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Sensors in Water Pollutants Monitoring: Role of Material

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Sensors in Water Pollutants Monitoring: Role of Material

Springer

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Preface

Sensors have become an integral part of civic society to check on social, environmental, and strategic activities. The environmental sensors are required to ensure the safety and security of the ecological environment around us. Water being the key component for life existence on earth needs to be ensured for its quality as well as quantity to meet global demand. However, with increased intervention of humans, its quality is getting deteriorated, while ground water table is going down owing to over exhaustion of water resources. Thus development of sensors for field testing of these parameters is essential. The figure of merits associated with any sensor, such as sensitivity, selectivity, detection limit, reproducibility, accuracy, precision, reusability, etc., is mainly defined by the type of sensor material and the transduction mechanism used. Amongst various analytical techniques, colorimetry, absorbance, fluorescence, surface-enhanced Raman scattering, electrochemical, and electrical techniques are widely adopted to develop a water quality monitoring sensor. Various materials, beginning from organic ligands to the nanomaterials (nanoparticles, quantum dots, nanotubes, nanowires, thin films, nanofibers, etc.), are widely adopted to develop a sensitive sensor. For selectivity, various chemo linkers and bio receptors (antibodies, enzymes, aptamers, oligomers, etc.) are utilized for field usability of the developed sensor platform. This book provides a comprehensive overview of the above sensing techniques, materials, and receptors for water quality/pollutants monitoring, and it would be a handy guide for the students, researchers, engineer, etc., working in field of environmental engineering, material science and engineering, and water.

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Dr. Pardeep Singh is presently working as Assistant Professor (Department of Environmental Science, PGDAV College ,University of Delhi, New Delhi, India). He obtained his doctorate degree form Indian Institute of Technology (Banaras Hindu University) Varanasi. The area of his doctoral thesis is degradation of organic pollutants. He has published more than 55 research and review articles in the international journals. His research interest is towards materials design for water pollutants remediation, e-waste recycling, and photocatalyst design. He has also edited several books of reputed publishing houses including Springer and Elsevier.

Dr. Sandip Patil is the founder Director of E-Spin Nanotech Pvt. Ltd and Technorbital Advanced Materials Pvt Ltd. Dr. Patil has extensive experience in nanofiber membrane technologies and Ultra Hollow Fibre (UHF) membrane technology for senor and water purification applications. Dr. Sandip Patil received his Ph.D. from Indian Institute of Technology Kanpur, India. He research has been published in very prestigious journals such as Soft Matter, Macromolecules, Langmuir, ACS Omega, ACS Applied Materials & Interfaces, and other peer-review journals. Dr. Patil is also the inventor of US and Indian patent. He has awarded various prestigious awards which includes, Technopreneur Promotion Program (TePP) award, IIChE Shah-Schulman award for the best PhD thesis in the area of Colloid and Interface Sciences and IICHE M. P. Chary Memorial Medal award for being an outstanding young chemical engineer for the year, Spirit of Manufacturing Award for Most Promising International Business Leader, Indian Leadership award for industrial development by All India Achievers Foundation, Rajeev Motwani Young Entrepreneur award by Motwani foundation, Indian School of Business Hyderabad Scholarship award, UICT Jalgaon alumni award for Young Entrepreneur.

Introduction: Role of Materials in Sensors for Water Pollutants Monitoring

D. Pooja, Pardeep Singh, Sandip Patil and Praveen Kumar

Abstract Water is a vital for the existence of any form of life on earth. However, the current century is witnessing the declining groundwater level as well as increased pollution of water resources. Both these challenges require utmost global attention to ensure safe and enough water supply to every human being as a fundamental human right. Sensors has a critical say to monitor the quality of available water as well to prevent its contamination by anthropogenic activities. They can be used as a tool by regulatory bodies in policy making as well as decision for selection of necessary remedial systems for water pollutants. Most of the conventional as well as emerging organic, inorganic, and biological pollutants has a life-threatening impact on the ecosystem, which necessitates the serious and periodical water quality monitoring. This monogram at first introduces these pollutants and their health effect. We further discuss the various existing analytical tools for water pollutants detection. The transduction techniques as well as materials role to achieve desired sensitivity and selectivity of sensor are discussed in the chapter dedicated for plasmonic sensors, electrical sensors, colorimetric, fluorescent chemo-sensors, electrochemical sensors, biosensors, nucleic acid-based sensors, etc. Finally, we deliberate the futuristic development to be taken up for reliable and field level detection of these pollutants in reference to technique and material selection.

Keywords Sensors · Water · Pollutants · Organic · Inorganic · Biological · Optical · Electrical · Materials · Sensitivity

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Amongst the fundamental human right, safe and sufficient water for human consumption is on the topmost priority since water is the origin and sustenance of life. However, the increasing industrial growth, urbanization, and related geogenic disturbance have degraded the water resources. The sensor system has a critical role to play in assessing the type and level of water pollution. Besides, it has a critical role to play in monitoring the performance of water pollutants remedial system. Over the conventional method of analysis of water pollutants, the various other analytical approaches such as electrochemical, colorimetric, fluorescence, absorbance, electrical, etc., have found significant potential in the design of a portable sensor system. However, the sensitivity, selectivity, and response time of these techniques are highly dependent upon the sensor material characteristic. The present book aims to contain and discusses these aspects of water pollutants sensors to severe as handy information in the present context for the students, researchers, engineers and technologist working in this field to address various challenges. The emphasis has also been given to specific techniques, including electrochemical, colorimetric, fluorescence, and biosensing with respect to materials innovations. As to make the sensors, the required materials need to have specific, structural, optical, chemical, electrical properties; therefore, the selection of materials to make different sensors becomes very critical. The first chapter of the book starts by explaining the role of different materials to develop the sensors for water pollutant monitoring, followed by the origin of different pollutant in the second chapter. Detecting pollution timely and locating the pollution source is of great importance in environmental protection. Numerous water pollutants have been discovered, consequently, to differentiate we discuss the conventional and emerging water pollutants in Chapter "Types of Water Pollutants: Conventional and Emerging". Having known about the various pollutants, we further discuss their original sources and their impact on the environment and human health in Chapter "Water Pollutants: Sources and Impact on the Environment and Human Health". Up to now, we can establish the background which we require to understand the issue of the pollutant and their side-effects on our day-to-day life, and conceived that efficient and selective sensors are required to monitor the exact quantity of these pollutants in the water. Thereby, we discuss in detail the analytical methods available to monitor these pollutants in Chapter "Analytical Methods of Water Pollutants Detection".

As there are plentiful types of water pollutants are reported including the emerging pollutant and most of them are having different specifications and also a source of origin. Therefore, to detect them efficiently and selectively, different types of water quality monitoring sensors are needed. Most important parameters when we design and select the sensors types include the chemical nature of the pollutant, sensitivity, selectivity, response time, size and speed of the possible sensors. Based on these requirements sensors can be divided into categories depending on the type of sensor being used, and the environmental factors that an analyst is looking at. From Chapters Plasmonic Nanoparticles Decorated Graphene Sheets for Detection of Water Pollutants to Immunochromatographic Strip Based Sensor for the Detection of Water Pollutants, we discuss various sensors in details which include plasmonic sensors, electrical sensors, colorimetric, fluorescent chemo-sensors, electrochemical sensors, biosensors, nucleic acid-based sensors, and immune-chromatographic strip based sensors. Further, we discuss the futuristic materials development for emerging water pollutants detection followed by the emerging advance sensing techniques, including nanofibres based sensors as sensor materials for their detection in Chapters "Materials in Emerging Water Pollutants Detection" to "Nanofiber Based Sensors for Water Pollution Monitoring".

Overall, this monograph presents a detailed, synergized and focused discussion on the various water pollutants, their origin, and possible sensors to detect them using the existing analytical methods, such as electrical, optical, colorimetric, electrochemical, nucleic acid, plasmonics, etc. The monograph further discusses the emerging techniques and materials for the advancement of the monitoring of conventional as well as emerging water pollutants in a holistic way. Specific topics covered in the monograph include:

- Role of Materials in Sensors for Water Pollutants Monitoring
- Water Pollutants: Origin and status
- Types of water Pollutants: Conventional and emerging
- Water pollutants: Sources and impact on the environment and human health
- Analytical methods of water pollutants detection
- Plasmonic nanoparticles decorated graphene sheets for detection of water pollutant
- Materials for electrical detection of water pollutants
- Materials in Colorimetric Detection of Water Pollutants
- Fluorescent chemosensor for the detection of water pollutants
- Materials in electrochemical detection of water pollutants
- Materials in biosensing of water pollutants
- Nucleic acid Technologies for Contaminants of Emerging Concern sensing
- Immunochromatographic strip based sensor for the detection of water pollutants
- Materials in emerging water pollutants detection
- Emerging techniques and materials for the detection of water pollutants
- Nanofiber-Based Sensors for Water Pollutant Monitoring.

Water Pollutants: Origin and Status

Jyoti Singh, Priyanka Yadav, Ashok Kumar Pal and Vishal Mishra

Abstract Water is the core of life that helps us to exist and also, the most vivacious that keeps us alive. It is essential for all to drink clean and pure water. Due to natural and anthropogenic sources, water becomes polluted that results in the origin of different water pollutants. These water pollutants need to be eliminated from the water for liveliness of people and protect them from various diseases. For instance, water pollution in Rajasthan is due to the indulgence of different industries. Likewise, in Rajasthan many states are affected by water pollution badly. Not only India, whole world suffers from the identical issues. The discharge of chemicals as well as heavy metals through industries and factories are the major sources of water pollution. It is reported that one of the largest sources for this is untreated sewage, discharge into rivers that ultimately affects environment and thus, finally human beings. Human beings contribute in an enormous way to pollute water. Education related to environment should be given to the students and common people so that this problem can be reduced to a certain level. This chapter focuses mainly on the origin of different water pollutants and their current status in the environment.

Keywords Water pollutants · Status · Origin · Diseases · Humans · Environment

1 Introduction

Water is the most vital component in the origin of life. Without water, life is not possible. But it got contaminated by various toxic, inorganic industrial pollutants that results in several problems such as unsafe for consumption for humans and irrigation activities. This leads to water scarcity because it limits its availability for humans and ecosystem.

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The main reason behind water crisis is water pollution. It should not be polluted to a certain threshold value for being used in irrigation and drinking water purposes [1].

The issue of social justice is compounding the water crisis; poor people are more likely to lack clean water and hygiene in comparison to rich one in related areas. Worldwide, enriching water safety, hygiene and sanitation could evade up to 9% of all diseases and 6% of all deaths. Apart from the worldwide waterborne disease crisis, global water quality is threatened by chemical pollution from agricultural activities, industries, cities, and mining areas. Certain chemical pollutants have severe health effects, while many others have long-term that are poorly known. More than 40,000 water bodies in the U.S. currently suitable the EPA description of "impaired," that means they can't sustenance a healthy ecosystem or meet water quality standards. Water pollution is contamination of water by an excess of a substance that can cause impairment to the people and/or the ecosystem [1]. The water pollution level subject to pollutant's abundance, pollutant's ecological impact, and water use. Pollutants derive from chemical, biological, or physical actions. Whereas natural activities such as volcanic eruptions or evaporation can sometimes cause water pollution, the major pollution is a consequent of human activities based on land. As water progresses all the way through stages of the water cycle, water pollutants can move through different water reservoirs. Water residence time (the average time spent in a water reservoir by a water molecule) is extremely imperative for pollution problems as it have an impact on the potential for pollution. Water in rivers has a relatively short period of residence, so there is generally only pithy pollution. Naturally, river pollution can merely move to another reservoir, for instance the ocean, where it can be the reason for further problems. Groundwater is characteristically categorized by sluggish flow and extensive residence time, that can pose a particular problem to groundwater pollution [2]. Lastly, residence time of pollution is greater in comparison to water because a pollutant can be used in the ecosystem for a long time. Pollutants arrive in the water supplies from different kinds of point sources that are easily recognizable and comparatively small, or nonpoint sources that are larger and greater diffuse areas. Point pollution sources comprise of farms in the animal factory that produce huge number and high livestock densities such as cows, pigs and chickens. Collective sewer systems for bringing together street sewage and storm water runoff for treating wastewater can be major point pollutant sources. Storm water runoff may overdo sewer capacity during heavy rain, triggering it to back up and directly spill untreated sewage into surface waters [3]. Agricultural fields, cities and abandoned mines are nonpoint sources of pollution. Rainfall runs across the land and through the ground for collecting contaminants from agricultural fields and lawns such as herbicides, pesticides, and fertilizers; oil, animal waste, and urban road salt; and acid and toxic elements from abandoned mines. This pollution is then transferred to surface and groundwater [1].

2 History of Water Pollution

Ancient Times: Water forms like rivers, lakes and streams were in the ancient times the source of drinking water. However, human waste was deposited in the same water bodies. Therefore, in rivers became so polluted that in order to obtain clean drinking water, these ancient cultures needed to build aqueducts [4]. The main cause for polluted water was that its way to rivers and streams that were originate by human waste.

Medieval Times—1800s: During this time, people were unaware of what was good for them and what was bad. Mercury was frequently dumped into water and was allowable to run freely into lakes and streams from most of the humans and farm waste. Most people living in metropolises just dumped their waste and garbage onto the street that smelled very bad, probably.

Civilization made many great strides during the latter half of this period, frequently to the damage of the ecosystem. Individuals even consumed chemicals at that time

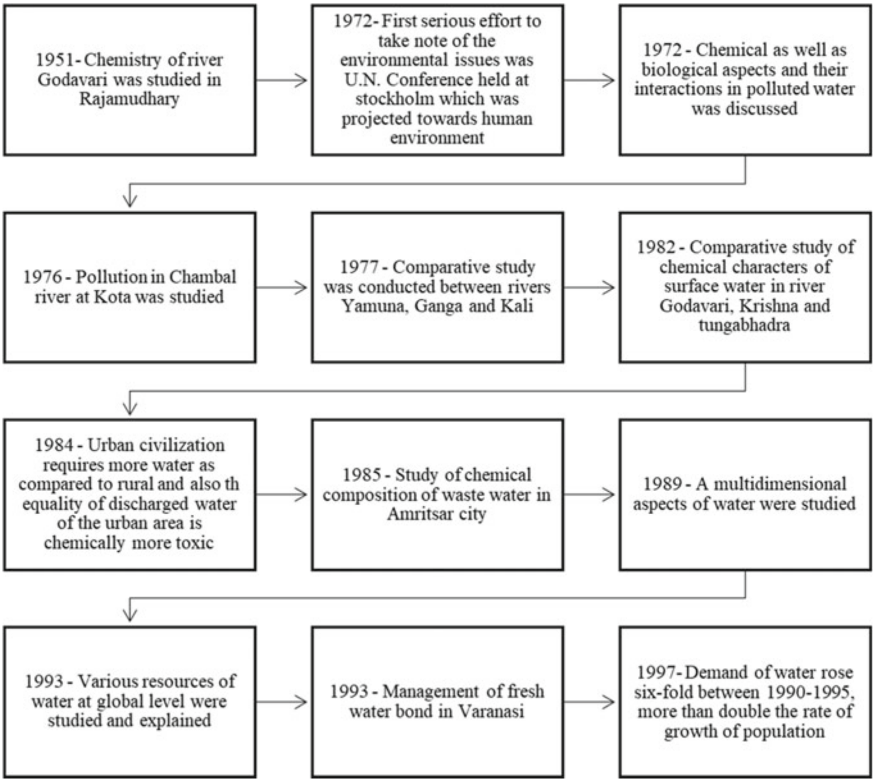


Fig. 1 Flow chart representing different studies on the water contamination at different sites

as they thought, it’s good for their health. For the benefit of industry, the Industrial Revolution of the 1800s saw little care for the ecological impact. Many chemical substances have been dumped into the rivers. At that time, people were not concerned about the environmental impact of their inventions [5].

After World War-II: Besides contaminants such as human waste, composts, leather tanning and slaughtering waste, the development of industries and factories had also resulted in much water pollution problems. As waste from industries dumped into river freely without care about the environment were affecting ecology and humans, including flora and fauna [6].

1969: After a series of fires on the Cuyahoga River in 1969, it was realized that fires were triggered by oil slicks and dumped into it by flammable industrial waste. The government then began the studies that allowed the 1972 Clean Water Act to be enacted [4].

Present Day: Many people still do not know how to guard themselves against chemical toxins and waterborne diseases, even with this act. Many cleanups on a large scale have been going on for years [1] (Fig. 1 represents different studies that had done in different sites to check contamination of water).

3 Origin of Water Pollution

The origin of pollutants can be attributed to their fundamental occurrence on earth, the development of natural products by transformation, and their man-made synthesis. The particulates might well arise indeed very naturally to form part of the ecological background exposure levels Many of them are excreted by the organisms or detoxified. Examples of some pollutants that occur naturally are nitrogen oxides, heavy metals. Hydrocarbons and substances that are radioactive [7].

Some pollutants can be formed during their domestic, agricultural or industrial use by concentration and transformation of naturally occurring compounds. The generation of sewage and waste waters comprising agrochemicals, pesticides, petrochemicals hydrocarbons, heavy metals, and radio nuclides are some important examples of pollutants that have emerged from this.

Many of the chemicals do not occur in the nature and the pollution they cause is entirely manmade. For example, the synthesis of various pesticides, surfactants, plastics and petrochemicals has created a large number of chemicals in the environment that have created serious environmental problems [2].

Figure 2 represents how the release of toxic chemicals can be done and how humans and animals get affected with the contaminated water.

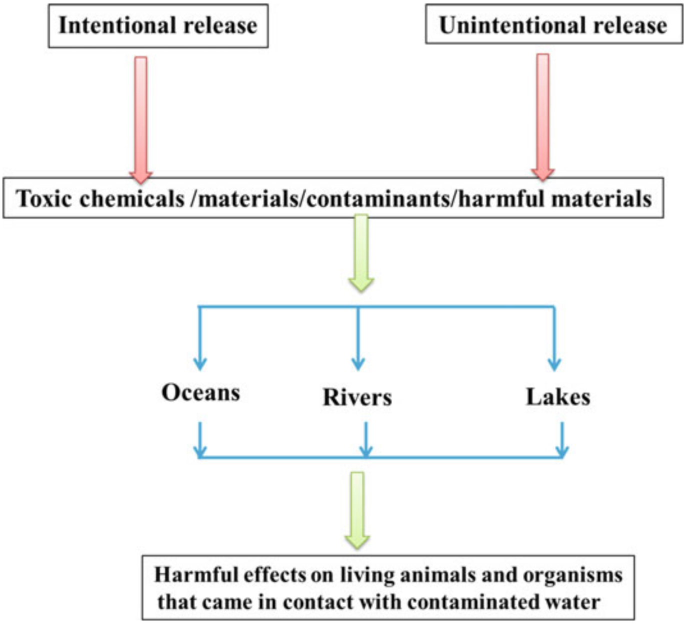


Fig. 2 A diagrammatic representation of release of toxic chemicals in various water bodies

4 Sources of Water Pollutants

The major sources of water pollution that result in contamination are direct and indirect ones, in addition to other sources.

Direct pollution is caused by releasing fluids directly into the water, such as a company that expels contaminated water or toxic solids mixed directly with water into the sea or river. This makes the water poisonous, every so often resulting in death, for fish and other aquatic creatures. Nevertheless, animals also drink this water, which also bring to them ill health or death. It can also affect to humans. In developed countries, people no longer depend on drinking water from the stream or river. There is still a risk for those who swim in or participate in activities such as canoeing on polluted water, as some of them can cause illness and even death [8].

Indirect water pollution is not caused by the introduction of contaminants directly into the water, but by those that end up there. An example includes fertilizer and pesticide chemicals that are washed slowly through the soil and find their way into groundwater and then into various watercourses. In addition, air pollution can cause acid rain to fall to the ground, which can be extremely harmful to wildlife, including polluting lakes, streams and shores, and make the water deadly for those creatures that leave in and near it [8].

Whether it's direct or indirect water pollution (Fig. 3), the results can still be the same, i.e. disease and possibly death to any living thing that lives in it or takes in

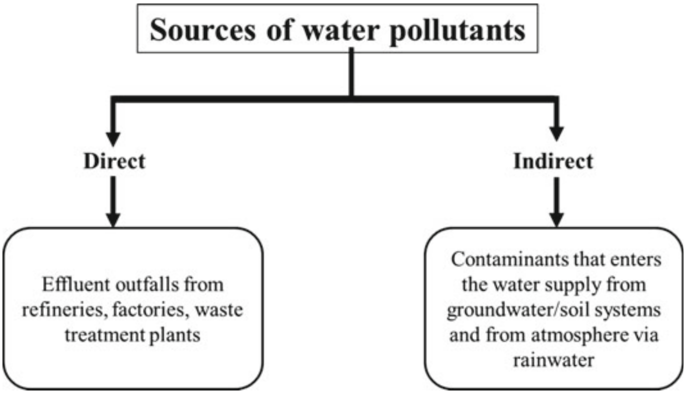


Fig. 3 Sources of water pollutants

water. Therefore, it is imperative that individuals and businesses take steps to reduce their levels of pollution and reduce their environmental impact [9].

The common sources of water pollution can vary from wholly natural to man-made sources such as release of domestic and industrial waste waters.

(a) Natural Sources and Runoff

The natural entry of pollutants in water reservoirs can be done through various activities as given below.

1. Rain water
2. Atmosphere (dust, storms)
3. Underground rocks and volcanoes
4. Natural run off
5. Surrounding vegetation

Rain water is an important natural source of water pollution, which dissolves the pollutants from air and brings down the entrained particulate matter with it. E.g. Occurrence of acid rain formed due to the dissolution of acid gases such as oxides of Sulphur and nitrogen in rainwater. The direct deposition of particulate by gravity is called dry deposition is another way of causing water pollution.

The falling of leaves, twigs and other parts of surrounding vegetation can also enrich waters. Presence of underground rocks and volcanoes beneath the water bodies may also be the source of certain kinds of salts [5].

(b) Domestic Sewage

Domestic Sewage comprises of waterborne wastes of the public and contains about 99% of water and 1% of solids. Of the solids existing in sewage, 70% are organic and 30% are inorganic in nature. Out of the organic constituents 65% are proteins, 25% carbohydrates and 10% fat. Inorganic fraction of sewage constitutes grit, salts and metals in varying proportions.

The major problems associated with sewage are production of odors and spread of enteric diseases besides organic pollution which leads to oxygen depletion and fish-kill. Sewage also contains huge quantities of nutrients in the form of N_2 and PO_4^{3-} even after secondary treatment that often result in the problem of eutrophication.

Another common way of sewage disposal is its land treatment or crop irrigation. However, disposal in this way, without scientific considerations, can lead to the severe health hazards and deterioration of land in the long run [10].

(c) Agricultural Wastes

Agricultural waste is the waste that originate generally from run-off from cultivated arenas and animal farms. In the recent time, for promoting the growth of fruits and vegetables, farmers add various kinds of agrochemicals that cause many kinds of pollution problems. It can cause toxicity to aquatic life also [11].

(d) Industrial Wastes

Industrial waste is a waste that possess the potential for polluting water reservoirs directly. Nature of industrial waste can vary from industry to industry and also on time as it depends on the usage and type of raw materials used, different processes and also operational factors. It is mentioned that industrial wastes are rich in organic matter [1].

A Table 1 described above to show different sources of pollutants. These pollutants have different components and their respective effects on humans. Thus, there is a need to control these pollutants so that it will not affect humans at a toxic level. That’s why some solutions are given in table that needs to be consider.

Table 1 Sources of water pollutants with their effects and corresponding solutions [28, 29]

Sources	Components/pollutants and their effects	Solutions
Agricultural run-offs and mill-waste	NO_3^- and PO_4^{3-}(in fertilizers) • Excess amount results to **eutrophication**	Control its use by (a) using only when crops are growing (b) not using on bare fields (c) not applying when there is a prediction of rain (d) not disposing in river
	Herbicide and pesticide residues • Accretion of pesticides and herbicides have lethal effects on organisms in the water and also to the humans • Level of pesticides start to build up as it passes over the food chain • High dose of pesticides may collect in the tissues of	• Use pesticides that are biodegradable • Use methods to control biological pest • Plant must be genetically modified so that it can resist attacks by pests as this may reduce the need of chemical insecticides

(continued)

Table 1 (continued)

Sources	Components/pollutants and their effects	Solutions
	ultimate consumers that are mostly carnivores	
Untreated sewage consisting mainly of human faeces and domestic waste	Suspended solids • Reduced penetration of light • If suspended solids are biodegradable, microorganisms can decompose them and their processes require a high oxygen requirement	• Before entering rivers, treat sewage • Help to stop the farm slurry (liquid manure) from entering into rivers and ponds
	NO_3^- and PO_4^{3-} • Results into eutrophication	
Domestic waste includes detergents and food waste	**Detergent** • 'Hard' detergents create foam that reduces oxygen supply to water-borne organisms • Soft detergents are biodegradable but it may contain high phosphate levels that can sometimes give rise to eutrophication	• Use low-phosphates biodegradable detergents
Animal waste from farm	Microorganisms such as bacteria and protozoa • If water would be used to drink, perhaps it will cause waterborne diseases namely cholera to be properly treated	• Drink water that is properly treated and boiled
Effluents from industries • Electronic and electroplating plants • Food and beverage processing industry • Rubber product processing industry	**Heavy metals** such as Cu, Hg, Zn and Cr • Highly toxic accumulation through the food chain in the organism • Mercury can cause acute human nervous disorder. Waste water contains numerous contaminants, including sulphide of hydrogen	• Treat effluent before discharging it into bodies of water • File a law suit against hazardous waste dumping
Underground pipes	**Lead** • Lead is highly poisonous heavy metals that could build up in living organism tissues • Lead may affect children's mental capability	• Use copper pipes in plumbing rather than lead pipes

5 Types of Water Pollutants

There are various types of pollutants categorized as:

(a) Organic Pollutants
(b) Inorganic Pollutants
(c) Radioactive Pollutants
(d) Suspended Solid
(e) Pathogens
(f) Nutrients and Agricultural Pollutants
(g) Thermal Pollution.

These pollutants are described as follows:

(a) **Organic Pollutants**

Organic compound consists of carbon, hydrogen, oxygen, nitrogen and Sulphur. Organic compound emitted from sewage, urban waste water, industrial wastewater and agricultural waste. Example is Oleic acid, Palmitic acid, Dodecanoyl chloride and Docosanoic anhydride [12].

(b) **Inorganic Pollutants**

Developing countries are concerned about contamination of harmful chemicals such as nitrite, ammonium nitrate and heavy metals in drinking water. The high levels of inorganic nitrogen pollutants (nitrate, nitrite, ammonium) and inorganic phosphates in river water resulting from draining water from agricultural fields, releasing municipal/industrial sewage, etc. lead to many health problems. Nitrite is carcinogenic in nature, which increases the risk of stomach, liver and esophageal cancer and can lead to high levels of ammonium in the body [13].

(c) **Radioactive Pollutants**

Naturally radioactive material comes from earth crust and dissolves in surface drinking water. Anthropogenic radioactive material emitted from nuclear power plant, nuclear weapons testing and manufacture and application of radioactive material. Generally, radionuclide appeared in drinking water have series of uranium, thorium and aluminum and with naturally occurring materials of radium, uranium and the radioactive gas radon. These contaminants cause dangerous effect on human being. Radium causes bone cancer. Uranium also causes cancer in bone and toxic effect on kidney [7].

(d) **Suspended Solid**

Suspended solid are the pollutants municipal and industrial wastewater treatment plants and sewage treatment plants. There are three different types of suspended solid are found (a) sand and other material at washing steps (b) organic content that cannot used for final product (c) suspended solid in the wastewater [1].

(e) Pathogens

Pathogens are small microbes that cause disease, including bacteria, viruses, pillows, and certain parasites. Viruses generally present in wastewater are Hepatitis and Norwalk virus and a common fungus is Candida. A salmonella bacterium causes food poisoning whereas *Vibrio cholera* is the pathogen that causes cholera. Parasites such as Cryptosporidium and Schistosoma can cause diarrhea and all wastewater pathogens can lead to serious gastrointestinal illness [1].

(f) Nutrients and Agricultural Pollutants

As a result, the use of large quantities of chemical fertilizers in agriculture causes so many environmental problems as some fertilizers contain heavy metals (e.g. cadmium and chromium) and high radionuclide concentrations. Non-organic fertilizer contains salts of phosphate, nitrate, ammonium and potassium. Manufactured fertilizer industry contains excess heavy metals such as Hg, Cd, As, Pb, Cu, Ni, and Cu. Heavy metal fertilizer is deposited in the soil and plant system. Plants absorb fertilizers through the soil; they can enter the food chain that contaminates the water [11].

(g) Thermal Pollution

The temperature alteration in water bodies, as a result thermal pollution occurs. The thermal power plants discharge causes raise in temperature of aquatic system of 10 °C. Therefore, very serious effect on aquatic life due to global warms by thermal effect. Use of wind and solar energy in place of thermal energy. Thermal pollution decreases by plantation and reduce the emitting of carbon dioxide in environment [14].

6 Status of Ground Water

As we know that the groundwater is found beneath the surface water as it occupies fissures, pores, channels as well as other types of void spaces in the rock framework which are not filled with other materials like liquid hydrocarbons, solid mineral matters as well as various gases including air [2].

Globally the annual requirement of water is 6000–7000 km^3 and the globally reserve groundwater is about 7,000,000 km^3 [15]. Due to the pressure of the modern agriculture, urban lifestyle, industries the spread of contamination in water will doubles their speed and as a result cause many hazardous things like various types of diseases. In China’s Northern provinces about 10 larger cities are using ground water which was a major concern in China [16]. Most of the sources of the private groundwater are located in the rural areas that are characterized by the ubiquity of animal as well as human contaminant sources with a lot of unregulated in the terms of treatment, design, location and maintenance and are associated with the low levels of institutional as well as consumer awareness [17].

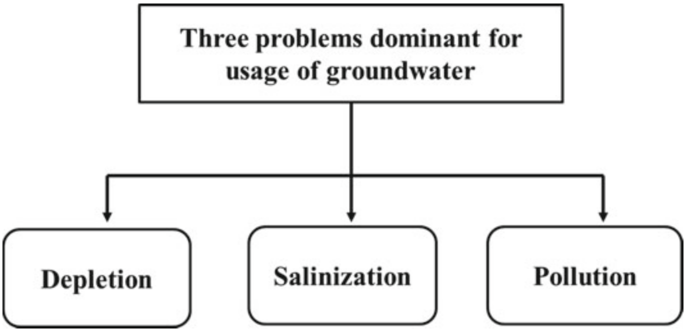


Fig. 4 Problems dominant during regular usage of groundwater

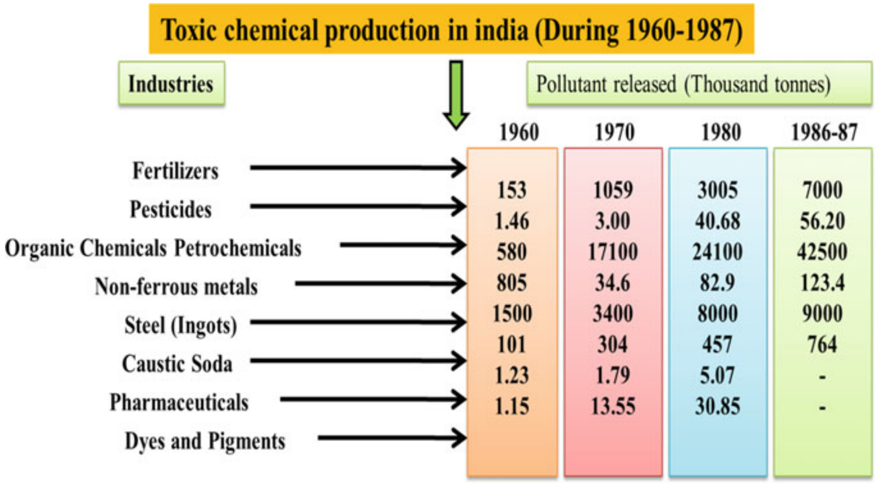
Figure 4 depicts the use of groundwater that are problem dominant like the depletion which are caused by over drafting as well as waterlogging, and salinization which are caused due to insufficient conjunctive use as well as due to inadequate drainage, and the third one is the pollution that are caused because of industrial, agricultural as well as the human activities [18]. In 2004, it was also found that the in North China Plain a sustainable groundwater resources were used for agriculture and was focusing on the major groundwater problems but a more process has to be done to utilize their groundwater. Many groundwater pilot projects were carried in country level and out of which Guantao is one of them. From about last 25 years China's institutional as well as legal framework was carried on the utilization of water resources [19]. Unlike the water which are present on surface or can say the surface water the groundwater is hard to measure, conceptualize but further it was analyzed in terms of timescale much longer than those of the analysis process used for the management of surface water [20]. According to the recent report on IWMI, it was stated that about 1.4 billion people's lives in the region where they face severe water scarcity within the first quarter of the next century [21].

7 Status of Surface Water

As we know that water occupies about 71% of earth surface and water is considered to be one of the scarcest commodities mainly in the developing countries and is one of the most demanding of all rural as well as urban amenities [22].

Figure 5 shows the toxic chemical production in India during the period of 1950–1987. It is observed that most of the pollutant released are from organic chemicals and petrochemicals and the rate of pollutants increases from 1960 to 1987 onwards.

According to the Water Framework Directive of European Union (WFD 2000), the Timia-Bega watersheds were selected a lot of watercourses, used for the



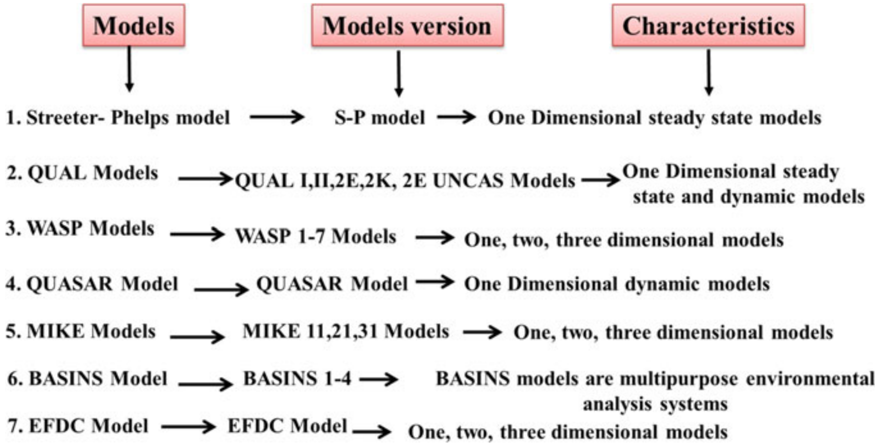
Toxic chemical production in india (During 1960-1987)

Industries	Pollutant released (Thousand tonnes)			
	1960	1970	1980	1986-87
Fertilizers	153	1059	3005	7000
Pesticides	1.46	3.00	40.68	56.20
Organic Chemicals Petrochemicals	580	17100	24100	42500
Non-ferrous metals	805	34.6	82.9	123.4
Steel (Ingots)	1500	3400	8000	9000
Caustic Soda	101	304	457	764
Pharmaceuticals	1.23	1.79	5.07	-
Dyes and Pigments	1.15	13.55	30.85	-

Fig. 5 Toxic Chemical production in India (1960–1987)

operational monitoring of the groundwater as well as for the surface water and are also responsible for the water quality determination and was found that 8 monitored ground water bodies, 3 surface reservoirs, 12 surface water bodies that are artificial as well as heavily modified and on the other side 14 surface water bodies found in natural status [23].

Figure 6 shows 7 models of the surface water with their versions and characteristics. The Streeter-Phelps provides the first S-P model in 1925. Mainly the S-P model focuses on the oxygen balance as well as the one-order decline of the demand for biological oxygen and is a one-dimensional stable-state model. USEPA



Models	Models version	Characteristics
1. Streeter- Phelps model	S-P model	One Dimensional steady state models
2. QUAL Models	QUAL I,II,2E,2K, 2E UNCAS Models	One Dimensional steady state and dynamic models
3. WASP Models	WASP 1-7 Models	One, two, three dimensional models
4. QUASAR Model	QUASAR Model	One Dimensional dynamic models
5. MIKE Models	MIKE 11,21,31 Models	One, two, three dimensional models
6. BASINS Model	BASINS 1-4	BASINS models are multipurpose environmental analysis systems
7. EFDC Model	EFDC Model	One, two, three dimensional models

Fig. 6 Major surface water models with the model version as well as their characteristics

gave the model QUAL I in 1970. These models are suitable for both dendritic and non-point source pollution and are either a one-dimensional stable-state or dynamic model. USEPA developed a WASP model in 1983, and these models are appropriate for water simulation in lakes, rivers, coastal wetlands, estuaries, and reservoirs including one, two, and three-dimensional models. Whitehead provides model QUASAR in 1977 and is suitable for dissolving simulation of oxygen in larger rivers and is a one-dimensional dynamic model such as modes PC QUA SAR, QUESTOR and HERMES. The MIKE model has been developed by the Denmark Hydrology Institute that is suitable for simulating water quality in lakes, rivers, tidal wetlands, estuaries and is one, two or three-dimensional. In 1996, USEPA developed the BASINS model and these models are a multi-purpose environmental analysis system and are suitable for watershed-scale analysis of water quality and can also integrate non-point and point source pollution. Virginia Institute of Marine Science developed the EFDC model. USEPA listed this model as a water quality management tool in 1997 and these models are suitable for simulating water quality in estuaries, lakes, rivers, reservoirs and wetlands [24].

Table 2 Key issues, limitations and advantages regarding Large dam reservoirs, Small surface water reservoirs as well as Groundwater storage [25]

	Large dam reservoirs	Small surface water reservoirs	Groundwater storage
Key issues	• Sedimentation • Dam safety • Environmental impact • Social impacts	• Environmental impacts • Adequate design • Dam safety • Sedimentation	• Groundwater Salinization • Rising water levels • Groundwater pollution • Management of access and use
Advantages	• Multipurpose • Large • Reliable yield • Carryover capacity • Low cost per m^3 water stored • Flood control hydropower Groundwater recharge	• Groundwater recharge • Multiple use • Ease of operation • Responsive to rainfall	• Water quality • Operational efficiency • Little evaporation loss • Ubiquitous distribution • Available on demand
Limitations	• Sedimentation • Environmental impacts • Social impacts • Dam safety	• Environmental impacts • Adequate design • Dam safety • Sedimentation	• Groundwater salinization • Rising water levels • Management of access and use • Declining water levels • Groundwater pollution

Table 2 depicts the major advantages, issues as well as the limitations of large dam reservoirs, Small surface water reservoirs as well as Groundwater storage in which groundwater were used for further uses. In groundwater storage the water were used to store in underground aquifers and with an advantage that groundwater can be stored for a year and is also purified of biological pollutants due to the slowly percolations of water into aquifers. On the other side small reservoirs are considered to be operationally efficient and flexible in use. And the last one is the large reservoirs have great yield related to the small reservoirs [25]. Groundwater is considered to be India's most vulnerable as well valuable resource as groundwater is a major source of drinking water for various rural communities as well as for cities communities [26]. In 1998, about 43.57 million hectare-meters per year is the estimated total replenishable groundwater resource in India [27].

8 Conclusion

Are we not aware of the various problems that occur in our nature, particularly in different water bodies? The causes of our undisciplined actions and irresponsibility are water pollution. We, humans, only create problems that we will bear the burden of these problems as well. We all know that water pollution can have a serious and serious impact on our health. It can cause such diseases and sicknesses that will have a serious impact on our health. We all know that water is so important. Water is our body's essential. Without water, neither we nor any living thing can survive. So, we should keep, protect, save, and help prevent pollution of our waters, we should act as early as now, we should save rivers, seas, and oceans, and other bodies of water, because we will bear the burden of this problem as well. We should not wait until people compete to get enough, fresh and clean water, the time when clean water is insufficient for humans and animals, and the time when our water sources are diminishing or when there are absolutely no water sources. And so, let's be disciplined and responsible enough to save, protect and preserve not only water sources but also our mother nature because our nature provides and helps us in our everyday lives. It's our only living source. Let's not destroy it or contaminate it. Let's take action for a change. We need and should help to save and preserve the nature of our mother, especially the various water bodies. Absolutely, in how we can help there are many simple ways. Change before we make changes in our nature.

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Types of Water Pollutants: Conventional and Emerging

Arif Ahamad, Sughosh Madhav, Amit K. Singh, Ashutosh Kumar and Pardeep Singh

Abstract Among all natural resources water is the most valuable resource existing on this planet. In present scenario, around the globe more than 0.78 billion people do not have access to safe and potable water which ultimately deteriorating their health. It is the right of every individual to have contamination free water but due to rampant urbanization, industrialization and uncontrolled population growth the pressure has been increased on existing available water resources (surface/ground water both) which leads to shrinkage of quantity and degradation of its quality. Various types of pollutants (organic and inorganic) released from different sources into the environment are increasing day by day. Conventional water pollutants include F^-, NO_3^-, and trace heavy metals (Pb, Cd, Cr, Ni, Zn, As, Hg, etc.), while emerging water pollutants include steroids and hormones, endocrine disrupting compounds (EDCs), pharmaceuticals & personal care products, artificial sweetener, surfactants, etc. The existence of these cocktail of pollutants in the water resources is more dangerous, which could lead to undesirable synergistic consequences.

Keywords Water · Pollutants · Trace metals · Nitrate · Pharmaceuticals & personal care products

1 Introduction

Water is the key constituent of all the existing lives. Being an essential component the freshwater comprises 3% of the total water on our earth. Out of which only a little amount (0.01%) of this fresh water is available to us for all purposes [46, 55].

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Due to various reasons like rapid growth population, urbanization and unsustainable use of water in agriculture and industries, this small portion of freshwater is now under in serious stress [2]. Non polluted water is a fundamental need of community and public health. On the event of World waterday 2002, a press release of UNO Secretary General highlighted the significance of accessibility of high quality drinking water. According to their report- an estimated 1.1 billion people are unable to get safe water for drinking purpose, 2.5 billion people are not getting proper sanitation, and more than 5 million people lost their lives due to water borne as well as water-related diseases which is equal to ten times the number killed in wars, on average, every year. So far where sufficient or plentiful water supplies are available, they are growingly at risk from contamination and increasing demand. They also reported that two thirds of world's population is expected to live in countries with moderate or severe water crisis by 2025 [5].

Polluted water mainly bears various infectious pathogens (like bacteria, virus and protozoa) as well as carcinogenic organic anions and cations (NO_3, PO_4, SO_4, F, Ca and Mg) and inorganic pollutants (acids, salts and toxic metals). When these substances exceed the permissible limit can become very dangerous and can cause serious diseases in humans and other organisms of the ecosystem [5]. Natural activity like volcanic eruption can contribute a small part of the sources of water pollutants but basically the key sources of water contaminants are anthropogenic like poorly treated or untreated municipal wastes, discharges from individual septic tanks, agricultural wastes like fertilizers, pesticides, industrial chemical wastes, spilled petroleum products, mine drainage, spent solvents, etc. [3]. Pollutants can be added into water bodies (both surface and ground water) through various processes e.g., discharge processes, surface runoff, subsurface infiltration, or atmosphere precipitation etc. Once the mixing of pollutants with water bodies occurs they are immediately carried into the water cycle in a global context. Consumption of polluted water can cause various water borne diseases like gastrointestinal illness by pathogenic microbes and also affect liver, kidney, nervous system and immunity [119]. Such pollutants are familiar to the society since long back termed as conventional pollutants because various researchers have reported their sources and the adverse effects on ecosystem in detail.

In recent years, the study of so-called "emerging contaminants" gains more attention than from conventional pollutants. Harmful effects of these emerging contaminants on human health is so far not known and have been detected at very low concentration (ng L^{-1} to μg L^{-1} levels) [33, 101] in the environment, particular in waters. With rise in population as well as globalization has not only increase the quantity of wastes but has also produced various emerging water pollutants which include pharmaceuticals, personal care products, pesticides, herbicides and endocrine disrupting compounds in last few decades [119]. Everyday emerging contaminants are added to our environment and the main source of formation of these is the byproducts of our modern lifestyle. We use chemical based products every day and these chemicals remain in wastewater due to lack of proper wastewater treatment plants. Likewise the industrial processes having their own treatment plants cannot remove all these chemicals and finally such chemicals end up in lakes and rivers of our environment. Therefore we are worrying about the harmful effects caused by those chemicals that they might be having on organism including human. Yet various pollutants have been detected in drinking water supplies but their negative effects on human body are still unknown. The sources of both natural and anthropogenic emerging contaminants having the levels between ng L^{-1} and μg L^{-1} (also called micropollutants) have been reported by various researchers in their publications including pesticides, industrial compounds, pharmaceuticals and personal care products [12, 57, 85–85].

There are several sources of these micropollutants in natural water. It is reported that industries and municipalities use about 30% of the world available renewable freshwater [19] resulting generation of vast quantity of wastewaters having various chemicals in varying concentrations. Some other remarkable sources of such pollutants are agricultural inputs [10] which use several million tons of pesticides each year; inputs from oil and gasoline spills; and from the human-driven mobilization of naturally occurring geogenic toxic chemicals [27]. Besides these, there are also enormous municipal and especially dangerous discarded industrial and earlier military waste sites from which poisonous compounds may enter into water body, mainly into the groundwater. As more than 100,000 chemicals are recorded and most of are used as daily basis [90], one can easily predict various probable ways of entering these chemicals into our aquatic environment [89]. Most compounds are mainly the resultant of urban waste water and can penetrate into drinking water via water cycle owing to their hydrophilic nature and poor elimination at drinking water and wastewater treatment plants [62, 71, 76, 122]. In several region of the world including rising economies like China, the wastewater having micropollutants are still untreated or undergo improper management which is unable to remove these kinds of pollutants [93]. Therefore, it was highly recommended to monitor the emerging compounds in the environment and basically in water because of their chances of open out via water and other unidentified eco-toxicological character [82, 83].

This book chapter deals with the various kinds of chemical pollutants in water resources including traditional as well as emerging.

2 Conventional Water Pollutants

People are aware about conventional pollutant like Fluoride, Nitrate and trace metals and metalloids because their desirable and permissible standard limit are known and also the causative effects on ecosystem and human health are also well described in the literature.

2.1 Fluoride

There are around 12 million tons of fluoride stores in the ground in India of the estimated 85 million tons present in the world [104]. The fluoride is highly scattered in our environment accounting for 0.3 g/kg of the earth's crust, resulting thirteenth in abundance. When fluorine reacts with other elements and forms ionic compounds like hydrogen fluoride and sodium fluoride in water and after dissociation it results into negatively charged fluoride ion [4]. Fluoride's chief natural source in soil is its parent rock itself [118]. In granitic rocks, fluoride, the only principal mineral of fluorine occurs chiefly as an extra mineral which contain sits concentrations of 20–3600 ppm [107, 112]. Apatite, amphiboles, biotite, hornblende, micas, muscovite, pegmatite, certain types of clays apart from villiaumite also contain fluorine [13, 34, 39]. There are other sources of fluoride into environment such as aluminum smelters, glass, enamel, textile dyeing, brick and tile works, plastics factories, phosphate fertilizer plants, industrial plants manufacturing hydrofluoric acid, along with the thermal power plants which consume high sulphur non-coking coal. At present high-tech industries like those involved in manufacturing semiconductors and integrated circuits generate large quantities of industrial effluents that contain fluoride [23, 25, 69, 73]. Though Fluoride with a very precise amount is an indispensable component for the normal mineralization of bones and development of teeth enamel, but its unnecessary intake could result into fluorosis [7, 59]. Low calcium and high bicarbonate alkalinity has been observed to favor high fluoride content in groundwater [15]. The water with high fluoride is normally soft, having high pH and high quantity of silica. In groundwater the amount of fluoride depends on various factors like aquifer's geological, chemical and physical characteristics, texture of soil and rocks, temperature, the action of other chemicals and the depth of wells [59]. The maximum limits of fluoride in drinking water as per WHO guidelines must not exceed 1.5 mg/L [116].

2.2 Nitrate

Nitrogen in the form of NO_3^-, NO_2^-, NH_3^+ and organic nitrogen could be groundwater's one of most common contaminants [66]. Besides, nitrate is also found naturally in very small concentrations in groundwater [28]. The nitrate exposure could occur from various environmental sources even as the drinking water remains the chief source. Though the ground and surface water normally have low concentrations of nitrates but because of issues like run off and leaching from agricultural lands, it could increase to high values [67]. In environments like oxygen-rich nitrate is generally a stable compound. It is highly water soluble and is easily leached from soils which have negative charges or with moderate to high pH, without being influenced by adsorption and precipitation reactions. For decades, the nitrate compound has the ability to remain in groundwater and get accumulated to higher levels since more and more of nitrogen is consistently used to the land surface on yearly basis. It has been observed that the water with greater than 50 mg/l of nitrate concentration could create health problems in humans and animals [36, 115]. If the nitrate polluted groundwater is discharged to the low nitrate concentration water bodies, it may result in eutrophication [98]. Various researches have observed that the increased nitrate concentration in groundwater can serve as an indirect indicator of the existence of other pollutants that are derived from human activities [28, 77]. The NO_3^-, component of nitrogen cycle in nature, signifies the most oxidized chemical form of nitrogen found in the natural systems and forms an important part of building blocks of living organism, i.e. DNA, RNA, hormones protein, vitamins, and enzymes [75]. Therefore human health consequences for humans because of high nitrate level exposure remain a great concern. The NO_3^- binds itself to the hemoglobin and therefore its increased concentration levels decreases the oxygen-carrying capacity in the blood which causes methemoglobinemia or "blue baby syndrome", a condition that may result in the mortality due to asphyxiation especially in the new born babies [2]. The infants (of <6 months of age) remain at highest risk because their digestive systems have bacteria which speedup the binding process. It is reported that nitrate can be endogenously reduced to nitrate, undergo nitrosation reactions in stomach with amines and then amines to form a variety of *N*-nitroso compounds (NOC) and are mostly carcinogens [106, 100, 113].

2.3 Trace Metals and Metalloids

Natural water dissolves the impurities of trace elements/heavy metals which are already present in water while seeping downward as a part of hydrological cycle [48]. Additionally, several human activities including large scale use of agricultural pesticides, fertilizers, dyes and improper disposal of industrial and municipal wastes introduce these metals to both the surface as well as groundwater [56]. Though for human health many of these metals are considered essential [44], however, their increased concentrations result in water pollution and lead to acute health issues in humans and other organisms. The speciation or the form in which they exist in a given water system determines the fate and toxicity of these metals even as it is a metal's freely dissolved form which is normally the most toxic. The EPA has included metalloids, metals & organics under priority water pollutants [64]. The metals and metalloids include Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Zn and Th. Most of them are transition elements, like Cd and Cu, or heavy metals like Pb and Ag and have tendency to form complexes with organic or inorganic ligands. In a solution ligands easily supply a pair of electrons to positively charged metal ions in solution and hence form complex ions with one to six ligands bound to the central metal atom. In fact, metal cations in water are hardly ever present as just the freely dissolved ions. If nothing else, water molecules can serve as ligands and tie to metal ions forming aquo-complexes. The ability of formation of various complex species is the fundamental feature of metals as the concentration of ligands in the water alters. The form of the dissolved metal can vary considerably as in an estuary transition of freshwater to seawater is caused by the metal [91].

Iron, one of the earth's most plentiful metals, occurs in various oxidation states while Fe (II) and Fe (III) are its two common forms in water. $Fe(OH)_3$ (oxidizing environment), Fe^{+2} and $FeHCO_3$ (reducing environment) are the species observed in water at neutral pH [103]. For the normal functioning of living organisms, Iron is an vital element and its deficiency as well as overload could be very harmful for the plants and animals [108]. The WHO has set a standard limit of 0.3 mg/L for iron in the drinking water. So the increased concentration of iron in natural water reservoirs poses a potential risk for human health system as well as the surroundings. Though compared to iron insufficiency, the overload or the overexposure of iron occurs less commonly but poses several serious health issues related to heart and liver [60], diabetes [29], cancer [6, 68], along with neurodegenerative disorders [9].

Manganese (Mn) occurs naturally in surface water and groundwater; however, its addition to water is largely contributed by human activities also [110]. It is an indispensable micro nutrient for all forms of life [30] since it combines to and/or control a number of body enzymes [20]. Manganese, tenth most abundant element in earth's, crust is a redox sensitive and is found in different oxidation states. In the aqueous environment, Mn^{+2} (reducing environment), MnO_2 and Mn_2O_3 (oxidizing environment) are the most prominent species. The exposure to too much doses of Mn results in severe nervous disorders and prominently targets brain [20] and in worst case scenario may permanently lead to a neurological problem which shows similar symptoms like Parkinson's disease [49]. Moreover, it has been observed that the exposure to Mn from food is generally higher than the intake from drinking water [110].

Chromium forms one of the most frequent elements in both earth's crust as well as water. The WHO permits 0.05 mg/L value of chromium in drinking water. In water it is unable to occur as freely as cation and appears as polyatomic anions chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$, respectively) [105]. Though this is not poisonous in itself and holds an significant role in the carbohydrate metabolism in our body, however, certain compounds of chromium mainly in its hexavalent state-chromium (VI) (carcinogenic form) cause irritants and diseases related to the digestive, excretory, respiratory and reproductive system, skin diseases ultimately cancers [41].

Nickel is a broadly dispersed component present in air, water and soil, and was dubbed as the "Allergen of the Year 2008" [26]. It can naturally enter the environment through processes such as weathering of minerals and rocks as well as from anthropogenic sources. In the aquatic environment more than 90% of the nickel is linked with particulate matter of sediments [45]. In natural waters, nickel occurs in the +2 valence state. Ni^{+2} form of nickel has been considered to be mainly responsible for evoking a toxic effect in aquatic organisms. The WHOs has put the limit of nickel concentration in water at 0.02 mg/L. Its compounds risk causing number of adverse effects like skin disease in the form of dermatitis, kidney problems, various heart diseases, respiratory tract cancer and lung fibrosis [58, 92].

Lead (Pb) is a normal component of the earth's crust and occurs naturally in very low concentration in soil and water [74]. It exists in two oxidation states of 0 and 2 and the dominant species found in normal water pH are Pb^{+2}, $PbOH^+$ and $PbHCO_3^+$. Of these Pb^{+2} is more common and reactive form. Lead is less mobile in soil and therefore usually found in minute quantities in deep aquifers in comparison to other heavy metals like Hg, As and Cd. Various sources contribute to the lead contamination in drinking water such as industrial wastes, vehicle exhausts and household paint. The WHO admissible limit for Pb concentration in drinking water is 0.01 mg/L. Lead usefulness in human physiology is unknown [74], but on contrary, its overdose exposure for longer times could affect major body organs and systems like neurological, gastric, haematopoietic, heart, reproductive system and immune system and also affects skeleton and kidneys [80, 111]. Lead has hazardous effects on pregnant women which can cause delay in development, under weight of fetus and cases of miscarriages are also recorded [8].

The naturally occurring compound Mercury (Hg) is considered as "persistent bio accumulative toxin" [114]. The WHO permissible limit for mercury in drinking water is 0.001 mg/L. Inorganic form of Mercury is less toxic than its organic forms owing to the differences in bioavailability [11]. In aquatic environments bacteria can transform mercury to methyl mercury which is highly toxic in nature [32] and can easily accumulated by fish and biomagnification takes place in the food chain. Coal fired power plants, smelting, alkali processing, apart from other industrial activities contribute to the mercury in environment. Historically, mercury was used in number of ways until its adverse effects became known. In the environment, the mercury cycles between air, water, soil, sediment, and biota. This causes difficulties in determination of its proper source. Occurrence of mercury in nature is also recorded in the sediments after the volcanic eruption which causes its mixing in atmosphere. Besides, the fly ash of power plants also contains mercury which directly mixes with atmosphere [91]. Only mercury has the property of biomagnification in the food chain and has serious detrimental effect on human health as well as the environment. Being a potential cellular toxin it has various harmful effects on our nerve cells, production of neurotransmitter even on the rate of production of thyroid and testosterone hormones [32].

Cadmium (Cd) exists in 0 and 2 oxidation states and is found in relatively low concentration in aquatic environment [61]. Its concentration could increase due to different activities like mining, seepage from hazardous waste site, wastewater disposal from industries or continuous use of Cd containing phosphate fertilizers. Cd is widely used in industrial applications including manufacture of batteries (NiCd), pigments, plastics etc. Its dominant form in pure water is Cd^{2+} (in fresh water the aquo-complexes are sticked to humic matters) and at high salinity, it forms a mixture of chloro-complexes, with $CdCl_3^-$ overriding in seawater [91].

Therefore the toxicity of same metal varies in different aquatic systems with diverse conditions. There are some metals and metalloids of polyatomic anions like arsenic, which are basically found as either arsenite (contains As (III) or as arsenate (contains As (V) in the water. The metal speciation also depends upon the oxidation-reduction conditions. As (III) species are predominate under reducing conditions, while under oxidizing conditions, the As (V) species are more constant. A good example of wood preservative (generally insecticide) is the lead arsenate—a form of arsenic was widely used for many years. After the decomposition, the wood pieces release arsenic into soil which mixes with surface water and finally makes its way to groundwater. Another chief source of arsenic and lead is smelting operation by which these metals are added into water directly or transported atmospherically. Presently the arsenic poisonings are caused mainly due to the consumption of well water where the ground water is naturally enriched in inorganic arsenic. Its over-exposure may cause reduction in the production of WBC and RBC, damage blood vessels and cause "pins and needles" sensation in hands and feet [1]. Its elongated exposure could result in leuko-melanosis, melanosis, neuropathy, hyperkeratosis, black foot disease, and cancer [17].

Selenium (Se) is often found in association with sulfur containing minerals in the earth's crust. Selenium is a metalloid component, a naturally existing trace element, available in five oxidation states in the nature: −2, −1, 0, +4 and +6, under the forms of elemental selenium, selenide, selenite, selenate and organic selenium [86]. The most familiar forms of selenium in water are selenite (Se (IV), SeO_3^{2-}) and selenate (Se(VI), SeO_4^{2-}). It is a slow process of emergence of selenate from selenite and both forms are found together in solution. Neither can be oxidized or reduced easily [97]. Selenium contamination of aquatic environment could happen due to mine drainage, agricultural drainage water, oil refineries, and sediments produced from fossil fuel thermoelectric power industries and metal ores [63]. The largest utilization of selenium compounds is in electronic and photocopier elements. A key nutrient at the level of low concentration, the permissible limits for selenium in drinking water has been set at 40 μg/L [117]. However, EPA has found that selenium has the potential to cause a number of health issues in case people are unmasked to it beyond MCL levels for relatively short time periods: fatigue and irritability, damage to the peripheral nervous system; hair and fingernail changes. A longer period exposure at levels above MCL have harmful effect on hair and fingernail loss; kidney and liver tissue damage, and the nervous as well as circulatory systems (www.freedrinkingwater.com).

3 Emerging Water Pollutants

Although the risk of health hazardous are not yet understood, all the drinking water supplies around the world is under contamination of chemical pollutants at least at trace level. Such problems lack scientific research and as well as there is scarcity of literature. But this issue is an urgent one and should be considered as emergent issue. There are several ways to define emerging contaminants.

The first one is the chemicals which are newly established into the ecosystem e.g. industrial chemicals which formed recently. The second one is regarding those compounds which have entered in environment in the past but are detected recently in the environment. The third one is same as the second one but they have caused harmful effects on ecosystems or humans [70].

Sources of ECs pollution may be point such as urban and industry or diffuse like agriculture. Point sources directly discharge the ECs into water bodies where their concluding fate is of primary concern as they may transport in the aqueous phase, degrade, adsorb into sediments [37]. However, in the case of diffused source of pollution, various properties of ECs such as their volatility, polarity, adsorption efficiency, persistence as well as interacting compartments determine their transport from source to the sink [31, 38]. Various types of emerging pollutants are displayed in Table 1.

3.1 Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceuticals and personal care products or PPCPs broadly consolidates the products pertaining to healthcare or medical requirement of humans and/or animals. PPCPs have been lately recognized as emerging contaminant owing to their continual presence in the aquatic environment thereby increasing the interest in their safety PPCPs over past three decades [88]. PPCPs are released in the environment through various sources including domestic wastewater, water treatment plants (WTPs) and hospital discharge [52, 54]. Amongst these, hospital effluents often show high frequency and concentration of pharmaceuticals [51, 65]. It is possible that the contaminants released into the aqueous environment from the source may preserve their initial concentrations and/or change their structure and convert into active or inactive forms throughout their lifespan. Generally, PPCPs are found in surface water, groundwater, drinking water as well as sewage at concentrations ranging from ppt (ng/L) to ppb (μg/L) [22]. It is likely that from the all the pharmaceuticals products sold approximately 65% are never ingested [84]. Additionally, enormous amounts of pharmaceutical products including inflammatory drugs and antibiotics do not even pass the sewage treatment. These are used by veterinarians for treating cattle feedlot and from there directly enter the surface water through run off during rainfall [14, 24].

PPCPs have been classified into multiple categories on the basis of their characteristics and usage. Pharmaceuticals classes include antibiotics, analgesics, steroid hormones, anti-inflammatory drugs, cytostatic drugs blood lipid regulators and β-blockers etc. [79] whereas types of Personal care products (PCPs) include fragrances, bactericides/disinfectants, insect repellents, preservatives and sunscreen ultraviolet (UV) filters [51, 54, 120]. Parabens are basically esters of para-hydroxybenzoic acid and may either contain an alkyl or benzyl group as side chain. These are mostly used in the form of preservatives in various products including food, cosmetics and pharmaceuticals [43, 53]. DEET is widely used

Table 1 Typical class of emerging contaminants and their representative compounds

Distinctive classes	Representative compounds
A. Pharmaceuticals	
A1. Broad-spectrum antibiotics	
1	Fluoroquinolone
2	Sulfonamide
3	Cephalosporin
4	Nitroimidazole
5	Tetracycline
6	Penicillin
7	Macrolide
A2. Hormones	
1	17-β-Estradiol (E2)
2	Estriol (E3)
3	Estrone (E1)
A3. Non-steroidal anti-inflammatory drugs (NSAIDs)	
1	Diclofenac
2	Ibuprofen
3	Naproxen
A4. β-blockers	
1	Metoprolol
2	Propranolol
3	Atenolol
4	Sotalol
A5. Blood lipid regulators	
1	Clofibric acid
2	Gemfibrozil
3	Bezafibrate
B. Personal care products	
B1. Preservatives	
1	Parabens
B2. Bactericides/disinfectants	
1	Methyltriclosan
2	Triclocarban (TCC)
3	Triclosan (TCS)
B3. Insect repellents	
1	N, N-diethyl-m-toluamide (DEET)
B4. Synthetic musks	
b1. Nitromusks	Musk moskene
1	Musk tibetene
2	Musk xylene
3	Musk ketone
4	Musk ambrette

(continued)

Table 1 (continued)

Distinctive classes	Representative compounds
b2. Polycyclic musks	
1	Celestolide (ADBI)
2	Galaxolide (HHCB)
3	Toxalide (AHTN)
4	Phantolide (AHMI)
5	Cashmeran (DPMI)
6	Traseolide (ATII)
B5. Sunscreen UV filters	
1	2-Ethyl-hexyl-4-trimethoxycinnamate (EHMC)
2	4-Methyl-benzylidene-camphor (4-MBC)
3	Octyl-methoxycinnamate (OMC)
4	Octyl-triazone (OC)
C. Endocrine disruptors (EDCS)	
C1. Pesticides	
1	DDT
2	Chlorpyrifos
3	Atrazine
4	2,4-D
5	Glyphosate
C2. Plasticizer	
1	Phthalates
C3. Food contact materials	
1	Bisphenol A (BPA)
C4. Flame retardants	
1	Polychlorinated biphenyls (PCBs)
C5. Textile/clothing	
1	Perfluorochemicals (PFCs)
C6. Antimicrobial	
1	Triclosan
D. Artificial sweetner	
1	Acesulfame
2	Saccharin
3	Cyclamate
4	Sucralose
E. Surfactants	
E1. Anionic	
1	Linear alkylbenzenesulphonic acid (LAS)
2	Sodium dodecyl sulphate (SDS)
3	Sodium lauryl sulphate (SLS)
4	Alkyl sulphate (AS)

(continued)

Table 1 (continued)

Distinctive classes	Representative compounds
E2. Cationic	
1	Quaternary ammonium compound (QAC)
2	Benzalkonium chloride (BAC)
3	Cetylpyridinium bromide (CPB)
E3. Amphoteric	
1	Amine oxide (AO)
E4. Nonionic	
1	Alkylphenolethoxylate (APE)
2	Alcohol ethoxylate (AE)

active constituent in insect repellents and is known to persist in the water bodies for long durations [120].

Synthetic musks have been used as economical substitutes for natural musks since 1930s as fragrances in wide variety of products (domestic and industrial) such as food, perfume, detergent, shampoo, cosmetics and cigarette additives [81]. Synthetic musks have been widely categorised into two groups namely, polycyclic and nitro musks. Amongst them, nitro musks were the most frequently used synthetic musks initially but eventually their usage was reduced by 1950s because of their toxic nature towards humans and environment [102]. Polycyclic musks has replaced the nitromusks, which accounted for around 85% of worldwide production whereas remaining 15% is contributed by nitro musks [18, 102]. UV filters are generally used in sunscreens, cosmetics and lotions for protecting the skin against UV radiation. Their usage has seen a surge owing to increased awareness of people regarding the detrimental health consequences caused by UV radiation. These filters are discharged into water bodies as effluents and through various water based recreational activities [18].

3.2 Endocrine Disruptors (EDCs)

EDCs has been described by the Endocrine Society, (the largest international group of scientists and physicians which work in the area of endocrinology), as: “an exogenous [non-natural] chemical, or mixture of chemicals, that interferes with any aspect of hormone action” [40]. EDCs disrupt the endocrine system by either mirroring the structure of the natural hormone or by obstructing its functional pathway. These have been characterized as artificial chemicals that either mimic or block hormones after entering the body thereby affecting its usual operation. The Environmental Protection Agency (EPA) has described EDCs as foreign factor that may interfere with the development, release, attachment, transport, activity and/or replacement of natural hormones which help in maintaining bodily functions like homeostasis, reproduction, development and behavior [109]). It is now widely accepted that the three main kinds of EDCs are estrogenic in nature and they operate by either mimicking or blocking the pathway of natural estrogens, androgens or thyroids (triggers instant or oblique consequences to the thyroid) [95]. Natural and engineered EDCs are released in the surrounding by human acts, creatures and industries; primarily passing via sewage treatment before finally being discharged into surface water, groundwater, soil and silt. Based on the aforementioned reasons, a lot of research has been carried out just on estrogenic compounds.

These compounds are found in very low concentrations (ng L^{-1} or μg L^{-1}) in wastewater. EDCs are of deep concern since their long period of exposure and effect on humans is unidentified. Today, there are more than 85,000 chemicals that are manufactured out of which thousands may just are EDCs. A list of typical EDCs along with their categories is presented in Table 1. Triclosan which is a antimicrobial compound, is widely used since decades in varieties of PCPs (personal care products) like cosmetics, soaps, shampoos, skin-care lotions and creams, deodorants, toothpastes and mouthwashes [18]. Polychlorinated biphenyl, a flame retardant, is a category of chemical compounds and are utilised in textiles, plastics, and furnishing foams. They have majorly provided towards reducing the risks of fire [72]. Perfluorinated compounds have extraordinary chemical properties such as their ability to repelwater, lipids and oil. These compounds are used in water, grease or dirt repellent platings, in sprays for leather and textiles and in non-stick cookware as PTFE (Teflon) coating [47]. Bisphenol A (2,2-Bis-(4-hydroxyphenyl)propane) is weakly estrogenic and also possesses some anti-androgenic activity [96]. It is a plasticizer manufactured in large quantities and is used in the manufacturing of polycarbonate and epoxy resins, flame retardants and unsaturated polyester-styrene resins as a monomer [99]. Its end product is applied in the platings of cans, dental fillings, and additives in thermal paper, powder paints and antioxidants in plastics [99]. Their discharge in our surrounding occurs throughout the production as well as through leaching from the end products [35]. Being a ubiquitous type of plasticizers Phthalates are widely utilised various products like cosmetic products, playing things, packaging of foods, and medical equipment. Di (2-ethylhexyl) phthalate, one of the most common phthalates, presents a definite public health concern because 100% of population of the US shows significant and detectable levels of this EDC [42].

3.3 *Artificial Sweeteners*

Being a newest group of emerging contaminants the artificial sweeteners are ate up as substitute of low-calorie sugar in large quantities in a lot of food items and drinks. Examples of these compounds include saccharin, acesulfame, sucralose and cyclamate [78]. Some of these are heat-stable like acesulfame and are used in baking. They are used in soft drinks having long expiry dates owing to their persistency in liquid [47]. Besides, certain class of sweeteners cannot be degraded by human body and become risky since these compounds may end up in large quantities in surface waters after use. This has already been shown in a study of German waste and surface waters by Scheurer et al. [87].

3.4 Surfactants

Another diverse group of chemicals viz. Surfactants (surface-active agents) which is structurally divided into two parts: first, a polar, water-soluble head and second, a nonpolar hydrocarbon tail, insoluble in water. Surfactants have higher solubility and cleaning abilities due to which they has occupied higher rank amongst the detergents and other cleaning substances [50]. A large amount of surfactants are used in various industries as well as household purpose in daily basis resulting in dispersion of them into soil, water, sediment etc. Surfactants have been classified, depending upon the charge on the head group, into cationic, anionic, nonionic and amphoteric.

Here, the most common and oldest type of surfactant is the anionic surfactants which are normally found in detergents or common soaps. Quaternary ammonium compounds (QAC) is the most commonly used cationic surfactants. They are primarily used in hair conditioners, fabric softeners and detergents. The best studied amphoteric surfactants are amine oxides (AOs). At very beginning, these were functioned as alternatives to fatty alkanolamides as foam boosters in dishwashing [16]. AOs are also used in textile industry, in rubber industry, and in deodorant bars as anti-static agents, as foam stabilisers and polymerisation catalysts and antibacterial agents respectively [94]. Nonionic surfactants are mostly used in various biotechnological processes and in facilitating solubilisation as well as increasing the carrier stability of the drug [21].

4 Conclusions

Pollutant in water is a most important topic to discuss since long back years because it is directly linked with health of the ecosystem including human beings. In current situation due to uncontrolled urbanization, industrialization and unmanaged activities, a diverse group of pollutant has been entered in our water resources. People are aware about conventional pollutant like Fluoride, Nitrate and trace metals and metalloids because their desirable and permissible standard limit are known and also the causative effects on ecosystem and human health are also well described in the literature. Since last ten years due to advancement in instrumentations techniques and detection limit researchers have discovered different types of new contaminants (emerging contaminants) in water resources which are unknown to our society. Although these emerging contaminants are measurable in different types of samples, even at present they are not usually monitored, due to the comparatively high charge of analysis and the inadequate number of experts. Scientists are trying to discover another new emerging contaminants and generating a huge number of data but very few knowledge about their fate and transport in water and their effects on organisms making it more complex. Hence regular surveys and monitoring of water resources and waste water resources should be carried out to acquire an understandable picture of these conventional and emerging contaminants. Actually we know that prevention is better than cure hence public awareness program should be initiated to alert the population about these traditional and emerging type of contaminants and their sources so that people will think about it and make some changes in their lifestyle.

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Water Pollutants: Sources and Impact on the Environment and Human Health

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Abstract Water is the most crucial commodity for life support process in organism. Water is basic and mandatory need for the humans and the entire living creature on earth. Therefore, the consumption of water by human should be safe, easily accessible, adequate and free from any kind of contamination. Pollutants in water bodies pose a severe threat to human health as well as aquatic ecosystem. There are numbers of water pollutant which has been categorized into inorganic pollutants, organic pollutants, pathogens, thermal pollution, and radioactive pollutants etc. In the current review an endeavor has been made to recognize the water pollution based on biological and chemical indicator and categorize the water pollutant on the basis of different source and origin. A brief discussion on different water pollutants, their source in atmosphere and impact on environment and human health is also done in this study. In this study a concise discussion has been done on some traditional water pollutants like nutrients (NO_3 and PO_4), Halogen (Cl, Br and F), heavy metals (Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr, Ni and Hg), organic pollutants (POPs, EDS and pesticides), and microbial pollutants. Some emerging crisis related to water pollution in recent past is like microplastic, thermal pollution, radioactive pollution and suspended solids and sediments are also included in this study.

Keywords Water pollution · Nutrients · Halogen · Heavy metals · Organic pollutants · Human health

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1 Introduction

Water is the most valuable reserve among all natural assets present on the Earth. Earth is recognized as a blue planet because of the occurrence of plentiful water on its surface [1, 2]. Owing to its exclusive structure and characteristics, water is taken as a matrix of life [3, 4]. It is projected that 97.3% of the whole water present on the earth is saline. The entire freshwater which is only 2.7% of whole water, approximately 68% is frozen in form of ice and glaciers 30% as groundwater and leftover about 1.3% is found on the surface of the earth in lake and rivers (C.G.W.M. 1990).

Freshwater, especially is very important in context to sustenance as it is required for household consumption and also as industrial and farming use. The water applied for human utilization should be "safe and wholesome" i.e. odorless, colorless, and fine in taste and liberated from dangerous chemical agents and pathogen [5]. The quality of water being used is, however, an important issue as a decrease in quality of water reduces its utility for a human being and other organisms [6].

Any alteration in the physical, chemical and biological features of water that has a destructive consequence on human health and living creatures can be expressed as water pollution [7]. Water, not only, supports a range of human actions such as drinking, bathing, and household use, irrigation etc., but also, act a key function in the biogeochemical reaction below the surface [8, 9]. In the past few decades, this scant resource has arrived at a position of crisis because of the exceptional enhancement in arguing for freshwater demand due to a remarkable amplification in population, mechanization, urbanization, and passionate farming actions [10].

Many industries causing water pollution through their effluents are sugar mills, thermal power plants, distilleries, fertilizer, and cement industries, oil refineries, paper, and pulp industries, tanneries, pesticides, pharmaceuticals, and textiles with dye and dye-intermediates [11]. Usually, these manufacturing units release their bilge water into the nearby sewage system, water bodies in close proximity or adjacent undeveloped lands which originate the environmental crisis [12, 13].

2 Indicators of Water Pollution

There are two major methods of determining the eminence of water. One is to take water samples and evaluate the amount of various constituents that it holds. If the constituents are unsafe or the values are too high, we can consider the water as contaminated. This type of evaluation is known as chemical indicators of water quality [14]. A different method to determine water excellence engages investigating the fish, insects, and other invertebrates who sustain in water. If numerous diverse varieties of living organism can survive in a water body, the class is expected to be very good; if the water bodies sustain no fish existence at all, the quality is apparently much inferior. Assessment like this are named as biological indicators of water eminence [15, 16].

2.1 Classification of Water Pollutants on the Basis of Origin

There are diverse categorizations of water pollution.

1. The two principal sources of water contamination can be observed as Point and Non-Point.

Point indicates to the contaminants that belong to a lone supply. An example of this would be effluent discharge from industries in water bodies.

Non-Point, in contrast, means contaminants coming from many sources. Polluted water after rains that has pass through numerous areas may also be believed as a Non-point source of contamination.

2. On the bases of source there are two kinds of contaminants natural and anthropogenic.

Water pollution can be categorized as having whichever natural or anthropogenic sources. Natural groundwater pollution chiefly owes to geological configuration with shallow groundwater mass, percolation from low-quality surface water bodies, salt water invasion, or owing to the consequence of geothermal fluids. Anthropogenic water pollution is normally attributed to intense application of farming pesticides and manures, mining desecrates, dumping of industrial effluents, waste dumping locations and defective well formation [17].

The ionic composition of groundwater is governed by many natural as well as human induced aspects. Natural factors which have power over water composition includes precipitation model and quantity, a geological attribute of watershed and aquifer, meteorological factors and diverse rock-water interaction courses in the aquifer [12, 13]. Human actions which manipulate the chemical composition of water comprise discarded of solid devastate, household and industrial desecrate and mining and farming actions [18]. Sources of water pollution can be either geogenic or anthropogenic. Anthropogenic activities causing pollution can be further classified into industrial, agricultural and domestic [19]. Despite the fact that industrial consumption of water is very little in comparison to farming purpose, the unmanaged dumping of industrial waste matter on land and/or on surface water bodies make water resources inappropriate for further uses [20, 21].

3 Different Pollutants, Their Sources and Environmental Impacts

3.1 Nutrients

Nitrate (NO_3^-)

Domestic sewage and animal excreta water gains N content by degradation of organic N(R-NH_2) by different pathways. Microbial enzymes degrade the organic nitrogen in ammonia. As nitrogen is a vital element for the plant growth, farmers apply a large number of nitrogenous fertilizers for the better yield but there is an imbalance between plant uptake and nitrate availability, such as application of fertilizers when it cannot be taken by plant or may be planted density is too low to absorb the nitrate, then the excess fertilizer not used by plant may get concentrated during evaporation, later contaminate the aquifer by seepage [22]. Numerous human induced actions the use of nitrogenous manure, community wastewater, septic system seepage, urban drainage discard, reject dumps, sewage ejection, industrial effluents, polluted ground, polluted sanitation performs, landfills, animal waste, and soluble nitrogen compounds contained by geologic materials—make worse the nitrate pollution [23]. The urine and dung of farming animals like cows and buffaloes [24] and deprived casings [25] have also been associated to nitrate pollution in shallow groundwater.

High values of nitrate in water are connected with health troubles like methemoglobinemia in newborns which may cause mortality by asphyxiation and stomach cancer in adults. NO_3 goes to reaction with amines and amides in the human body and forms cancer-causing nitroso compounds [26–28]. Higher nitrate incoming human body via water can cause birth imperfections and gastrointestinal diseases [29]. Nitrate toxicity in human increases by frequent boiling of nitrate-rich water for drinking, preparation of dry milk powder with high nitrate-containing water, and weaning with nitrate-rich vegetables [30].

Phosphate (PO_4^{3-})

PO_4 is a vital nutrient for plants, animals and human. It is available in three forms, that is organic phosphorous (associated with organic molecules), orthophosphate and polyphosphates. In few water bodies, the value of phosphorus is small adequately to limit the growth of algae and/or aquatic plants. In this matter, researchers state that phosphorus is the restrictive nutrient. Therefore, eutrophication and water excellence is sustained by calculating the access of the PO_4 [31]. Natural disintegration of rocks and minerals, farming discharge, erosion and sedimentation and through input by animals is the non point sources, while point sources are sewage wastewater and industrial effluents [32]. A little concentration of PO_4 may boost the development of algae and aquatic plants directing to eutrophication of the aqueous ecosystem. PO_4 in water may cause algal bloom development in water bodies [33, 34].

3.2 Halogens

Commonly, halides present in natural water are chloride, fluoride, bromide and iodide. These ions are highly soluble and present in all natural water sources i.e. lake, streams, rivers and groundwater. The source of halides includes hard rock weathering, industrial runoff, pesticides and fertilizers etc. Chloride and bromide are conservative in nature and their ratio is used as the source of salinity in coastal aquifers. The conservative nature of these elements reduces the biological uptake as well as sedimentation [35].

Fluoride (F^{-})

Fluoride is the highest electronegative element among all the chemical elements. It has an affinity to form fluoride ion in the solution. It is found in only solid salt and ion in aqueous solution as it is very reactive [36, 37]. Fluoride is found in almost all type of water from trace to high concentration. Various factors such as temperature, pH, and solubility of fluoride bearing minerals impose the impact on the concentration of fluoride in the water. Fluoride contamination in groundwater is a common problem in semi arid and arid climate having alkaline soil and crystaline igneous rocks [36, 38]. Geogenic sources mainly from igneous (granite) and metamorphic (gneisses) rocks are considered as the primary source of fluoride in groundwater [39]. Fluorite, apatite, mica, amphiboles and some clay are the fluoride wearing minerals. Moreover anthropogenic sources also contribute fluoride in water such as chemicals used in agriculture and bricks industries [40].

Both the lower (0.6 mg/l) and upper (1.5 mg/l) limit of fluoride in groundwater have heath effects. Very low limit of fluoride (<0.6) in drinking water leads to tooth decay while consumption in higher concentration (>1.5 mg/l) causes dental fluorosis even more concentration (>3 mg/l) leads to skeletal fluorosis [41]. Due to high concentration of fluoride in water about 62 million people in India including 6 million children suffers from fluorosis [42].

Chloride

Ion exchange processes, halite dissolution, precipitation, farming overflow, untreated effluents from industries, sewage wastes etc. are source of chloride in water resources. Owing to extremely less or insignificant biological uptake of chloride my cause higher chloride concentration once it released in water. The dichloromethane present as a byproduct during conventional water chlorination procedures and other carcinogenic substances by reacting with naturally occurring compound [43, 44]. High values of Cl in water disgrace the water quality. It also contributes to the corrosion of many metals, including man-made structures, such as dams.

Bromide

Naturally, bromide enriched in water as inorganic salt in natural water resources. In fresh water, bromide concentration may naturally derive from rainfall, but significant level may be caused by the combustion of leaded gasoline containing ethylene dibromide. The elevated level of bromide caused due to industrial dumping and agricultural runoff. Bromide is conservative in nature. Due to its conservative nature, it has been used as an indicator of saltwater intrusion and source of salinity and contaminant in coastal aquifers [44, 45]. But high concentrations of Br may cause fatal consequence on aquatic organisms. The impact of high bromide in plants can cause the stunted growth and poor germination.

3.3 Heavy Metals

Heavy metals are regarded as a metal or metalloid having high atomic weight and specific density and are often assumed as toxic even at very low concentrations [46]. The heavy metal sources may be geogenic or anthropogenic. Chemical weathering of rocks with their constituent minerals, decomposing vegetation and animal matter and also atmospheric dry or wet deposition is natural sources. Anthropogenic sources such as mining, discharge of industrial effluents, industrial emissions (both in elemental or compound form), fertilizers used in agricultural activities, roadside and automobiles etc. are considered as prime contributors for heavy metal contamination in water [47].

Iron (Fe)

Fe found in soil and minerals mainly as insoluble ferrous oxide and iron sulphide form. CO_2 present in groundwater react with ferrous carbonate and release Fe^{+2} in solutions form [48].

$$FeCO_3(s) + CO_2 + H_2O = Fe^{+2} + 2HCO_3^-$$

Weathering of Fe iron from silicate minerals is a time-consuming process, but near surface weathering of Fe containing silicate may produce an accumulation of ferric oxide and ferric hydroxide. High concentration of Fe in water is owing to the organic material of municipal household waste and occurrence of Fe minerals in the soil/weathered material favorable for the reduction of ferric iron into ferrous iron in the circulating water (Raju et al. 2010).

The brown color of groundwater after extraction from the aquifers is the main problem in the Fe containing water. The color of water turned into cloudy and then brown caused by $Fe(OH)_3$ precipitation The reducing environment producing by the organic matter degradation. The solubility of Fe-bearing minerals boost in reducing conditions. It directs to increase in Fe concentration [49]. High concentration of Fe in water originates awful taste, staining, turbidity and equipped problem in water supply. High concentration of Fe in water may cause red rot disease. Red rot disease is caused by bacterial precipitation of hydrate oxide of ferric ion. Iron containing water has clear appearance when pumped but when it get exposed to air, water become rusty and turbid due to the precipitation of iron by oxidative process [50]. The undue ingestion of Fe may direct to chronic intoxication while the unnecessary ingestion of Mn can causes lung embolisms, bronchitis, impotency, and nerve dent, even to the point of Parkinsonism [51].

Arsenic (As)

Ar is a broadly dispersed metalloid, taking place in rock, soil, water and air. Inorganic arsenic is found in groundwater applied for drinking in numerous countries all over the globe. Smelting of non-ferrous metals and the manufacturing of power from fossil fuel are the two key industrial procedures that direct to arsenic pollution of water and soil. Currently, very large population is affected by arsenic contamination worldwide, therefore, the toxicity problem arising from its contamination in drinking water is a matter of global concern [52]. The World Health Organization (WHO) and U.S. EPA have suggested 10 μg/L of arsenic concentration in drinking water as the safety limit for human consumption.

Both natural and anthropogenic sources are responsible for arsenic contamination into surface and groundwater. Arsenic is a rare crystal element constituting approximately (0.00005%) of the Earth crust [53]. The arsenic content in soils of different countries has been reported to range from 0.1 to 40 mg kg^{-1} with an average value of 6 mg kg^{-1} (Bowen 1979). Its higher concentration present in certain minerals such as pyrite (up to 5–10% by weight) causes its release in environment. In addition to its natural occurrence, many microbes in nature transform arsenic into various oxidation states. During anaerobic respiration certain microbes respire As (V) and release As (III) in surrounding groundwater [54]. Among anthropogenic sources mining operations, copper smelting industries, fossil fuel burning and other combustion processes are known to release arsenic into environment. Presence of arsenic containing sulfide minerals has significantly contributed to its release into the environment [55]. Arsenic has been commonly used in variety of dyes, paints, herbicides, pesticides, insecticides, wood preservatives and animal feeds [56].

Inorganic arsenic is extremely noxious and ingestion of big magnitude directs to gastrointestinal signs, cruel anarchy of the cardiovascular and central nervous systems, and ultimately death. In survivors, bone marrow despair, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy may be experienced. Populations exposed to arsenic via intake water confirm intemperance risk of death from lung, bladder and kidney cancer, the risk rising with escalating exposure. There is also an augmented threat of skin cancer and other skin lesions, such as hyperkeratosis and pigmentation alterations. Arsenic (As) is a notorious carcinogenic element and its intake severely affects various human organ systems including hepatic system, cardiovascular system and central nervous system (Farrell et al. 2001) [57, 58].

Manganese (Mn)

Mn is found in the association of Fe because chemically it is very similar to Fe. Mn is an essential element. Mn is found in manganese dioxide form in the soil. Manganese dioxide is very insoluble in water containing CO_2. Mn is positively correlated with Fe and it is an essential component of plants and animals [50]. Ferromagnesium minerals release the Mn in groundwater. High concentration of Mn causes damage of central nervous system.

Zinc (Zn)

Zn is also an necessary trace element acting as a micronutrient for human health. Zn is essential for male reproductive activity therefore consider as masculine element [59]. Zn is also helpful for plant growth as it reduces the Ni toxicity and increase ATP/chlorophyll ratio [60]. Zn is utilized as an anticorrosion agent where it is layered on iron pipelines to shield them against corrosion. Galvanized pipelines are utilized during the construction of the boreholes [61]. It acts a significant function in the development of male reproductive system, therefore, considered as the masculine element. It also serves as a co-factor for a number of enzymes for their activation such as carbonic anhydrase. Deficiency of Zn may cause anaemia, growth and reproduction impairment, when consumed in excess it causes toxicity which includes irritation, muscular stiffness, loss of appetite, nausea, etc. Though, Zn is an essential element but high concentration causes muscular stiffness, nausea and loss of apetite [62].

Copper (Cu)

Copper is a vital trace element which helps in human, animal and plant metabolism. The natural source of Cu in water is probable enrichment from aquifer resources such as feldspar, biotite, and muscovite minerals. Sometimes, the corrosion of copper pipes becomes the major source of Cu in drinking water. Organic and inorganic compounds of copper are extensively applied as farming pesticide sprays. The big amount of Zn intake may cause Wilson's disease. High concentration of Cu causes discoloration and corrosion of pipes and utensil and amplifies the risk of lung cancer in human [48].

Aluminum (Al)

Al is the third most plentiful element present in the earth's crust [63]. Al found naturally in the environment. Mining and handing out of Al raises its amount in the environment. The mobilization of noxious Al ions, consequential from transform in the pH of soil and water owing to the acid rains and rising acidification of the neighbouring atmosphere, has an undesirable consequence on the environment [64]. Al in elevated values is extremely noxious for aquatic animals, particularly for gill breathing living such as fish, originating osmoregulatory collapse by decimating the plasma and hemolymph ions [65]. Metabolic path in the living organism concerning Ca, PO_4, F and Fe metabolism are influenced by Al. Al has been establish to be very injurious to nervous, osseous and hemopoietic cells [64].

Lead (Pb)

The increasing concentration of Pb in water may be due to the liberation of Pb adsorption of marine sediments, from dust transferring via atmosphere and continental shell erosion (chemical weathering), precipitation and deposition of airborne aerosols containing Pb (Hem 1991) [61, 66]. Commercial products such lead storage batteries, electroplating, constriction material, ceramic and dyes, paints, glassware and gasoline are the main source of the lead in the environment [67]. Low concentration may be harmful to the human if taken for a long time period as it stored and accumulated in bones [68]. Lead is a non-biodegradable and a teratogen which is extremely harmful as it can cause cardiovascular diseases and damage the central and peripheral nervous system (Singh et al. 2011). Toxicity of Pb, also known as lead poisoning, can be either acute or chronic. Acute contact can cause thrashing of hunger, headache, hypertension, abdominal pain, kidney dysfunction, tiredness, insomnia, arthritis, hallucinations and dizziness. Chronic exposure of Pb may cause intellectual retardation, birth faults, lunacy, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain injure, renal dent and may even cause death [69, 70].

Cadmium (Cd)

Cd found naturally in ores jointly with Zn, Cu and Pb. Cd compounds are utilized as stabilizers in PVC commodities, colour pigment, numerous alloys and, now most frequently, in re-chargeable Ni-Cd batteries. Metallic Cd has chiefly been utilized as an anticorrosion agent. Cd is also found as impurities in phosphate fertilizers. Cd is associated with Pd minerals so Pd mining is a source of Cd in the groundwater [70]. Tobacco is the key source of Cd intake in smokers as tobacco plants, like other vegetations, can take Cd from the soil [67]. High concentration of Cd causes renal dysfunction, kidney damage and gastrointestinal disorder. Long term exposure of Cd may also causes Cancer. Premature birth and reduced birth weights are the problems that occur if Cd exposure is elevated during human pregnancy [71].

Chromium (Cr)

Chromium is a naturally found element in rocks minerals and very much persistent in water sediments. Chromium is present in two oxidation states +3 and +6. Cr (+6) is more toxic to Cr (+3) as its rate of adsorption is high [50]. The higher content of Cr is found in ultramafic igneous rocks. Chromite is concentrated in the residues of laterite which is underlying the ultramafic rocks. Industrial sources of Cr comprise shielding metal coatings, metal alloys, magnetic tapes, paint pigments, rubber, cement, paper, wood preservatives, leather tanning and metal plating [70]. Chromium based dyes are one of the chief source of contamination in soil and groundwater. Chromium (VI) compounds are extremely noxious and carcinogenic in nature. Chromium (III), in contrast, is vital nutritional supplement for animals and humans and has a significant function in glucose metabolism [67]. Contact to elevated values of chromium compounds in humans can direct to the reserve of erythrocyte glutathione reductase, which in turn diminish the ability to reduce methemoglobin to hemoglobin [72].

Nickel (Ni)

In aqueous chemistry Nickel is considered with Ni^{2+} oxidation state. It substitutes the iron in ferromagnesian igneous rock mineral. It coprecipitates with the oxides iron and manganese. Ni is largely used industrial element for making stainless steel. WHO (1993) prescribed 20 µg/l Ni as permissible limit for drinking purpose. It is an essential trace element in lesser amount but uptake in of large quantity may cause cancer in lungs, nose, larynx and prostate, respiratory failure, asthma, birth defects, heart disorders and renal and skin diseases.

Mercury (Hg) [73]

The Hg amalgam cinnabar was applied in ancient cave painting for red colours, and metallic Hg was recognized in early Greece where it was applied as a beauty product to improve the skin color. Metallic Hg is utilized in thermometers, barometers and appliances for determining blood pressure. A chief application of Hg is in the chloralkali manufacturing, in the electrochemical practices of Cl production, where Hg is applied as an electrode [74]. Inorganic Hg is transformed to organic compounds, like CH_3Hg, which is extremely stable and accumulate in the food web. Methylmercury is a neuro toxic compound which is accountable for microtubule damage, mitochondrial harm, lipid peroxidation and gathering of neurotoxic molecules like serotonin, aspartate, and glutamate [75, 76]. Acute mercury contact may give go up to lung damage. Chronic poisoning is considered by neurological and psychological symptoms, such as tremor, change in behaviour, agitation, nervousness, sleep anarchy and sadness. Metallic mercury is an allergen, which may cause contact eczema, and mercury from amalgam fillings may give increase to oral lichen [67, 77]. The Minamata tragedy in was initiated by methyl mercury poisoning from fish infected by mercury discharge to the neighbouring sea.

3.4 Organic Pollutants

Organic pollutants broadly alienated into two categories: oxygen demanding waste which is degraded by bacterial activities and another one is synthetic organic pollutants which cannot be degraded by the bacterial actions. The effluents and waste water from domestic outlets, municipal sewage, canning industries, food processing units, butcheries, paper and pulp industries, tanneries, breweries, distilleries, etc. have significant amount of biodegradable organic compounds in all forms, suspended, colloidal and dissolved. These pollutants consume whole oxygen present in the water body and create anoxic condition in the ecosystem. Moreover, synthetic organic pollutants are not biodegradable and stay in water body for an extended duration. Synthetic organic pollutants comprise synthetic pesticides, synthetic detergents, food additives, pharmaceuticals, insecticides, paints, synthetic fibers, plastics, solvents and volatile organic compounds (VOCs). Synthetic inorganic cation exchange materials are excessively applied in elimination of radioactive cations from water is also one of the sources of the organic pollution in water body [78].

Among the organic pollutants some of the poses a immense risk to aquatic animals, plants, and humans are dyes, cosmetics, petroleum organic pollutants. They can cause chemical burns, nausea, convulsions and direct to chronic health turmoil with carcinogenic property.

Persistent organic pollutants (POP’s)

A compound is usually defined as a POP if it shows the subsequent 4 features:

1. Determined in the environment, i.e. chemical, photochemical, and biological alteration processes do not direct to a considerable elimination of the compound in any environmental compartment;

2. Prone to lengthy transfer, therefore to global circulation, yet in isolated areas where the compound has not been utilized or dumped, due to the compound's physical-chemical properties;
3. Bioaccumulative during the food web; and
4. Noxious to living creatures, together with humans and wildlife.

POPs containing polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins, organochlorine pesticides (OCPs), perfluorooctanoate (PFOA), polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonate (PFOS) has been traced into the river and costal aquifer [79]. PCBs in rivers and coastal aquifer may cause possible human health hazard [80]. It is known that Dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) has been applied as pesticides in the agricultural function but now it is banned by the government due to its toxic and carcinogenic effects. But new sources of DDTs and HCHs have investigated and associated to local usage of lindane, dicofol, and DDT-containing anti-fouling paints [79]. In the perspective of global water contamination, POPs create a rigorous crisis chiefly because of their great bioaccumulation and biomagnification prospective in aquatic food webs [81].

3.5 Endocrine Disruptive Chemicals (EDC)

One of the emerging organic pollutants groups is Endocrine disruptive chemicals which create the hormonal imbalance affecting the normal homeostatic reproduction, development or behavior. These also caused irregular endocrine behavior and amplifies cancer hazard in human [82].

Pesticides

In the previous 4 decades, the utilization of pesticides has amplified considerably all over the world. It endeavours at safety of crops from pest invasion to attain elevated crop yield with improved features [83]. An approximate amount of 2.5 million tons of pesticides is applied in the world yearly with incessant augment [84]. An approximate quantity of merely 0.1% of pesticides used arrive at the objective organisms and the residual 99.9% go away through air, soil and water, therefore consequential in the pollution of natural ecosystems and distressing human health [84]. Clinical features like headache, vomiting, dizziness, muscle weakness, shortness of breath, skin rash and burning sensation in the urinary tract owing to pesticide contact have been founded in human [85].

Dyes: Now a days industry are heavily using dyes, water soluble toxic chemicals. Dyes are generally used in textile, food, paper, leather and tanning industries to give color code on products [12, 13]. The untreated effluents of these industries are continuously contaminating the water and soil. This is the reason that humans are getting affected to this toxicity by consuming the vegetables, fruits and grains which have sown in soil and irrigated by water contaminated by dyes. The use of colored papers, towels in wiping body and in cooking is an additional way of revelation to human [86]. Dyes are considered as one of the carcinogenic and mutagenic chemicals.

3.6 Microbial Contaminants

Pathogens enter in the water through various sources such as sewage discharge, industrial wastewater. Virus and bacteria such as *Cryptosporidium*, *Campylobacter*, *Salmonella*,

Shigella, can lead into water born diseases. Cholera, typhoid, dysentery, polio, hepatitis are some of the common diseases which are seen in human beings caused by the water pollutants.

Exposed water is easily contaminated by saprobic microorganism when comes under the contact of air, soil and sediments [87]. Microbial contagion of water can be identified by inspection for few organisms counting heterotrophic bacteria, coliforms, and *Escherichia coli* in such samples. Microbial contamination is more in lake water and abundant in heterotrophic bacteria [88]. Some of the studies have shown that, contamination by *E. coli* and coliforms were beyond the allowable limit in the stagnant water bodies. Untreated disposal of sewage into water body and human excreta has induced the high level of pathogens in the water ecosystem. Some of the common examples of the water pathogens are under fecal contamination are total coliforms, *Escherichia coli*, fecal coliforms, fecal streptococci/enterococci, coliphage, and *Clostridium perfringens*. Coliforms are parts of the family Enterobacteriaceae. The 38 Water Challenges of an Urbanizing World are facultative anaerobic, Gram-negative, nonsporing, rod-shaped bacteria that ferment lactose with gas formation within 48 h at 35 °C. Humans and animals are one of the biggest sources of fecal contamination.

3.7 Micro Plastics

Microplastics are tiny plastic piece <5 mm lengthy which can be destructive to our sea and marine life. Microplastics can be classified by their origin. There are two key varieties, primary and secondary. Primary microplastics are firmly made to be that size, on the other hand secondary microplastics are minute piece of plastic that crack down from bigger pieces. The complexity with microplastics is that they are so tiny that they are generally not pulled out up by water filtration and make it out into rivers and oceans. Microplastics are awful for the reason that fish and other aquatic animals eat them and they die or have health troubles [89].

Microplastics are physical risks to organisms if ingested. The effects comprise obstruction of the intestinal tract, reticence of gastric enzyme discharge, condensed feeding stimulus, and diminish steroid hormone levels, interruption in ovulation and malfunction to reproduce [90, 91]. The high surface area to volume ratio of microplastics makes them an efficient carrying medium for noxious contaminants, for e.g. trace metals and persistent organic pollutants (POPs), additionally endangering human health and marine wildlife [92].

3.8 Accidental Oil Leakage

The utilization of oil or of other natural resources without wastage is impracticable; wastage happen in operation, shipping, refinement and utilization. Oil spill create a great concern as a big quantity of oil go into the sea and does not dissolve with water; thus opens trouble for local marine wildlife such as fish, birds and sea otters. For example a ship shipping a big amount of oil may spill oil if meet with an accident and can cause unreliable harm to species in the ocean depending on the amount of oil spill, size of the ocean, the toxicity of contaminant [93]. Being less weight than water it extends above the facade of water, unravelling the exposure of water with air, therefore ensuing in decline of DO. This contaminant is also accountable for endangering water birds and coastal plants owing to shell of oils and unfavourably disturbing the usual activities. It in addition results in drop of light diffusion through surface waters, thus dipping the photosynthetic action of the aquatic plants. Oil contains polycyclic aromatic hydrocarbons (PAH), a few of which are identified as carcinogenic [94].

3.9 Suspended Solids and Sediments

The idiom suspended solids (SS) refers to the amount of inorganic and organic matter, which is detained in the water column of a waterway, river, pond, lake or dam by instability. SS classically contain particulate matter with a diameter of <62 mm [95]. The consequence of SS on aquatic biota is reliant on 4 key factors, these comprise: (1) the quantity of SS, (2) the period of contact to SS quantity, (3) the geochemistry of SS and (4) the particle-size allocation of SS. Attendance of suspended solids can obstruct the sunlight infiltration in the water, which is necessary for the photosynthesis by benthic flora. Finer suspended solids may harm the gills of fishes and originate asphyxiation [96].

3.10 Thermal Pollution

Thermal pollution is the release of hot water from industry in water body which disturb the normal aquatic life and hydrogeochemical processes of the water body. Substantial thermal pollution consequence owing to release of hot water from thermal or nuclear power stations, and factories where water is utilized as coolant. As an outcome of hot water exonerate, the hotness of water body amplify. Ascend in temperature diminish the DO content of the water, disturbing negatively the aquatic existence. This modifies the spectrum of organisms, which can approve to live at that temperature and DO point. When organic matter is also found, the bacterial feat amplifies owing to increase in temperature; therefore, ensuing in speedy diminishes of DO. The release of hot water directs to the thermal layering in the water bodies, where hot water will stay on the upper level [97, 98].

3.11 Radioactive Pollution

Atomic energy is basis of clean-air and carbon free electricity but the radioactive ion contamination that is originated from, e.g., tailings and heap leakage remains of uranium mining (such as ^{226}Ra ions), nuclear fusions derivatives (such as ^{90}Sr), nuclear weapon tests, medical research and leakage and accidental explosions in the nuclear reactors can create a long-term effect in the form of a serious threat to human health [99, 100]. Nuclear power plants and industrial effluents are the source of radioactive pollution in water. The fission process released huge energy and this energy travels in the form of waves and even little bit of this is enough to cause damage in human cells, tissues and organs. These harmful waves cannot be treated physically, chemically and biologically. Radioactive effects persist in the environment for extended duration depending upon the elemental half-life [101].

Geologically long term deposition of all elements including radioactive minerals get exposed to the geological agents after weathering and erosion and radioactive elements get mobilized with time. The weathering rate depends on the mineral composition, environmental condition and geological agents also [102]. Minimum trace of radioactive element associated with all groundwater depending upon the geological rock and strata of that area.

Radionuclides either natural or artificial have been present in water due to their radius size and decay byproducts. Some of the examples of radioactive elements emitting low radiation energy are potassium-40 (^{40}K), tritium (^{3}H), carbon-14 (^{14}C), and rubidium-87 (^{87}Rb). While emitting high radiation energy alpha particles are radium-226 (^{226}Ra), the daughters of radium-228 (^{228}Ra), polonium-210 (^{210}Po), uranium (U), thorium (Th), radon-220 (^{220}Rn), and radon-222 (^{222}Rn), also present in trace amount in the water [103]. Among the oxo-anions, the pertechnetate (TcO_4^{2-}) ion, has significant attention as technetium isotope (^{99}Tc) is a radioactive element with a very high half-life time (2.1 * 10^5 years). In fission field, ^{99}Tc is byproduct of nuclear fission of ^{235}U or ^{239}Pu with a high fission yield [101].

4 Conclusion

Natural water is a vivacious chemical arrangement comprising in its composition a complex collection of gases, mineral and organic essences in the appearance of true solutions, and suspended and colloidal matters also. There are various natural and anthropogenic factors that affect the basic physical, chemical and biological properties of natural water. Among them waterborne pathogens and chemical contaminants are major concern for public health on local, regional and global scale, not only with respect to morbidity and mortality but by the high cost of their prevention and treatment. At present, the continuous rise in concentration level of these pollutants which reached up to alarming level, making the environment and habitat unsuitable to survive. The maintenance of quality water and its safety is an important to avoid long-term irreversible effects on human health. In this review we reviewed various water pollutants, their source in atmosphere and impact on environment and human health. Nutrients like NO_3 and PO_4 are responsible for eutrophication and poses various health impacts on human health are arise mainly from agricultural activities. The source of halogens in water is both natural and anthropogenic. Heavy metals in water come mainly through industrial activities but some heavy metals like, As and Cr are geogenic also. Microbial pollutants in water bodies are come mainly by human excreta and poses serious health consequences on human health. Radioactive pollution, thermal pollution and suspended soiled are the new dimensions in the field of water pollution also briefly discussed in this study.

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Analytical Methods of Water Pollutants Detection

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Abstract Due to the urbanization and industrialization, new pollutants have been reported in the water bodies and explored for understanding the status of this contamination. Surveying and managing these related natural hazards are getting overall consideration. In some cases, the concentration of these pollutants is higher as well as lower (in the range from ng/L to μg/L). Therefore, it requires highly sensitive and particular multicomponent-concurrent-investigation, which is imperative for distinguishing and evaluating these pollutants. The most imperative, but as often as possible ignored, advancement in water contamination control programs is the ideal structure of the water quality estimation programs. The plan of water quality surveillance and checking programs is to pursue a stepwise methodology, given a rationale conspire. This incorporates (a) meaning of short and long-haul targets, (b) determination of parameters of an investigation, and destinations and recurrence of estimation, and (c) choice of strategies for examination and information handling requirement. By following this protocol and making a preliminary model, will help in the better investigation that will accomplish the objectives. The cost-viability investigation may additionally tune the estimation program and related model. Ultimately, the result of this strategy will be optimized that results in good plans with the defined objectives. Discoveries of past research and contextual analysis investigations deal with a logical approach that joins solid phase extraction (SPE) and fluid chromatography—pair mass spectrometry (LC-MS/MS); this is an adaptable and dependable technique for recognizing and measuring contaminations in stream water and wastewater tests. Thus, this chapter focuses on analytical methods such as Mass Spectrometry, Solid Phase Extraction, Chromatography (HPLC/GC), and spectrophotometry.

Keywords Water pollutants · Solid phase extraction · Spectrophotometry · Chromatography

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1 Introduction

The world is confronting imposing difficulties in satisfying rising needs for clean water as the accessible supplies of freshwater are under serious worry because of broadened dry spells, general public development, progressively stringent wellbeing based guidelines, and contending requests from an assortment of users [1]. Access to adequate, sheltered and reasonable freshwater is imperative for human improvement and has been proclaimed by the United Nations (UN) as an essential human right. Currently, more than 1.2 billion people need access to acceptable clean water supply, and over 2.4 billion people do not have adequate sanitation [2, 3]. The World Water Vision reported an emerging water crisis in 2000 [4]. As a result of the risky supply of water, more than 2.4 million people (mostly children) bit the dust from water-related diseases each year [2]. The fact that more than one nation shares many water resources further exacerbates the situation, and many people fear that future 21st-century wars will be fought over water, not oil [4].

The fast-monetary development has additionally displayed extraordinary difficulties to water asset administrators, inferable from developing an interest for water and the shortage of accessible assets, combined with serious water contamination and other water-related natural concerns. Water contamination is extremely influencing individuals' wellbeing and personal satisfaction. It has also turned into a noteworthy currency improvement limit, with a forecast loss of financial movement in the US$14–27 billion request per year [5]. Water contamination makes a circumstance where both agrarian and recreational clients of water can be presented to huge well being dangers because of natural and inorganic mixes. Given the importance of consumable water in both created and creating nations and the concern about the adequacy of flow tests in meeting the expanding needs of all water clients, there is an unmistakable requirement for the advancement of imaginative new advances and materials whereby challenges related to safe drinking water management can be addressed [3].

2 Problem Statement

Industrial procedures have been known to create vast amounts of effluents that contain huge amounts of overwhelming harmful metals and natural pollutants. The existence of these organic (for example POPs, relentless organic poisons) and inorganic (for example cadmium, lead, chromium, mercury, arsenic, nitrates, and perchlorates) contaminants in water sources has tremendous public health, environmental and financial impacts [3]. These water contaminants have been related to high expenses as far as observing and expulsion from drinking water. They have additionally influenced antagonistically groundwater, business angling, recreational and social exercises related to streams, lakes and marine waters [6]. Therefore, the analysis and remediating of these poisons in our rare water assets are fundamental.

Minimal effort, quick, easy to utilize and convenient techniques which can discover pertinence in both provincial and urban settings will lighten the weight brought about by these poisons. The customary momentum strategies used to screen natural and inorganic water contaminations are, for the most part, chromatography and spectrometry.

3 Water Scarcity and Quality

As indicated by the Food and Agriculture Organization (FAO), the earth contains an expected 1351 million cubic km of water. Just 0.003% of this is delegated new water assets appropriate for drinking, cleanliness, farming, and industry. Anyway, crisp water is, in some cases remote from human advancement or too hard to even think about capturing for use [7]. FAO likewise detailed that the total populace is developing at a rate of about 1.2% per annum and is relied upon to increment by two billion by 2030. This suggests giving sufficient water to everybody will be a noteworthy test as different factors; for example, environmental change will no doubt irritate the circumstance.

The World Health Organization (WHO) additionally detailed that freshwater is a restricted asset, and its quality is under steady weight, consequently saving its quality is vital for drinking, nourishment creation, and recreational purposes. The proximity of irresistible operators, poisonous synthetic compounds and radiological hazards can undermine water quality, making it dangerous for residential use and general condition. There are currently countless people without access to safe water, even though the UN has declared this a fundamental right. To bear the cost of everybody this right, the world has promised to lessen the extent of individuals without reasonable access to safe drinking water and essential sanitation significantly as one of the Millennium Development Goals (MDGs) [8]. This is because the absence of water to address day by day issues is a reality today for one out of three individuals around the globe. All around, the issue is deteriorating as urban areas, and populaces develop, and the requirements for water increment in agribusiness, industry, and households [9]. It has been accounted for that the interest for water has been developing at more than double the rate of populace development in the only remaining century consequently an expanding number of districts are constantly shy of water [10].

4 Water Pollution

In early human progress, water was perceived as an image for the beginning of life and its restorative esteem, yet it was not assigned as a bearer of diseases. The disclosure made by Anton van Leeuwenhoek while utilizing a magnifying instrument began to change the impression of immaculateness which engaged researchers to see past the suspended particles from the modest material particles to the miniaturized scale organisms [11]. This changed the comprehension of unadulterated drinking water. As of now, it is apparent that the accessibility of water through surface and groundwater assets is turning into a major test because of contamination by harmful synthetics because of industrialization and urbanization. This further restricts the measure of accessible consumable water.

Various reports are accessible on the antagonistic impact on human wellbeing because of poor water quality now and then with genuine outcomes, including death [12]. Examples incorporate the flare-ups of loose bowels and cholera because of microbial sullying, and these could be diminished by access to safe drinking water. This is because water is one of the key media by which toxins transmit consequently it is of extraordinary significance to screen its quality to get profitable data on the poisons' transmission chain which can be utilized to demolish or remediate water bodies by proficient water contamination control [6]. Synthetic concoctions of various sorts have turned into a worldwide issue influencing human and ecological wellbeing over the limits of nations, districts, and economies. Once discharged into the earth, they may experience short or long-range transport because of characteristic natural procedures. They possibly changed into different synthetic substances and may cause neighbourhood, territorial as well as worldwide defilement, uncovering people and natural life and sometimes, causing poisonous effects [13]. Pollution brought about by these engineered synthetics is one of the major ecological issues since some of them have interminable lethality and they bother endocrine frameworks of living beings, produce cancer-causing impacts, and may influence the generation of organisms [6]. This is one reason why these toxins must be observed and managed productively.

Safe drinking water rules are presently set up worldwide to screen the nature of water. Water that agrees to the drinking water gauges is viewed as sheltered and does not represent a huge wellbeing hazard over a lifetime of utilization [14, 15] while levels higher than the suggested models can have genuine ecological and wellbeing impacts. It is along these lines essential to keep poison levels as low as conceivable to meet the MDGs set by the United Nations [11].

The World Health Organization (WHO) norms portray sensible least necessities of safe practice to secure the strength of consumers [14]. According to WHO, it is desirable over consider the rules with regards to nearby or national natural, social, efficient and social conditions [14]. The fundamental explanation behind not advancing the selection of universal measures for drinking water quality is the preferred standpoint given by the utilization of a risk—advantage approach (subjective or quantitative) in the foundation of national gauges and guidelines. Along these lines, the nature and type of drinking-water benchmarks may shift among nations and locales. In South Africa (SA), the nature of the local supply that is viewed as safe for human utilization is guaranteed by checking for consistency with the South African National Standard (SANS 241) [12]. In request to meet these rules, solid, quick and shoddy innovations ought to be grown subsequently the improvement of new and touchy multifunctional sensors in this work.

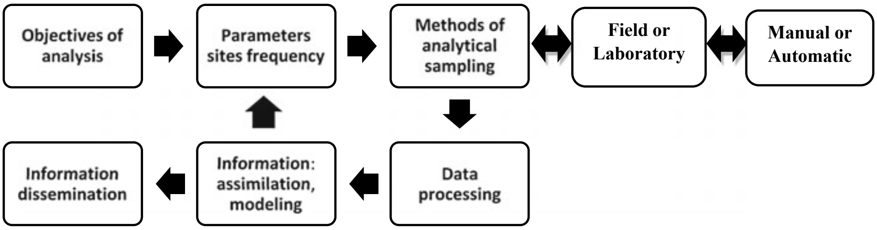


Fig. 1 Outline of a stepwise technique for the ideal plan of estimation frameworks [43]

5 Design of Measurement System

A stepwise technique for the ideal plan of estimation frameworks is given in the stream outline appeared in Fig. 1.

6 Analytical Methods Used for the Detection of Pollutants in Wastewater

In most of the time, the methods utilized for the identification of organic compounds are unique about those utilized for heavy metal contaminants. As already chromatographic techniques are typically utilized for the examination of organic compounds while atomic spectroscopic strategies are utilized for heavy metal investigation. To be noted, electrochemical methods can be utilized for the two kinds of pollutants.

6.1 Electrochemical

Ordinary strategies like, chromatography requires specialized pre-treatment, which may conceivably mean tedious procedures. In this unique situation, electrochemical biosensors have turned out to be valuable apparatuses to recognize little sample volumes, fewer convergences of biological components, and some of the reduced analytical gadgets [16, 17]. Continuous progress has been made in the manufacture and use of electrochemical biosensors for agri-food, biomedical and ecological tests [18]. Electrochemical-based procedures for detecting poisons can be sorted as conductometric, coulometric or amperometric, voltammetric (fusing pre-concentration and stripping steps), and potentiometric.

The capacity to structure exceptionally explicit acknowledgement makes biosensors an appropriate option in contrast to conventional chromatography-based techniques [19]. Electrochemical biosensors have several advantages among

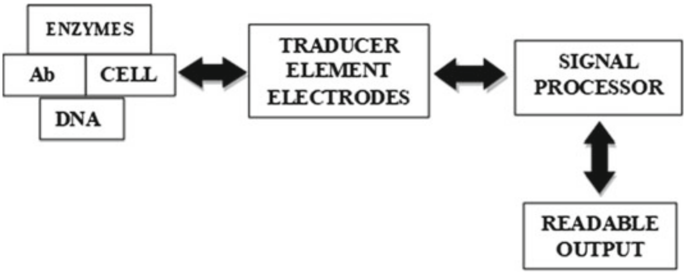


Fig. 2 An electrochemical biosensor plan. Components of organic detection are connected to terminals. These transduce the flag into a reporting yield [19]

existing biosensors, such as real-time monitoring, miniaturization and sensitivity and selectivity improvement. Moreover, electrochemical responses convey electrical signals, so the use of complicated signalling components is not important. This encourages the improvement of compact clinical testing frameworks and monitoring of the local environment [16]. Biosensors that utilize electrodes permit the change of organic signs into a decipherable yield flag. The affectability and selectivity of these signs can be accomplished using adjustment with explicit natural components, for example, DNA, cells or enzymes (Fig. 2). Figure 3 represents four distinct classes of biosensors and sub-classes, depending on the transducer type. Because of the idea of organic alteration, electrochemical biosensors can be called either biocatalytic or partiality sensors. With organic components that are

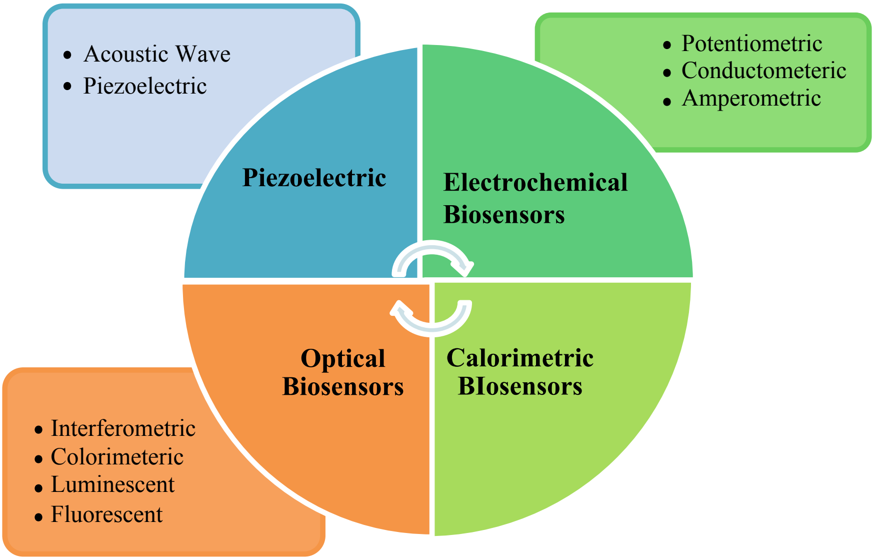


Fig. 3 Four distinct classes and sub-classes of biosensors based on the transducer

ready to perceive an objective and activate an electroactive molecule reaction (e.g. compounds), electrochemical biocatalytic sensors are changed. Then, electrochemical tendency sensors have a component of coupling recognition that releases a flag when coupling it to the target (e.g., antibodies) [20]. The use of biosensors to detect harmful overwhelming components in the environment, together with Pb, Cd, Hg, and Cu, is widely available [21].

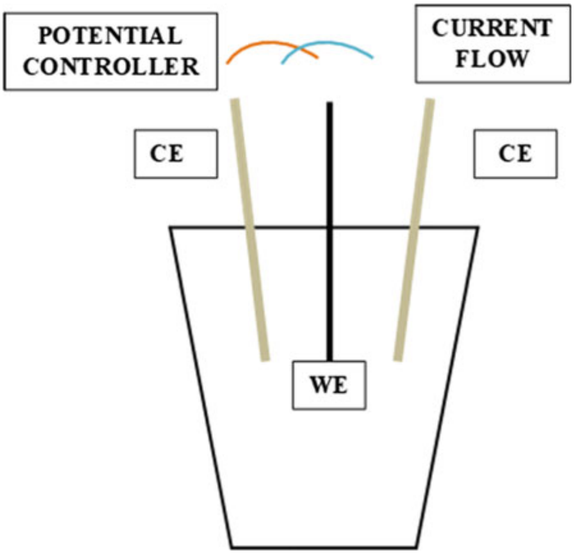
Electrochemistry is a part of science worried about the interrelation of electrical and substance impacts which incorporate the estimation of electrical amounts, for example, flow, potential, or charge and their relationship to concoction parameters [22]. A vast piece of this field manages the investigation of compound changes brought about by the entry of an electric flow and the generation of electrical vitality by synthetic reactions [23]. A wide scope of utilization has been found for scientific purposes utilizing these electrical estimations. Rather than numerous synthetic estimations that include homogenous mass arrangements, anode forms happen at the cathode arrangement interface [22]. These procedures are observed utilizing distinctive electro analytical methods. The distinctions between the different electrochemical strategies lie in the kind of logical flag utilized. There are two major types of electrochemical sensors, potentiometric and voltammetric methods:

(a) Potentiometric strategies—Involves the estimation of the potential (E) of a cell at zero current. For this situation, the potential is corresponding to the logarithm of the concentration of the substance being determined [24].
(b) Voltammetric or amperometric strategies—The terms voltammetric and amperometric scope of procedures including the use of a directly shifting potential between a working terminal and a reference anode in an electrochemical cell with a high concentration of an aloof electrolyte to make the arrangement conductive (i.e. electrolyte supporting) and an electroactive species. The current is continually checked through the cell. A hint of current is recorded against potential and is known as a voltammogram. The current through the cell is checked consistently. A hint of current against potential is recorded and is known as a voltammogram [24, 25]. Voltammetric systems subsequently manage the investigation of charge exchange at the anode arrangement interface. This procedure can be seen as connected electron weight, which powers the analytes to pick up or lose an electron which gets diminished or oxidized, respectively. The resultant current is an impression of the rate at which electrons move over the electron-arrangement interface [22]; consequently, these strategies can be connected for any species that can be decreased or oxidized.

6.1.1 Voltammetric Techniques

Irrefutably the potential at a cathode can't be known. Thus the potential difference between two terminals is estimated. The electrode of steady potential is named the reference electrode (RE) while another electrode of interest where the focused on

Fig. 4 Three electrode cell



electrochemical changes happen is known as the working terminal (WE) [22, 26]. A third terminal is normally expected to encourage current entry at the WE, and it is known as the counter anode (CE). Electrochemical examination in this manner ordinarily utilizes a three-cathode cell, which has a working, counter and reference terminals as appeared in Fig. 4. The potential is linked to the active cathode, which changes its potential in terms of the reference terminal's fixed capacity. It is estimated the subsequent current between the working and counter anodes. The counter anode is usually a platinum wire, while the Saturated Calomel Electrode (SCE) and Ag/AgCl electrode are reference cathode examples [23, 25]. There is a wide scope of the accessible working terminal, for example, Hg, Pt, Au and C terminals.

In an electrochemical cell, the recorded current will be involved two parts; faradaic and non-faradaic current. The faradaic current result from the adjustment in the oxidation condition of the analyte and it is that segment of the overall charge that pursues Faraday's laws. This infers it is connected to the entirety of the electron-exchange responses affected consequently relative to the convergence of the analyte. This can be accomplished by checking the charge exchange during the redox procedure portrayed in Eq. 1 as;

$$O + ne^- \leftrightarrow R \tag{1}$$

where O and R are the oxidized and reduced types of the redox couple. In any case, the measured current is normally more than the theoretical current. The additional current does not pursue Faraday's laws, and subsequently, it is said to be non-faradaic [24, 26]. Therefore, the general current watched is given in Eq. 2 as:

$$I_{Faradaic} + I_{non-faradaic} = I_{overall} \tag{2}$$

The non-faradaic current ought to be limited via the cautious decision of exploratory structure, reagents, and device as this can influence the sensitivity of these techniques. Luckily, some voltammetric apparatuses are designed to limit this non-faradaic current. The advantage of voltammetric procedures in this manner incorporate high selectivity, sensitivity towards electroactive species, a wide direct range, compact and low-cost instrumentation, speciation capabilities, and a wide scope of electrodes that permit examines in uncommon environments [22].

6.2 Chromatography

Chromatography is a method that can be used to separate the mixture and acquire both qualitative and quantitative data. Chromatographic divisions are practised through a consistent free phase, called a mobile phase, through a second sample-free phase, which remains fixed, called the stationary phase [25, 27]. It divides its segments between stationary and mobile phases as the sample moves through the mobile phase. Components whose distribution ratio supports the stationary phase will take longer to complete the framework, while those supporting the mobile phase will take a shorter time to complete. Given adequate time and stationary and mobile phase, it is possible to isolate solutes with similar distribution ratio. Chromatography includes, for example, several analytical chemistry systems, high-performance liquid chromatography (HPLC) and gas chromatography (GC).

6.2.1 Gas Chromatography (GC)

In GC, the sample, which could be a gas or fluid, is infused into a flood of a versatile idle vaporous stage (often called carrier gas, for example, helium, argon or nitrogen). The sample is delivered via a pressed or capillary column where the sample component is separated depending on its ability to disperse between the stationary and mobile phases. Column temperature control is essential to obtain a decent gas chromatography partition. The column is, therefore, located in a thermostatic oven [25, 28]. The section is kept at a constant temperature in an isothermal partition, whose decision is managed by the solutes. A detector such as a thermal conductivity detector (TCD), a flame ionization detector (FID), an electron capture detector (ECD) and a mass spectrometer (MS) generally combine the GC. It is widely used in clinical, environmental, pharmaceutical, forensic, biochemical, food science, and petrochemical research laboratories to analyze a diverse range of samples. GC is used for the analysis of various organic toxins in the air, water and wastewater applications [25]. Proper example pre-treatment and very much prepared staffs are basic for these techniques.

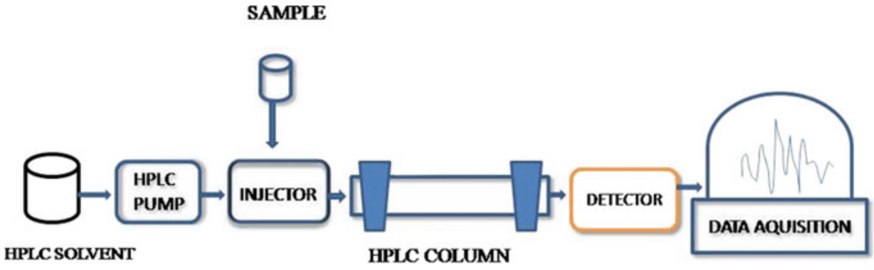


Fig. 5 Schematic diagram of HPLC [25]

6.2.2 High-Performance Liquid Chromatography (HPLC)

A sample (liquid or solid sample dissolved in a suitable solvent) is helped in HPLC through a mobile fluid phase through a chromatographic segment. Separation is controlled by interactions between the solution and the stationary phase. The detachment uses a single mobile phase of fixed composition in isocratic elution. Usually, it is not easy to locate a single mobile phase composition suitable for all solutes. Therefore, using a gradient phase is the only choice. The mobile phase's underlying composition is moderately polar to separate the reverse phase. The composition of the mobile phase is made less polar as the separation advances these separations. As with GC, different detectors have been produced for the monitoring of HPLC separation and incorporate spectroscopic detectors (e.g. UV/Vis absorption and fluorescence), electrochemical finders and ongoing advances in mass spectrometry have led to a growing enthusiasm for liquid chromatography-mass spectrometry (LC-MS).

HPLC (Fig. 5) is used regularly for both quantitative and qualitative pharmaceutical, environmental, criminal, clinical and industrial examinations. Usually, these chromatographic techniques are used for organic compound analysis. Chromatographic techniques are very efficient and give great sensitivity, especially when combined with MS, but require expensive, complicated equipment requiring qualified operators [25].

6.3 Atomic Spectroscopy

Atomic spectroscopy incorporates every single analytical technique that utilizes the emission and absorption of electromagnetic radiation by individual atoms. It is a great technique for the analysis for the trace levels of many elements in the periodic table [25, 29]. The particular wavelength of the radiation (emitted or absorbed) recognizes the element while the intensity of transmitted (or absorbed) radiation is proportional to the measure of the element present [30] (Fig. 6). Examples of these methods include inductively coupled plasma and atomic absorption spectroscopy.

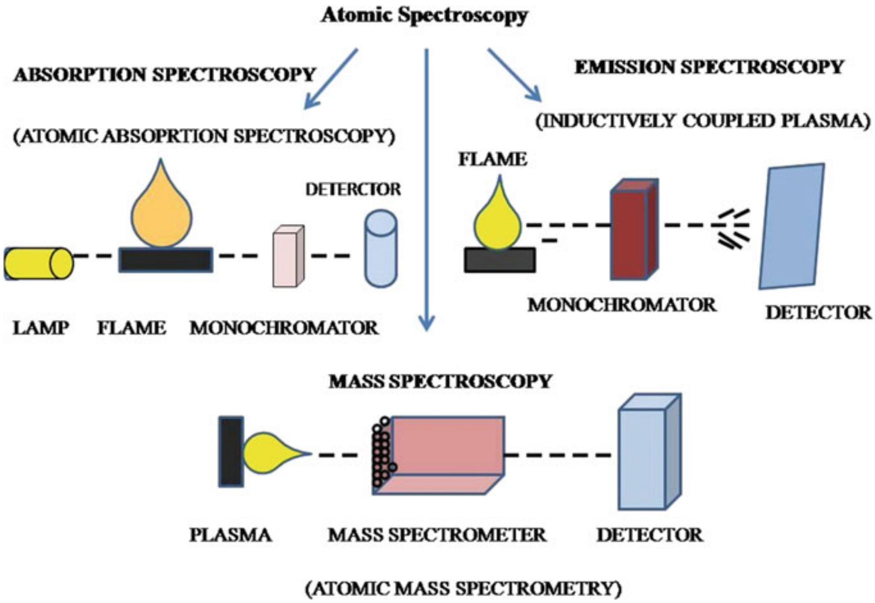


Fig. 6 Types of atomic spectroscopy [25, 29, 30]

6.3.1 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy estimates the discrete radiation absorbed by the absorption of a photon of energy by exciting the atoms of the ground state to higher energy levels. The radiant power of the absorbed radiation is identified using the Beer-Lambert equation with the absorption coefficient of the ground-state atoms. In a variety of test matrices, trace metals are widely examined by atomic absorption using either flame or electro-thermal atomization. The choice of strategy for atomization is mainly determined by the concentration of the analyte in the examples being analyzed. Because of how electro-thermal atomization has more sensitivity; for most components, identification limits are completely lower than when using flame atomization. A superior accuracy while using flame atomization makes it the choice technique when the concentration of the analyte is significantly higher than the flame atomization detection limit. But flaming atomization is less likely to interfere, takes into account a more prominent sample throughput and requires less operator mastery.

Atomic absorption gives great selectivity and can be used to analyze more than 60 elements at or below parts per million concentrations. The analysis time when using flame atomization is fast, using a fully automated system with a test throughput of 250–350 determinations per hour. However, analysis using this technique requires a wide sample preparation, which is not the case with electrochemical instruments [25].

6.3.2 Inductively Coupled Plasma (ICP)

ICP is an atomic emission spectroscopic technique which utilizes plasma for the atomization process. Plasma contains an amazing portion of electrons and positive ions which cancel out as well as neutralize molecules. The plasmas comprise of very energizing and ionized gases which are produced in inert gases like argon. They are helpful for dissociation of atoms as well as for the excitation and ionization to give atomic and ionic emissions. Comparing ICP with AAS, ICP gives lower detection limits but needs a highly skilled operator. The major drawback of all atomic spectroscopic methods is that they provide no data on the oxidation condition of the element or its speciation. Like AAS, this technique additionally requires a highly skilled operator and broad example preparation [31].

6.4 Fluorescence-Based Detection of Water Pollutants

Monitoring of water pollution is essential to avoid the health problem, the various method used for the monitoring of pollution level in the water, for the regular control of pollution level in water it requires a more rapid and fast technique to analysing the water quality.

This method is useful for detection of various pollutants like organic matter, trace organics and other pollutants which are found in marine, surface and ground water.

Currently, the various method has been used for the detection of water pollutants, which is centred on traditional detection of water quality like ANNs (artificial neural networks) and RVMs (relevance vector machines) [32]. However, this process of water quality parameters has several limitation like it take a long time for analysis, require various chemical reagent for analysis, not sensitive or less sensitive and generate various waste [33].

In comparison with the traditional method of water quality detection, the analysis based on spectra, detect the pollutants without separation or extraction, and this is very simple and rapid, and it does not require any reagent for the detection of contaminant [34]. Various researchers analyse the water contaminant or water quality using UV-visible spectrophotometry technique [35, 36]. While based on this method, the detection limit of some organic matter is not enough to achieve the standard.

For the many years, fluorescence-based method has been used for the monitoring of water quality, and also it is main technique for consistently measuring of organic matter which is dissolved in water, pigment like chlorophyll and algae [37]. It detects the organic matter at a lower limit than the UV-Visible spectrum, and also it provides more information. This method requires less sample, and detect the sample without processing; hence, it does not damage the structure of sample; it has high selectivity good reproducibility and high sensitivity [38].

The method of detection of water pollutants is based on the absorbance of contaminants under UV-vision.

Mechanism of Fluorescence-Based Detection of Water Pollutants

This method detects the water pollutants by detecting the light which is emitted by the contaminants after absorbance at a different wavelength (lower wavelength), which are more significant than the primary wavelength, the flow diagram of the overall mechanism of detection of water pollutants are given in Fig. 7.

This process detects an only specific number of molecules; this is a very selective method for detection of water pollutants.

6.5 *Colorimetric Detection of Water Pollutants*

Various technique is available for the detection of chemical contaminant in the water these technique include the inductively coupled plasma mass spectrometry, atomic absorption, X-ray fluorescence spectrometry and electrochemical analysis [39–42]. This technique gives accurate result for the presence of metal ions or other chemical contaminants in water, but this technique is very costly and available in only sophisticated lab hence it is challenging to handle this outside the lab or on the site of determination of water contaminant, and it requires a highly skilled person to handle this instrument and also it consumes more time.

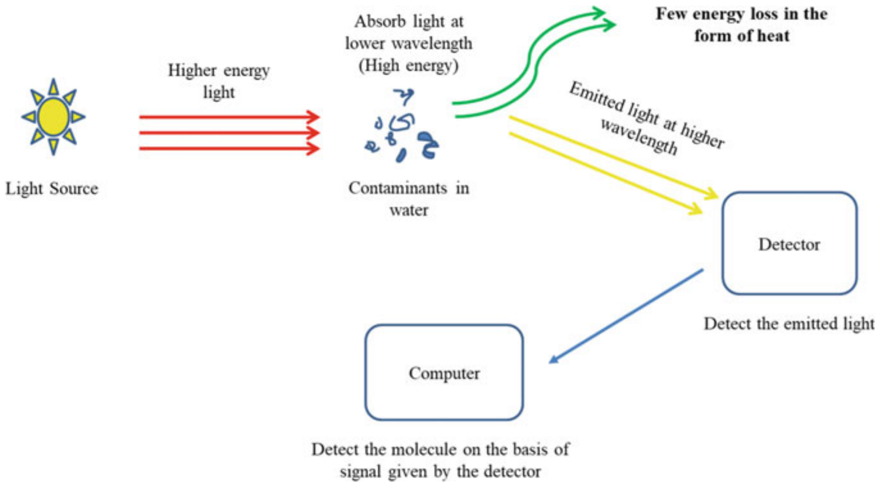


Fig. 7 Overall mechanism of fluorescence-based detection of water contaminants [38]

No of chemical contaminant present in water are generally colourless and cannot be detected by the human eye. To detect this various technique are used, one of this technique is the colorimetric technique, this technique measures the chemical contaminant which reacts with a compound which gives a specific colour, intensity of colour depending on the concentration of contaminant chemical, if intensity of colour is high then it indicates more elevated level of chemical it means intensity of colour is directly proportional to the intensity of chemical contaminant. By using this technique, we mainly measure the concentration of phenols, phosphorus, ammonia, chlorine, calcium magnesium, fluorine and heavy metals like arsenic, mercury, zinc, nickel, cadmium etc. And another chemical compound we analyse the concentration of calcium and magnesium to determine the hardness of the water.

7 Conclusion

From the information discussed above, it is clear that the future of analytical methods or biosensors will depend on the achievement of rising advanced technologies, both on a micro and nano scale, as well as material science, the biochemistry of electronics and physics. Environmental pollution is a genuine health concern throughout the world in various media. It is therefore important to plan and develop an analytical technique based on biosensors that can detect various pollutants from a wider range. Biosensors for natural pollutant detection, however, have some limitations that include (a) reaction time, (b) selectivity, (c) sensitivity, (d) affinity, (e) compatibility, (f) shelf life, and (g) stability, etc. These limitations should be removed as a competitive analytical device for more effective on-site implementation. It is important to know, apart from the above, whether the pollutant is gas (e.g., H_2S, O_2, CO, SO_x) or whether it is limited to a phase of the solution. It is important to note that this type of technique allows researchers to try different experiments with the varieties of sensor responses with different structural arrays when designing such structures. Consistently expanding public health concerns about the impact of pollution on the biological system will increase the demand for rapid detection of biosensors in the coming years. Despite past and current research in the advancement of biosensors, there is still a challenge to make biosensors better and more sensitive to avoid instrumental drift. A thorough study of the related techniques and sectors is required in this context. This will eventually have an impact on improving new techniques for biosensors in the future. Nevertheless, in the future, there will be the advent or requirement of user-friendly and more sensitive biosensors.

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Plasmonic Nanoparticles Decorated Graphene Sheets for Detection of Water Pollutants

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Abstract In the 21st century, human health, water safety, and environmental pollution are the main crucial issues all over the world. Many hazardous organic and inorganic pollutants present in the groundwater, surface water systems create havoc in the environment as well as drinking water. Waterborne diseases are dangerous for human health and other animals. Thus development of the simple and user friendly methods of for the easy detection of the water pollutants are necessary for healthy society. Graphene is one of the most promising and wonderful carbon hybrid materials as it possesses many outstanding properties like honeycomb structure, high surface area, unique physical, mechanical and chemical properties, etc. The nanoparticles such as Au, Ag, and Cu possess shape, and size-dependent surface plasmon resonance (SPR) absorption bands thus can be used to construct plasmonic-based sensors. Recently 2D graphene and its composites are widely used as a support to these metal nanoparticles to improve sensitivity and selectivity towards the analytes. These nanocomposites are widely used to detect hazardous environmental pollutants by different techniques like colorimetric, fluorometry, and electrochemical sensing. There are several reports on designing graphene quantum dots/metal nanoparticle based system for sensing application for water pollutants like organic pollutants, gold, silver, mercury, iron, etc. These techniques are very simple and do not require expensive facilities, highly skilled manpower, and easy to operate. This chapter is mostly focussed on the synthesis of monometallic and bimetallic plasmonic nanoparticles decorated graphene/graphene quantum dots system for the detection of water pollutants. The recent development of the detection of water pollutants by colorimetric, fluorometric, and electrochemical

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detection techniques using plasmonic nanoparticles decorated 2D nanosheet are also briefly discussed in this chapter.

Keywords Graphene · Plasmonic nanoparticle · Surface plasmon resonance (SPR) · Water pollutants

1 Introduction

In the 21st century, many of the major problems like human health, environmental pollution, water safety are the principle concern issues all over the world. In this century, the problem that humanity is facing related to the quantity and quality of water. These problems are globally recognized, and there is an adverse effect on climate change, water cycle intensification, melting of glaciers, etc. [1–4]. Many hazardous pollutants (heavy metal ions, organic contaminants, dyes, pesticides, etc.) present in the groundwater, surface water create a severe threat in the environment as well as in drinking water. Concerning human health, more than one-third of the people in the world facing severe problem like improved sanitation, lack of clean drinking water [5–7]. Water is the most vital part of human beings, which includes every field of energy, health, economy, food, etc. Some statistical reports show near about 10–20 million people die every year due to nonfatal and waterborne illness, and 5000–6000 children die due to diarrhea every day. It is a matter of serious havoc that the current water supply will be reduced by one-third after a couple of decades [8–12].

Single layered graphene sheet was discovered by A. K. Geim and his co-workers from graphite using a "Scotch Tape" approach in 2004 [13, 14]. For the discovery of graphene, A. K. Geim and Konstantin Novoselov were awarded jointly Nobel Prize in Physics in 2010. There are mostly two forms of functionalized graphene, e.g. graphene oxide (GO) and reduced graphene oxide [15–17]. There are different routes of reduction of graphene oxide, the partial reduction (physical and chemical) of oxygenated functional groups of GO is termed as reduced graphene oxide (rGO) [18, 19]. Another form of fluorescent graphene is graphene quantum dots (GQDs) which is prepared by cutting the larger lateral dimension of graphene sheets, making it 0D as well as lateral size of few nanometers. These carbon hybrid materials (graphene, GO, rGO, GQDs) possess some outstanding properties like optical, water-solubility, photostability, biocompatibility, nontoxic inexpensive, photo-stable, and environmentally friendly and many more. Thus, these materials are widely used in various field like in fluorescent biosensors, chemical-sensors, in which they either serve as fluorophores or quenchers, electronic devices, molecular sensors, nanocomposites, supercapacitors, batteries, hydrogen storage device, etc. As fluorophores, they show tunable photoluminescence emission (fluorescence) and excitation-dependent emission property due to "Giant Red-Edge Effect" [20, 21].

There are different techniques reported to date for the synthesis of graphene, functionalized graphene, and GQDs. The reported methods are exfoliation and cleavage, thermal chemical vapor deposition techniques (TCVD), plasma enhanced chemical vapor deposition techniques (PCVD), chemical methods, electrochemical process, etc. [22–25].

Graphene and functionalized graphene as a novel substrate for plasmonic nanoparticles decoration have been well studied and explored. Also, the 2D surface of these materials shows strong non-covalent affinity towards biomolecules, plasmonic nanoparticles (like Au, Ag, Cu, etc.) via π-π interaction, $d_{electron}$-pπ interaction, electrostatic force or sometimes hydrogen bonding, which provide an excellent platform for conjugation [26]. Thus, the graphene/metal top surface (e.g., Au, Ag monometallic or bimetallic) of such structures easily can be modified for chemical and biological sensing applications. Graphene interacted with plasmonic nanoparticles through localized surface plasmon resonance (LSPR) mechanism, offers a great platform for sensing applications like chemical-sensors, bio-sensors, etc. It is also used in transparent, physically flexible, and tunable (chemical) materials in electronics applications. The optical-electrical phenomenon arose when light interacts with a metal surface is called Surface Plasmon Resonance (SPR) [27]. These high charge density oscillations at metal-dielectric (or metal/vacuum) interface propagated in a parallel direction or the metal-dielectric interfaces. That's why SPR techniques are very sensitive to any change occurred in the boundary of the interfaces, for example, such as adsorption of nanoparticles to the 2D nanosheets.

The 2D graphene, GO, and 0D GQDs as a fluorescence, colorimetric, and electrochemical sensing platform have attracted the attention of the scientific community recently. These three detection techniques are mostly discussed in this chapter for the sensing of water pollutant. The fluorescent (optical) detection techniques have been recognized as promising and powerful tools for quantitative detection of anions and cations. Depending on the design of the nanomaterials optical method can be divided into three techniques, such as colorimetric, fluorometric, and chemiluminescent methods. The GO and GQDs are reported as fluorescent materials when their lateral size dimension becomes few nanometers. Thus, graphene-based materials decoration with plasmonic nanoparticles has been used in fluorescence sensing applications [28]. Again peroxidase mimic property (as artificial nanozyme) of plasmonic nanoparticles decorated graphene and their applicability in colorimetric sensing (naked eye detection) for water pollutant are well established. This interesting property of these nanomaterials can be analyzed by a redox reaction caused by reduction of H_2O_2 in the presence of oxidation of a variety of chromogenic substrates like pyrogallol, O-phenylenediamine (OPD), 3,3′,5,5′-tetramethylbenzidine (TMB), and 2,2′-azino-bis-(3-ethyl benzothiazoline-6-sulfonic acid) (ABTS), to produce orange, blue and green colour suspension respectively. It is interesting to note that compared to other substrates, TMB is less carcinogenic as well as products have high absorption coefficient value. Thus, it is the most common chromogen used to study horseradish peroxidase (HRP) mimics, in acidic conditions for naked-eye detection of ions and biomolecules. Usually, graphene decorated with monometallic or bimetallic nanoparticles shows better peroxidase mimic activity compared to bare graphene sheets [29, 30]. Generally, electrochemical sensor based on particularly stripping voltammetry technique and regarded as a very useful tool for on-site monitoring and detection of heavy metal ions in the environment. The benefits of these types of sensors are that these are highly sensitive and selective towards electroactive species, low detection limit, inexpensive, portable, high accuracy and easily packable device, etc. [31–33]. Carbon-based electrodes such as glassy carbon, graphitic carbon, etc. have been already replaced over other metal electrodes substances in electrochemical and analytical fields. These materials show some outstanding properties over metal electrodes like chemical stability, low cost, electrocatalytic activity for a variety of redox reactions and possess wide potential applications.

This chapter discusses mostly plasmonic nanoparticles decorated graphene and functionalized graphene system for the sensing application of hazardous water pollutant like heavy metal ions, organic pollutants, etc. The recent progress based on fluorometric, colorimetric, and electrochemical detection techniques using decorated graphene surface for detection of water pollutants mostly heavy metal ions is also briefly discussed in this chapter.

2 Synthesis of Graphene Oxide

The oxygen-rich functionality of graphene, which is prepared by the oxidation of commercially or naturally available graphite powder, is termed as graphene oxide. In 1958, Hummers and Offeman developed a faster, safer, and the most efficient route for the synthesis of oxidized graphite. Before this method, some other methods like Brodie methods 1859, Staudenmaier method 1898 were developed. But graphite oxide production was very slow, and the final product contains hazardous ions due to the use of concentrated H_2SO_4 and HNO_3. This method is regarded as a better method over other reported methods that time. In the Hummers and Offeman method, graphite oxidation is carried out with a mixture of H_2SO_4, $NaNO_3$, and $KMnO_4$. Nowadays, a modified Hummers and Offeman method are generally used [34]. In this method, oxidation has been carried out in the absence of $NaNO_3$. The reaction between $KMnO_4$ and H_2SO_4 leads to dimanganese heptoxide (Mn_2O_7), which acts as a strong oxidizing agent for this reaction to generate graphite oxide (Eqs. 1 and 2). The extensive oxidation of graphite to graphene oxide is depicted in schematically in Fig. 1.

$$KMnO_4 + 3\ H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3\ HSO_4^- \tag{1}$$

$$MnO_3^+ + MnO_4 \rightarrow Mn_2O_7 \tag{2}$$

Characterization of Graphene Oxide

The GO dispersion was characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), UV-visible spectroscopy, XPS and Raman

$$KMnO_4 + 3\ H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3\ HSO_4^- \quad (1)$$

$$MnO_3^+ + MnO_4 \rightarrow Mn_2O_7 \quad (2)$$

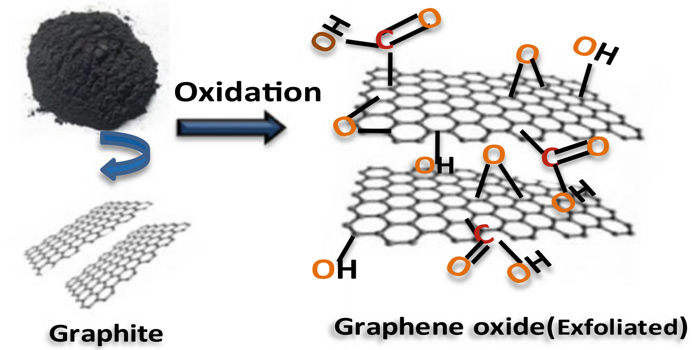


Fig. 1 Schematic representation of the synthesis of graphene oxide from graphite

spectroscopy. Figure 2a, b show AFM and TEM images of the GO sheets. The thickness, correspond to AFM image (Fig. 2a), is found to be 1.2 nm, which indicates the formation of double-layered GO nanosheets (Fig. 2c). The UV-visible spectra of GO and rGO were shown in Fig. 2d. There are two prominent peaks observed at 230 nm and 300 nm, due to n-π* and π-π* transition of C=C and C=O, respectively [35].

Raman spectroscopy is regarded as one of the most useful tools for analysis of defect and disorder present in the crystal structure. Generally, this technique is used to characterize graphitic derivatives. The ratio of G band to the D band (I_D/I_G) calculates the disorder in the graphitic structure. Figure 3 represents the Raman spectra of GO and rGO sheets. The D band is observed at 1365, 1364 cm^{-1} and corresponding G band are observed at 1597, 1607, for GO, and rGO, respectively. The origin of G band (sp^2 carbon) arises from C-C bond stretch, and first-order Raman scattering. The shifting of G band to a higher wave number is may be due to the oxygenated moieties presence in graphite after oxidation. The D band also broadened in case of GO due to defects, distortions, size reduction of the sp^2 domains after oxidation. The I_D/I_G shifted from 0.96 (GO) to 1.0 (rGO) confirms the attachment of oxygenated moieties to graphene sheets.

Figure 4a depicts the survey XPS of GO demonstrates the presence of C and O atoms in GO. The high-resolution C1 s XPS spectra (Fig. 4b), representing the peaks corresponding to four functional groups C–C/C=C, C–O, HO–C=O, C=O, suggests the successful oxidation to GO [37, 38]. The peaks at binding energy of 284.64 eV, 285.34 eV, 287.28 eV and 289.07 eV correspond to C=C, the C in C–OH, C(C=O) and (HO–C=O) (carboxyl-C) respectively. Again, O1s high-resolution XPS spectra are also recorded in Fig. 4c which composed of two

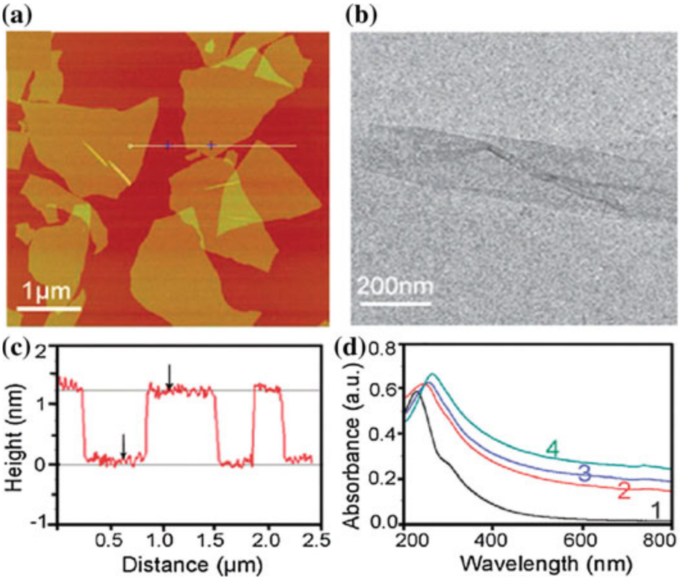
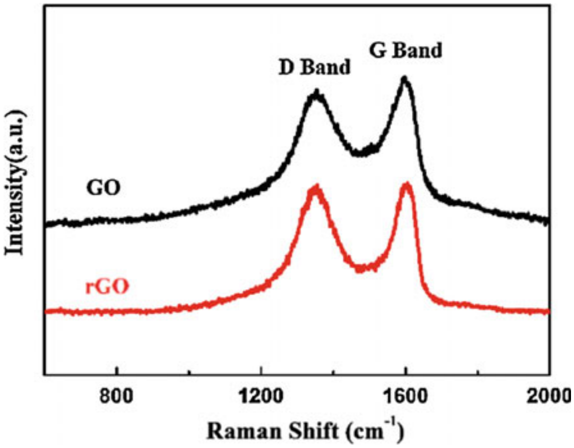


Fig. 2 **a** AFM image of GO, **b** TEM image of GO, **c** the height profile of GO, **d** UV-vis absorption spectra of GO and (1) and (2), (3), (4) UV-visible absorption spectra of GO after reduction (reproduced with permission from Ref. [35])

Fig. 3 Raman spectra of GO, and rGO (reproduced with permission from Ref. [36])



oxygenated constituents, one at 532.19 eV for C–OH and the other at 533.15 eV for (C–O–C).

X-ray diffraction (XRD) is a useful tool to characterize graphite and graphene oxide. This technique was carried out to determine *d*-spacing value as well as to confirm the GO synthesis. The XRD spectra of graphite and GO were depicted in Fig. 5. For graphite, there observed one sharp peak at 2θ values 26.4° for

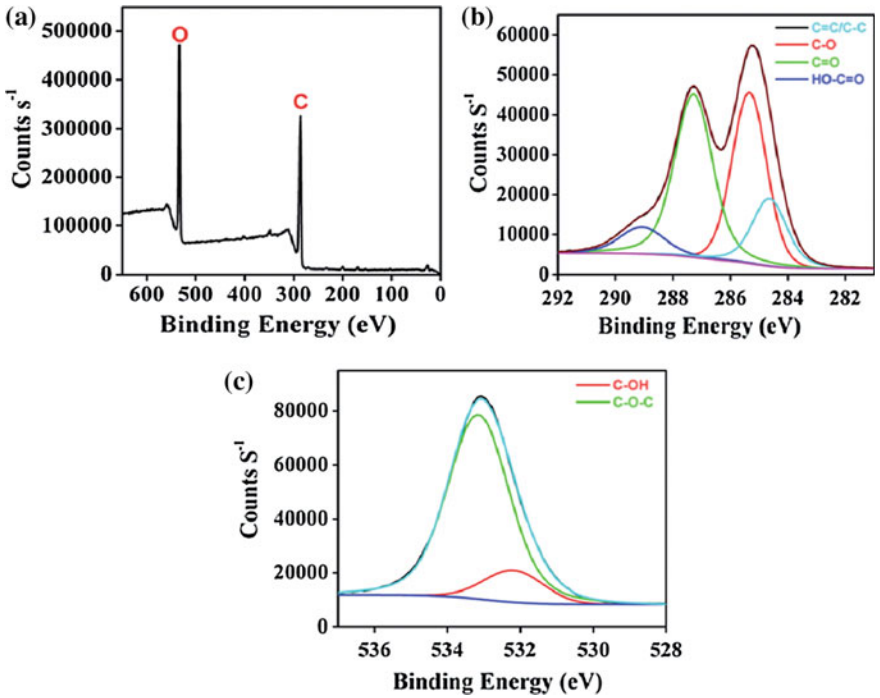
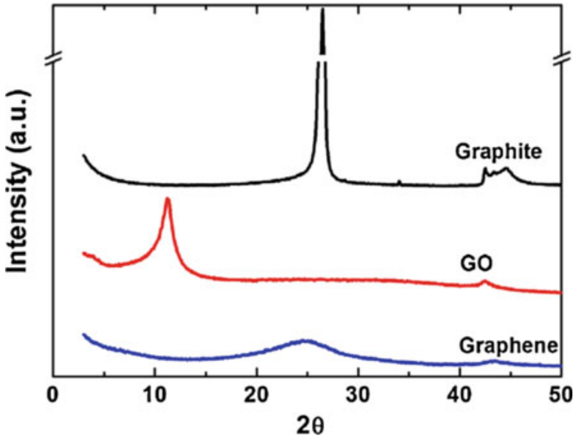


Fig. 4 **a** XPS survey spectrum of GO and high resolution, **b** C1s spectra, and **c** O1s spectra (reproduced with permission from Ref. [37])

Fig. 5 XRD spectrum of graphite, graphene, and GO (reproduced with permission from Ref. [39])



(002) plane with *d*-spacing value 3.45 Å. Interestingly after oxidation to GO, the XRD pattern depicts a characteristic peak at $2\theta = 9.9°$ for the plane (100) having a *d*-spacing value of 8.9 Å, which confirms the successful functionalization of graphite to GO [39].

3 Fluorescence (Fluorometry) Detection of Water Pollutants

The term fluorescence means the emission of light by material, and it is denoted as a specific type of luminescence phenomenon. When electromagnetic radiation falls on molecules or substance, the electrons gain the energy and are excited to higher energy level and produce luminescence. This process of emission is termed as photoluminescence. Mostly there are two types of photoluminescence, fluorescence and phosphorescence. In the case of fluorescent, the release of electromagnetic energy is instantaneous or ceases on the withdrawing of the exciting radiation and emission occurs between states of same spin multiplicity. But for phosphorescence, the energy release or emission is continuous or delayed after the existing radiation has been removed. Among the two techniques, fluorescence is extremely effective as the detectors on the machine are highly sensitive. Other than these two techniques, other luminescence processes are chemiluminescence, bioluminescence, electrochemiluminescence, electroluminescence, lyoluminescence, etc.

The fluorescent optical detection methods have also been recognized as powerful and promising tools over other techniques because of its better sensitivity, high speed, easy operation, and low cost for quantitative detection of anions and cation. The sensitivity of the fluorometric technique is approximately 1000 times greater than the absorption technique [40]. Thus, when working with low quantity or expensive materials fluorescence method is very useful as using a minute amount of the compound, can be achieved better sensitivity as well as detection limits. Only fluorescence active molecules or samples can be detected by this method, show better selectivity and specificity compared to UV/Vis and other techniques. In fluorescence, wide concentration range can be detected, e.g., more than three to six log orders of concentration. Again, in the case of fluorescence, sample preparation is also very easy and simple, shows accurate and precise reading [33–35].

Graphene and its analogs such as GO, GQDs, rGO have found extensive applications in fluorescent sensors for detection of water pollutants in recent years. Main benefits of graphene-based nanomaterials are that they can be employed as in tunable fluorophore as well as a potent fluorescence quencher. In this section, we want to focus the origin of fluorescence, its excitation dependent fluorescence, and strategies for sensor design based on plasmonic nanoparticle-decorated GO and GQDs.

Excitation dependant PL of graphene-based nanomaterials

GQDs and other derivatives of GO mainly possess excitation-dependent photoluminescence, and this is one of the most important properties of carbon-based nanomaterials. There are many debates on the origin of this property and yet not been well established. On the contrary, despite having considerable differences in shape, surface, functionalities, and sizes, all the carbon nanomaterials exhibit excitation dependant PL. Interestingly, some exceptions are also reported where there exists excitation independent PL behavior [41, 42].

The mechanism of excitation dependent or independent PL properties depends on some factors like size effect, quantum confinement effect, giant red-edge effect, edge effect, carbonization degree, surface traps, etc. [43, 44].

Z. X. Gan and his co-worker's studied the details of photoluminescence (PL) and photoluminescence excitation (PLE) spectra of rGO. The excitation-dependent PL and PLE spectra of rGO are demonstrated in Fig. 6a, b. Increasing the excitation wavelength from 300 to 500 nm, the corresponding emission occurred at 400 to 600 nm. Thus, emission intensity gradually increases attained a maximum optimal emission value, and then the intensity decreases. There are two bands (250 nm and 330 nm) observed for rGO in PLE spectra (Fig. 6b). The 250 nm peak is due to π–π* transitions and 330 nm peak for δ–π* transitions, respectively.

It is already reported that the excitation-dependent and independent PL co-exist in same PL spectra and the mechanism is depicted in Fig. 6. In the case of graphene and functionalized graphene, blue emission observed when excitation wavelength gradually increases from 300 to 350 nm. But in case of higher excitation wavelength greater than 350 nm greater red shifting occurs uniformly [45]. The reason and mechanism for this property are depicted in Fig. 6a, as the excitation-dependent and independent PL mainly consists of two parts, one emission generates from defects state and other is from size effect of sp^2 clusters [46–48].

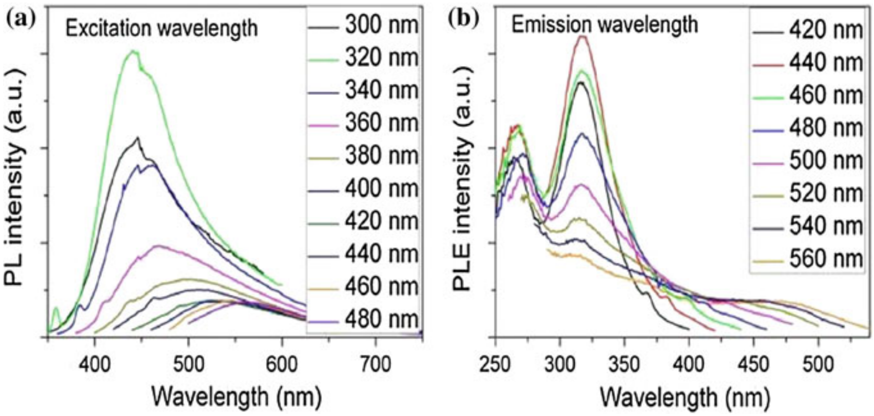


Fig. 6 **a** PL spectra and **b** PLE spectra of rGO (reproduced with permission from Ref. [45])

With taking advantages of PL (fluorescence) property of these graphene-based nanomaterials, these plasmonic nanomaterials decorated graphene/GQDs are used as a fluorescence sensing platform for water pollutant like anions, cations, heavy metal ions, dye, pesticide, etc. Due to their transparency and atomically thin nature, both pristine graphene and their functionalized analogs are reported as excellent substrates for plasmonic nanoparticles decoration. This strategy helps to construct plasmon-based sensors (biological and chemical) as well as transparent flexible electronics device. There are several reports for graphene-based fluorescence sensor for water pollutants.

Among the heavy metal ions, Au^{3+} or its salts are already reported as toxic to humans beings as well as environment. The ions may cause a serious threat and risk to the kidneys, nervous system, liver, heart, cell toxicity in living organisms. The permissible limit of Au^{3+} reported as 200 µM, so there is a need for a developed new method for the detection of gold ion also necessary.

A. Kundu and his co-workers have successfully demonstrated a method for sensing Au^{3+} by fluorescent graphene oxide polyvinyl alcohol (GO-PVA) hybrid and shown in Fig. 7. They have used polymer PVA in the composites for restacking GO nanosheets, passivation for electron-hole recombination. Thus, GO-PVA nanocomposites possess more quantum yield (higher PL intensity) than bare GO. Also, with Au^{3+}, the fluorescence intensity of nanocomposite has been quenched, where Au^{3+} acts as a fluorescence quencher. Figure 7a depicts the fluorescence quenching of GO-PVA in the presence of Au^{3+} (0–300 µM). Selectivity diagram for Au^{3+} and other metal cations are shown in Fig. 7b. Fluorescence of GO-PVA nanocomposites can selectively detect Au^{3+}. In aqueous medium minimum detection limit was found to be 275 ppb. As the reduction potential of Au^{3+} is higher than other cations, and they reported that this is the reason for being selective for Au^{3+}.

Fu's group have developed a new and effective fluorescence sensor of Pb^{2+} using Au decorated GO nanosheets. This is well explored that fluorescence

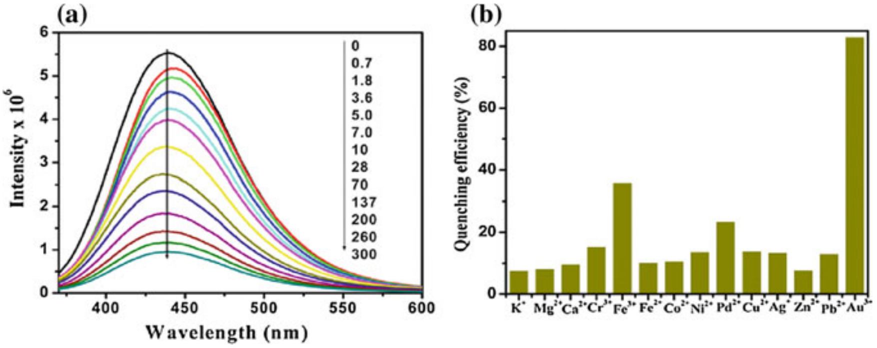


Fig. 7 **a** Fluorescence spectra of GO-PVA upon addition of Au^{3+}. **b** Selectivity diagram for Au^{3+} ion and with other cations (reproduced with permission from Ref. [49])

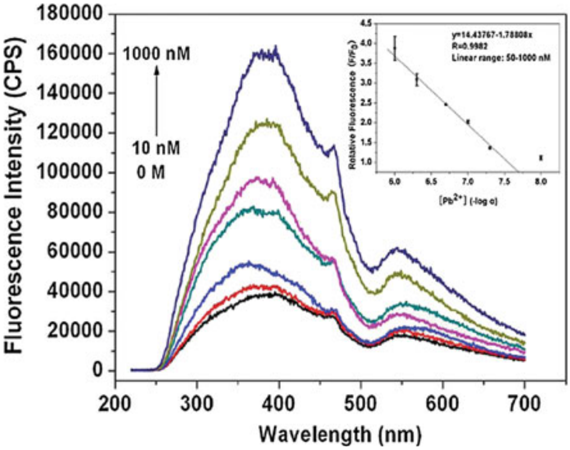


Fig. 8 Variation of fluorescence intensity of Au-graphene in 5 mM glycine solution at different concentration of Pb^2 ions (0 M–1000 nM) (inset: linear response of fluorescence spectra) (reproduced with permission from Ref. [50])

intensity of carbon nanomaterials is quenched interaction with plasmonic nanoparticles. Here, the fluorescence of GO after interaction with Au^{3+} is quenched due to fluorescence resonance energy transfer (FRET) mechanism. The intensity of quenched fluorescence intensity can be restored by addition of Pb^{2+}. The added ions accelerate the rate of leaching of Au nanoparticles on the decorated graphene surface. Thus, this is an on-off-on type fluorescence sensing strategy for Pb^2 ions using Au-nanoparticle (NP)-decorated graphene surface. The turn-on the fluorescence spectra of GO are depicted in Fig. 8. They have observed that the fluorescence properties of GO were strongly dependent on the size effect, presence of functionalities on the basal plane, edge effect, etc. It was shown that the small lateral size of less than 1 μm GO nanosheets show fluorescence and can be used for sensing application. The fluorescence intensity showed a good linear response in the concentration range of 50–1000 nM, and LOD was determined to be 10 nM. The sensor is also selective over other metal cations like (Ca^{2+}, Al^{3+}, Cd^{2+}, Mg^{2+}, K^+, Zn^{2+}, Li^+, Co^{2+}, and Ni^{2+}) and can be used for real samples also.

The 0D form of graphene, which possesses some extraordinary optical properties (e.g., fluorescent) recently attracted the attention of the scientific community. Xiaofang Niu et al. have utilized the 0D form of graphene, which is called GQDs and oligonucleotides strand modified Au nanoparticles to detect heavy metal ions, particularly Pb^{+2}. The sizes of the synthesis graphene quantum dots were confirmed by TEM. The optical property, as well as sensing, are characterized by fluorescence technology.

The morphology and sizes of Au nanoparticles, GQDs, and Au nanoparticles-GQDs were investigated by TEM analysis. The average size (diameter) of Au nanoparticles and GQDs was found to be 18 nm and 5 nm, respectively. They have observed that the dispersion was homogeneous and the particles well separated. The successful conjugation of Au nanoparticles and GQDs were also confirmed by TEM analysis.

The optical properties of these synthesis nanoparticles were characterized by fluorescence spectroscopy and UV-visible spectroscopy. In the presence of ultraviolet (UV) light (390 nm), the GQDs possess beautiful blue emission. The maximum emission is found to be at wavelength 470 nm. Compared to GQDs, the emission curve of GQDs-catalytic strand shows a red-shift of a peak, and the fluorescence intensity also gets reduced. This suggests the successful functionalization of GQDs and Au nanoparticles. Thus possess turn off fluorescence intensity.

The UV-visible spectra of Au nanoparticles and GQDs functionalized Au nanoparticles were studied and the absorbance peak appeared at 518 nm. After functionalization with GQDs, the peak was red-shifted to 523 nm, and the absorbance intensity also gets reduced. They provided one reason for reduction of absorbance intensity. The absorbance of nanoparticles is associated with the shape of the particles. The absorbance center of Au nanoparticles obtained at 518 nm. Thus, with the changing of the shape of nanoparticles, shifting of the absorbance center wavelength would occur. It may be due to as the Au nanoparticles were absorbed on GQDs surface, there is an enhancement of the surface plasmon resonance (SPR) band of Au nanoparticles and reduced the absorbance intensity.

Figure 9a demonstrated the turn-on the fluorescence of Au nanoparticles-GQDs in the presence of Pb^{2+} ions in different concentrations. It can be noted that with the increase of concentration of Pb^{2+} from 50 to 4000 nM, the fluorescence intensity gets enhanced from 1500 to 7000, and the emission wavelength also red shifted. They put forward a reason for this as the DNA strand from Au nanoparticles left on the GQDs surface, making a larger plasma resonance of quantum dots. In Fig. 9b. Corresponding Stern Volmer plot is also shown. From this plot, it is confirmed that the Pb^{2+} sensor has a broad linearity range of 50–4000 nM and limit of detection were calculated, and it was found to be of 16.7 nM. The selectivity study of the sensor also conducted with similar cations, and there is no such change observed in

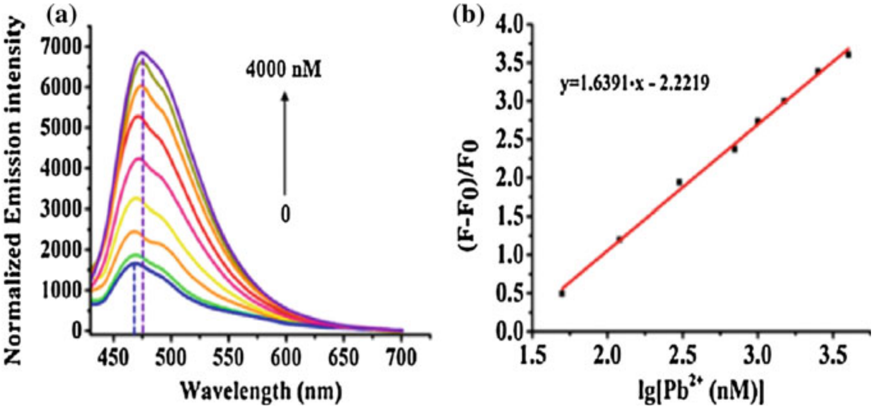


Fig. 9 **a** Fluorescence plot of Au-nanoparticles-GQDs in presence of different concentrations of Pb^{2+}. **b** Stern Volmer plots of fluorescence signal recovery after adding Pb^{2+} concentrations (50 nM–4000 nM) (reproduced with permission from Ref. [51])

fluorescence intensity for such ions. Thus, the fluorescence sensor was sensitive as well as selective for only Pb^{2+} [51].

Hua Wang and his group recently developed a GQDs based fluorescent nanosensor for silver ions in an aqueous medium as silver ions are also included highest toxicity class of heavy metal groups, that's why detection of silver ions is also essential. The commercially available GQDs are characterized by TEM and AFM characterization techniques. From the TEM and AFM images, the sizes of the GQDs are found to be below 10 nm, particles are well separated and show homogeneous the dispersibility. The corresponding particle size distribution curve also plotted, and the average particle size (diameter) is calculated at about 2.9 nm. From the atomic force microscopy (AFM) imaging the thickness was calculated from the height profile diagram and found to be 1.2 and 4.0 nm, which suggests stacking of a few graphene layers.

Under the optimization conditions (concentration range of $Ag^+ = 0–115.2\ \mu M$, GQDs concentration = 20.0 μg mL^{-1}, OPD concentration = 180 μM; at 10 mM PBS, pH 6.0), they have developed a quantitative sensors for Ag^+ (Fig. 10). The fluorescence spectra of GQDs-OPD (O-phenylenediamine) system with increasing concentrations of Ag^+ was recorded and displayed in Fig. 10a. The peak intensity of GQDs at 445 nm was diminished gradually as well as the peak intensities at 557 nm were increased upon continuously adding Ag^+. This proves that the ratiometric variation of fluorescence intensities was mainly due to the added concentration of Ag^+. The intensity ratios of (I557/I445) versus Ag^+ concentration was plotted and was shown in Fig. 10b. The ratio of intensities (I557/I445) possessed a good linear response to Ag^+ in range of 0–115.2 μM. The regression equation, and the R^2 values were calculated as $I_{557}/I_{445} = 0.08887 + 0.01649C$ and 0.9945 respectively. Figure 10b (inset) depicts photographs showing the changes of GQDs-OPD in the presence and absence of Ag^+ and colour change can be

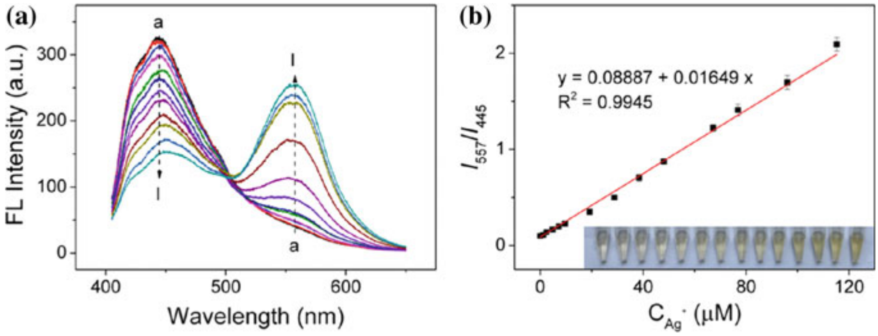


Fig. 10 **a** Fluorescence spectra of GQDs-OPD in presence of Ag^+ in the concentration range 0–115.2 μM, GQDs concentration = 20.0 μg mL^{-1}, OPD concentration = 180 μM; at pH 6.0 of 10 mM PBS. **b** Linearity plots between ratio of fluorescence intensity (I557/I445) versus Ag^+ conc. (inset: capturing images of GQDs-OPD in presence and absence of different concentration of Ag^+) (reproduced with permission from Ref. [52])

monitored visually. The standard deviation and LOD were calculated as 3.21% and 250 nM (S/N = 3). Thus, GQDs-OPD platform was established as a dual sensor for the detection of Ag^+.

4 Electrochemical Technique for Detection of Toxic Water Pollutants

The electrochemical sensing method is highly selective as well as a sensitive technique for the determination of non-UV-absorbing analytes. Nevertheless, the electrochemical sensor also potentially worked on the determination of UV-absorbing analytes. It is an easy detection technique for the simultaneous detection of single as well as multiple water pollutants. This is a very powerful sensing technique, which can detect electric current, generated from either oxidation or reduction reactions in the test mixtures. In this method, the sensing takes place on a cell containing a working electrode and existing a counter electrode which maintaining stable potential [53, 54]. The electrochemical sensor is classified as potentiometric, conductometric, and amperometric based on the property of the acquired sensor. The recognition element and physical transducer (electrode) is present in all kind of sensors. The sensor performance is fully depending on the interaction between the electrolytes of the test samples and the electrode surface [55]. The large surface and small size materials electrodes have high sensitivity towards the detection of target molecules [56].

Nanomaterials with high surface to volume ratio employed as highly selective as well as sensitive electrochemical sensors for the detection of different organic and inorganic pollutants materials [57]. Plasmonic nanoparticles such as Au, Ag, Cu have shape and size dependent optoelectric properties; these are widely utilized as sensing materials for environmental applications [58]. Plasmonic nanoparticles have promising approaches as electrochemical sensors, due to the high stability; these are produced the robust potential for on-site detection of water pollutants [59, 60]. Generally, carbon-based nanomaterials are widely used in electrochemical applications due to their low cost, high chemical stability, and electrocatalytic activity for the different redox reactions [61, 62]. Among the carbonaceous materials, graphene-based nanomaterials have wonderful potential for electrochemical application as unique electrode materials, which have enhanced electron transfer rate, high signal to noise ratio, and they increased the mass transfer rate [63]. The hydroxyl and carboxyl group present in the graphene surface may interact with organic pollutants molecules, and form complexes with pollutant metal ions result in high sensing activity of the graphene-based composite materials [64, 65]. Graphene-based electrochemical sensors have the ability to detect individual ions as well as multiple metal ions up to a low detection limit and which can detect metal ion concentration deviation in the groundwater sample.

Gong et al. synthesized monodispersed Au nanoparticles on graphene for the electrochemical detection of Hg (II) ion. The Au nanoparticles decorated graphene (Au nanoparticles-chi-graphene) could greatly enhance the electron transfer process between electrode and Hg^{2+}, which exhibited excellent performance for the detection of Hg^{2+} ion [66]. They have used three electrode systems such as glassy carbon electrode (working electrode), calomel electrode (reference electrode), and auxiliary electrode (platinum wire). Square wave anodic stripping voltammetry (SWASV) was utilized for the continuous determination of Hg^{2+} ions. SWASV responses of the modified Au nanoparticles decorated graphene sensor (Au nanoparticles-chi-graphene/GCE) against different concentrations of Hg^{2+} ions (from 0.025 to 60 ppb) are shown in Fig. 11. The sensitivity of the electrode was obtained 708.3 A/ppb for the detection of Hg^{2+}, which is much higher than the other method of the previous report [62, 67, 68]. The peak intensities of well-defined peaks are proportional to the Hg^{2+} ion concentration; it was obtained in two ranges from 0.025 to 0.05 ppb and 0.1 to 60 ppb. The Hg^{2+} ion concentration was determined from the known concentration calibration curve of Hg^{2+} (inset in Fig. 11) compared with the obtained peak response. The Au nanoparticles-chi-graphene/GCE sensor had high sensitivity and showed a lower LOD of 6 ppm, which is far below from the specified value of drinking water (1 ppb) fixed by the WHO [69]. They have expected that Au nanoparticles-chi-graphene should be easily usable towards the detection of Hg^{2+} ion in a real sample. However, selective detection of heavy metal ions is a challenging task in the real sample, since different metals ions exist in real samples. The selectivity of the Au nanoparticles-chi-graphene was studied for the detection of Hg^{2+} ion in the presence of different interfering ions like Cd^{2+}, Co^{2+}, Cu^{2+} Fe^{2+}, Zn^{2+}, and I^{-}. Figure 12 shows the effects of Cd^{2+}, Co^{2+}, Cu^{2+} Fe^{2+}, Zn^{2+}, and I^{-} ions on the electrochemical detection of Hg^{2+}. As clearly seen from Fig. 12, no any significant detection efficiency was changed for Au nanoparticles-chi-graphene/GCE towards 1 ppb of Hg^{2+} ion detection in the presence of 20 ppb of each Fe^{2+}, Cu^{2+}, Co^{2+},

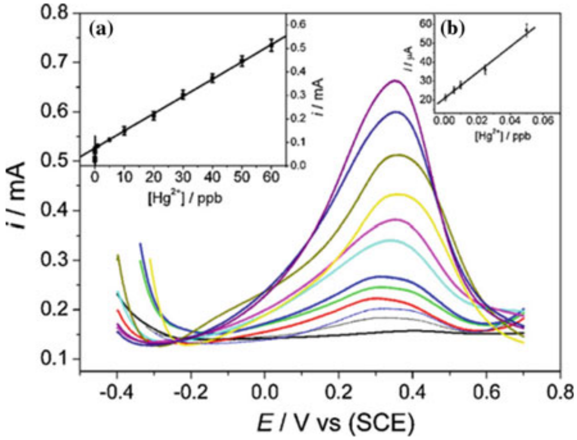


Fig. 11 SWASV of increasing the concentrations of Hg^{2+} (from 0, 0.025 to 60 ppb). The inset **a** calibration curve for the whole range of the Hg^{2+} concentration and **b** the calibration curve magnification for lower concentration region (reproduced with permission from Ref. [66])

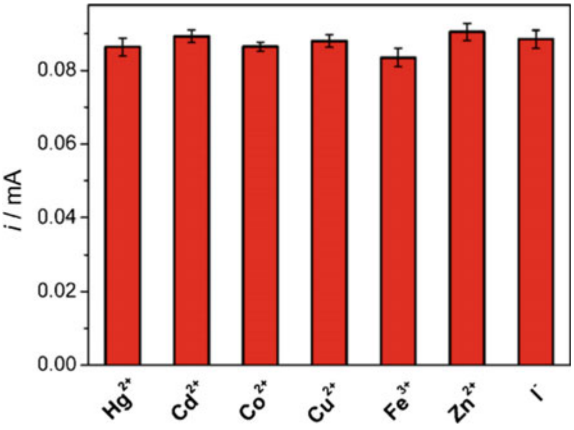


Fig. 12 Effects of Fe^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+} and I^- ions on the electrochemical stripping signals of Hg^{2+} at modified Au-chi-graphene sensor (concentration of Hg^{2+} 1.0 ppb and 20 ppb for each of the other metal ions) (reproduced with permission from Ref. [66])

Cd^{2+}, Zn^{2+} and I^- ions. Similarly, Zhang and his co-workers have developed Au/graphene nanocomposite sensor for the selective electrochemical detection Hg^{2+} ion [70]. They have observed a very low LOD of 0.001 aM in the linear range of 1.0 aM–100 nM.

Yang et al. and his co-workers have contrived a plasmonic Au nanoparticles deposited functionalized graphene and carbon nanotube (CNT) based composite materials for the electrochemical detection of various water pollutants [71]. They have observed a low LOD of 4.17, 1.00, 7.80, and 23.5 μM, for the detection of hydroquinone, catechol, resorcinol and nitrite ions. The electrochemical sensor based Au nanoparticles/rGO/CNT nanocomposite was established by Wang et al. for the detection of harmful phenolic compound bisphenol A [72]. They have obtained LOD of 800 pM in the linear range of 1.5–1490 nM for the electrochemical detection bisphenol A. The highly selective activity of Au nanoparticles/rGO/CNT was observed towards the detection of bisphenol A in presence of various interference molecules and ions like phenol, p-nitrophenol, pyrocatechol, 2,4-dinitrophenol, hydroquinone and Na^+, K^+, Cl^- and Ca^{2+}. Ma et al. have also been utilized Au nanoparticles-polyaniline-graphene nanocomposites (Au nanoparticles/PAN/graphene) based electrochemical sensor for the selective detection of NO_2^- ion with a low LOD of 10 nM [73].

Ikhsan and his co-workers have decorated plasmonic Ag nanoparticles on rGO sheets for sensitive as well as selective electrochemical detection of 4-nitrophenol (4-NP) [74]. Since nitrophenols are commonly used in the manufacture of dyes, pharmaceuticals, and pesticides, these are highly toxic, inhibitory, and anthropogenic compounds [75]. They have also chosen a SWASV detection method for the sensitive electrochemical detection of 4-NP. The electrochemical detection of 4-NP was thoroughly investigated by the modified Au/rGO electrode prepared with 2, 6, 10, and 15 h reaction times. The Au/rGO/GCE electrode displayed that, the current response is an increase in the 4-NP reduction process at different concentration of 4-NP ranging from 10 nM to 10 μM (Fig. 13a). Owing to the high

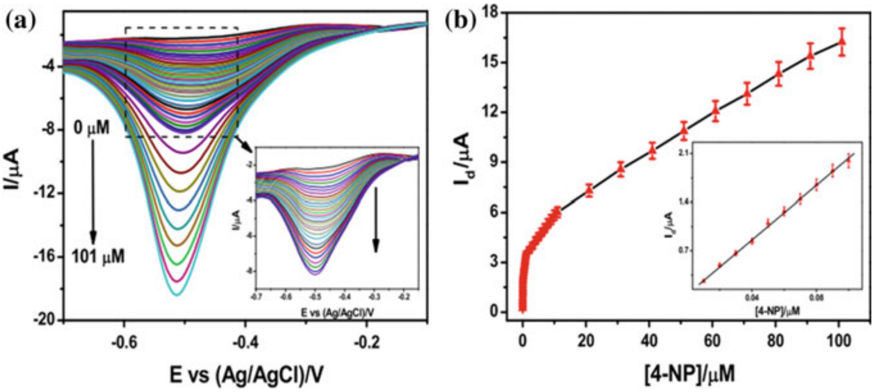


Fig. 13 **a** SWASV responses attained at Ag/rGO (15 h) modified electrode with various concentrations of 4-NP and **b** plot of peak current difference versus concentration of 4-NP (reproduced with permission from Ref. [74])

electrical conductivity of rGO, π-π interaction between 4-NP and rGO, and large surface area of the smaller Ag nanoparticles, the modified Au/rGO electrode is highly sensitive towards the current reduction response even with the addition of 4-NP up to the concentration of nM level. The calibration plot of the current response (I_d) difference versus different 4-NP concentrations is shown in Fig. 13b. The sensitivity of the modified Ag/rGO electrode was determined to be 19.83 ± 0.293 μA/μM for the detection of 4-NP. The LOD was calculated with the help of this calibration curve and found to be 1.2 nM in the linear concentration range of 10–100 nm. Roy et al. have been utilized Ag-ZnO bimetallic nanoparticles GO sheets modified sensor for the electrochemical detection *of E. coli* bacteria. The Ag-ZnO bimetallic nanoparticles graphene modified sensor has easily detected bacteria with a low LOD of 5.9 CFU mL^{-1} for the first time in the linear concentration range of 10 to 10^{9} CFUmL^{-1} [76]. The plasmonic NPs decorated graphene-based electrochemical sensor for the detection of different water pollutants are presented in Table 1.

5 Colorimetric Detection of Water Pollutants

While there are numerous methods for detection of hazardous material from water sources, air they need some inexpensive, high sensitive, simple, selective, fast reaction and easily monitored analytical method [77]. Among the different detection techniques, colorimetric detection is considered as an attractive method for point-of-use applications due to their visual and simple read out by the unaided eye [58, 78]. This method does not require any sophisticated instruments, and thus, the colorimetric methods demonstrate great potential for portable and inexpensive daily

Table 1 Selected plasmonic nanoparticles decorated graphene-based electrochemical sensor for the environmental pollutants detection (NPs = nanoparticles)

Electrode materials	Pollutants	Detection limits (LOD)	Linear range	Reference
Au NPs-chi-graphene	Hg^{2+}	1 ppb	0.025–60 ppb	[66]
Au NPs/graphene	Hg^{2+}	0.001 aM	1.0 aM–100 nM	[70]
Au NPs/graphene/ CNT	Hydroquinone	4.17 μM	54.5–120.5 μM	[71]
Au NPs/graphene/ CNT	Catechol	1 μM	11–126 μM	[71]
Au NPs/graphene/ CNT	Resorcinol	7.8 μM	43.5–778.5 μM	[71]
Au NPs/graphene/ CNT	NO_2^-	23.5 μM	86–7500 μM	[71]
Au NPs/rGO/CNT	Bisphenol A	800 pM	1.5–1490 nM	[72]
Au NPs/PAN/ graphene	NO_2^-	10 nM	0.1–200 μM	[73]
Ag/rGO	4-nitrophenol	1.2 nM	10 nM–100 nM	[74]
Ag-ZnO/GO	E. Coli	5.9 CFU mL^{-1}	$10–10^9$ CFU mL^{-1}	[76]

life applications [79, 80]. Amanulla et al. utilized chitosan stabilized Au nanoparticles incorporated on rGO for sensitive and selective detection of nitrite ions (NO^{2-}). They reported that with the insertion of various concentration of NO^{2-} ions, the color of the Au nanoparticles/rGO composites changes from wine red to purple. Based on this color change, the concentration of NO^{2-} was detected quantitatively by monitoring the UV-visible spectroscopy. The reported sensor was able to detect NO^{2-} ions with a limit of detection 0.1 μM in a linear range 1 to 20 μM by spectroscopic method in (Fig. 14) [81].

Dong and his group utilized a colorimetric technique based on the variation of color of gallic acid capped gold nanoparticles (GA-Au nanoparticles) for the selective detection of Cr(III) and Cr(VI). They reported the limit of detections (LODs) of a mixture of Cr(III) and Cr(VI) are 1.5 and 2 μM, respectively by naked eye vision whereas the LOD value was found to be 0.05, 0.1 and 0.1 μM, respectively when monitored by UV-visible spectrometer. They also reported the selectivity of the nanoparticles with other ion, which shows visual colour changed (Fig. 15) [82].

Ag-$CoFe_2O_4$/rGO nanocomposites synthesized by simple one-pot microwave assisted treatment was used as a sensing probe for colorimetric as well as detection of SERS for toxic Hg^{2+} ions based on its intrinsic oxidase-like activity towards the oxidation of TMB. The reaction between Ag and Hg^{2+} nanoparticles takes place within a very short period and results in the formation of Ag-Hg alloy with the simultaneous reduction of Hg^{2+}. The formation of such alloy can enhance the oxidase-like activity and makes it enable for sensitive towards Hg^{2+}. They reported

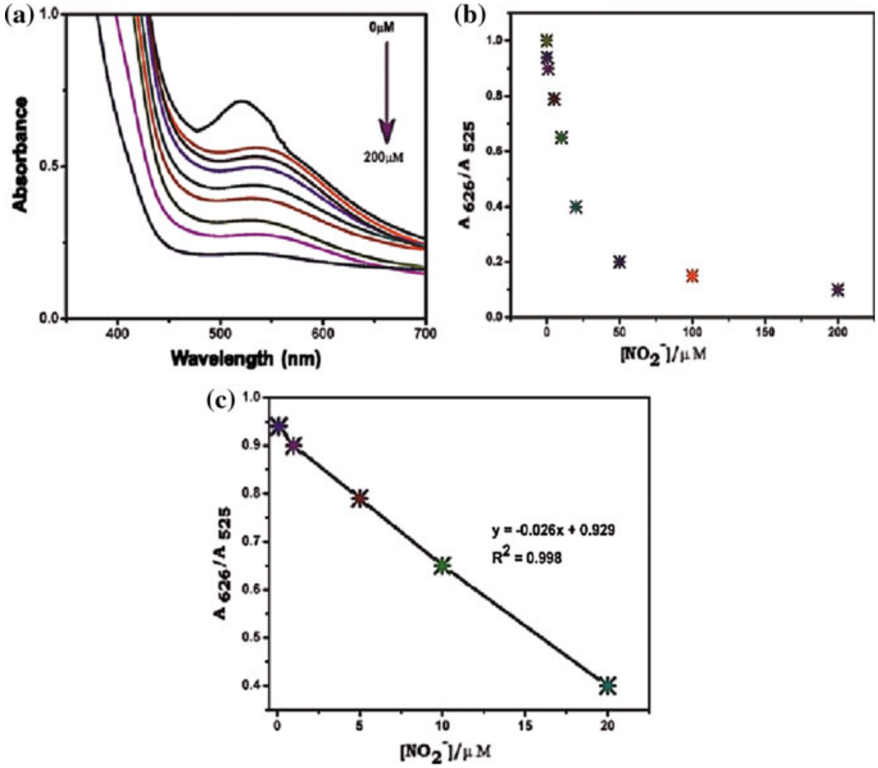


Fig. 14 UV-visible spectra of Au nanoparticles/rGO at various concentrations of NO^{2-} (**a**), plot of absorbance versus $[NO^{2-}]$ (**b**), calibration curve for NO^{2-} ion detection (**c**) linear plot of No^{2-} range 0.1–20 μM (reproduced with permission from Ref. [81])

the sensing ability up to 0.67 nM using SERS method and 10–7 nM based on the colorimetric method in acidic conditions [83] (Fig. 16).

Borthakur et al. utilized Cu(0) nanoparticles decorated hydrophilic glucose functionalized graphene oxide nanocomposite (Cu-frGO) for the detection of toxic Cr(VI) ions present in wastewater system. To explored the sensitivity of the proposed colorimetric probe, they have studied the peroxidase-like activity towards the oxidation of chromogenic peroxidase substrate TMB to it's blue colored oxidized (oxTMB) product. For the quantitative determination of Cr(VI), the absorbance of oxTMB is monitored by UV-vis spectrometer at 652 nm wavelength in presence of Cr(VI) ions, which enhances the peroxidase oxidation of TMB. They reported that the proposed colorimetric probe is highly selective and had sensitivity for Cr(VI) up to the lower concentration of 67.13 nM (Fig. 17b). They also reported the removal of Cr(VI) ion from environmental spiked samples [84].

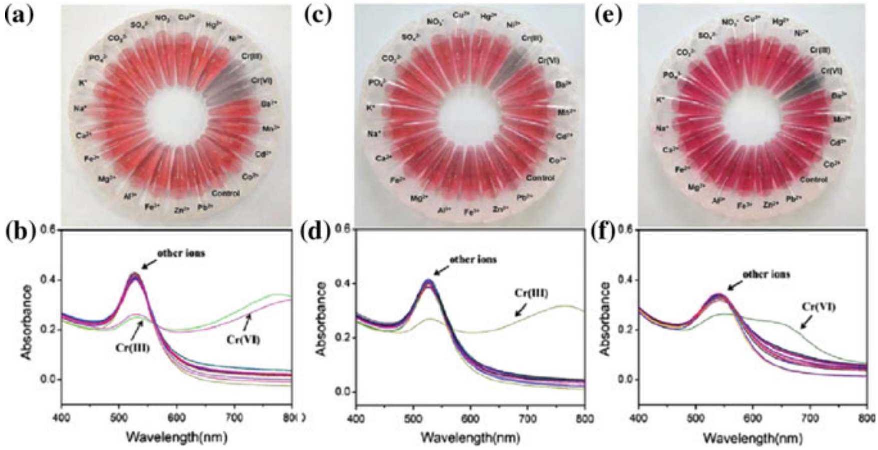


Fig. 15 Compared with other ions, the selectivity of the Au nanoparticles for colorimetric detection of Cr(III) and Cr(VI). Image of (**a**, **c**, **e**) various ions in the absence of masking agents, in presence of citrate and thiosulfate, with EDTA; UV spectra of the Au nanoparticles for Cr(III) and Cr(VI) (**b**, **d**, **f**) other ions in the absence of masking agents, in presence of citrate and thiosulfate, with EDTA (reproduced with permission from Ref. [82])

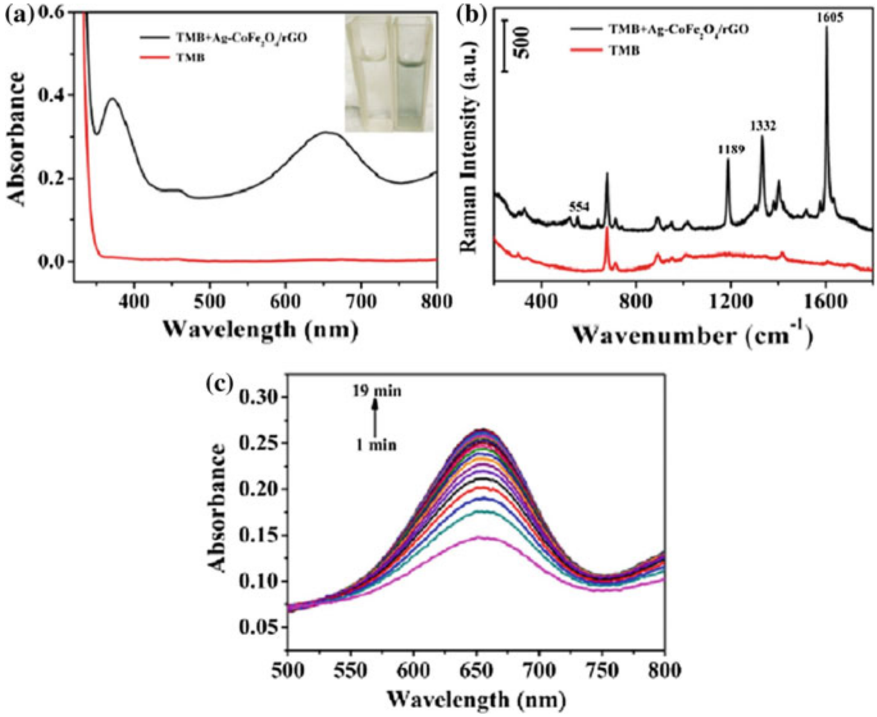


Fig. 16 **a**–**c** UV spectra of oxidation of TMB as prepared Ag-CoFe$_2$O$_4$/rGO NPs (reproduced with permission from Ref. [83])

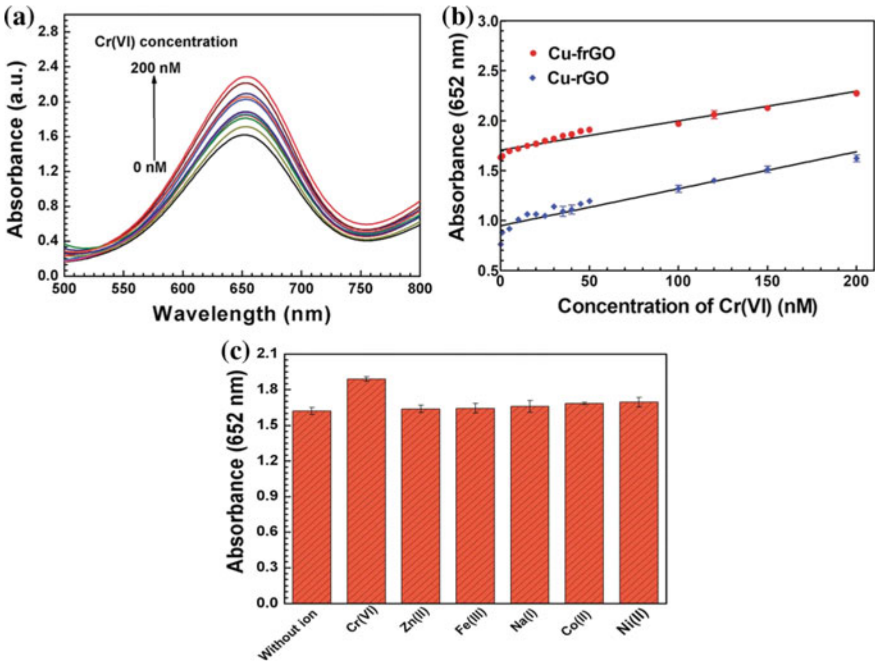


Fig. 17 **a** In the presence and absence of Cr(VI) ions UV-vis spectra of the ox TMB product, **b** linear calibration plots for Cr(VI) detection, **c** absorbance of oxidized TMB in the presence of 50 nM of different ions (reproduced with permission from Ref. [84])

Zhang and his group Au/Fe_3O_4/GO hybrid material for ultrasensitive detection of Hg^{2+} ions in an aqueous medium with the detection limit of 0.15 nM based on its peroxidase mimics (Fig. 18) [85].

Darabdhara et al. reported the magnetic Au@Ni loaded on rGO nanocomposites for colorimetric detection of phenolic compounds. Core-shell Au@Ni/rGO magnetically recoverable nanocomposites were prepared with size below 8 nm by a solvothermal method which exhibited enzymatic behavior towards the colorimetric detection and oxidation of TMB with LOD value 1.65 μM in range limit 1–300 μM. They reported that the addition of different phenol concentration in Au@Ni/rGO nanocomposite the colour changed from colorless to pink shown in (Fig. 19) [86].

In similar process Yanzhou J. and his group have utilized the (rGO)/Cu_8S_5/polypyrrole (PPy) nanocomposites with Cu_8S_5 nanoparticles and PPy layer decorated on rGO sheets as peroxidase like activity for colorimetric detection of phenol and H_2O_2. They reported that the synthesised (rGO)/Cu8S5/PPy nanocomposites exhibit higher catalytic activity towards 3,3′,5,5′-tetramethylbenzidine (TMB) oxidation in presence of H_2O_2 [87].

Liu Lu et al. reported that histidine capped gold nanoclusters (His@AuNCs) on rGO sheets possessed oxidase-like activity, in presence of TMB to ox-TMB without

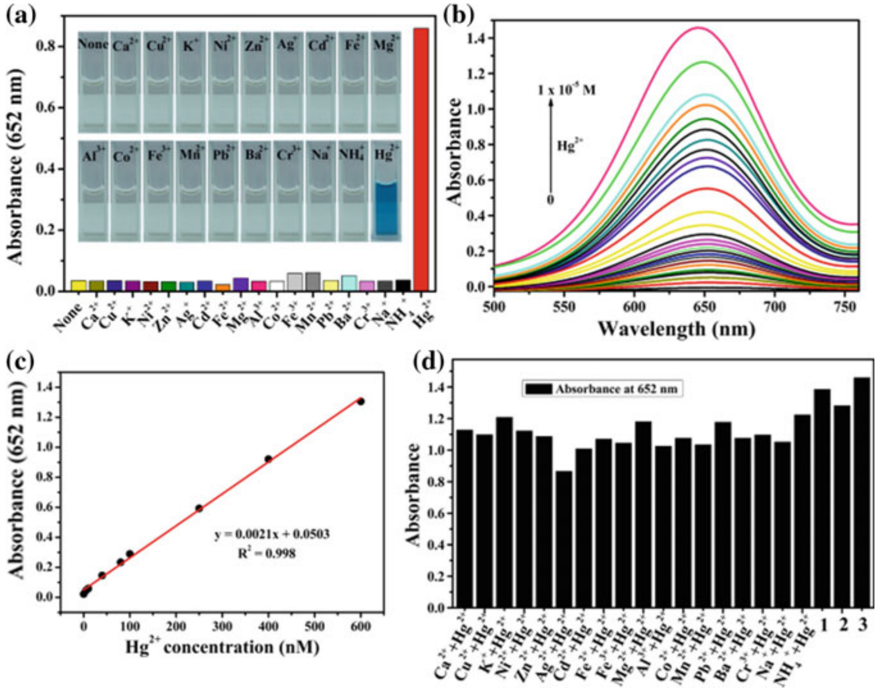


Fig. 18 **a** Catalytic activity of Au/Fe3O4/GO stimulated by various metal ions. **b** After the addition of Hg^{2+}absorption spectra. **c** Linear calibration plot for Hg^{2+} detection. **d** Absorbance effect of metal ions on catalytic activity of Hg^{2+} (reproduced with permission from Ref. [85])

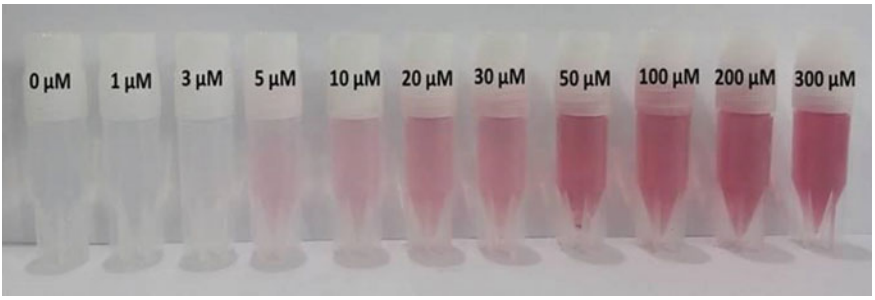


Fig. 19 Photographs of colorimetric change of Au@Ni/rGO containing different phenol concentrations (0–300 µM) (reproduced with permission from Ref. [86])

H_2O_2 which change to blue colour (Fig. 20). They reported that the His@AuNCs on rGO as on oxidase mimic by a colorimetric method to detection of nitrite with linear ranges of 10–500 µM and 2.5–5700 µM [88].

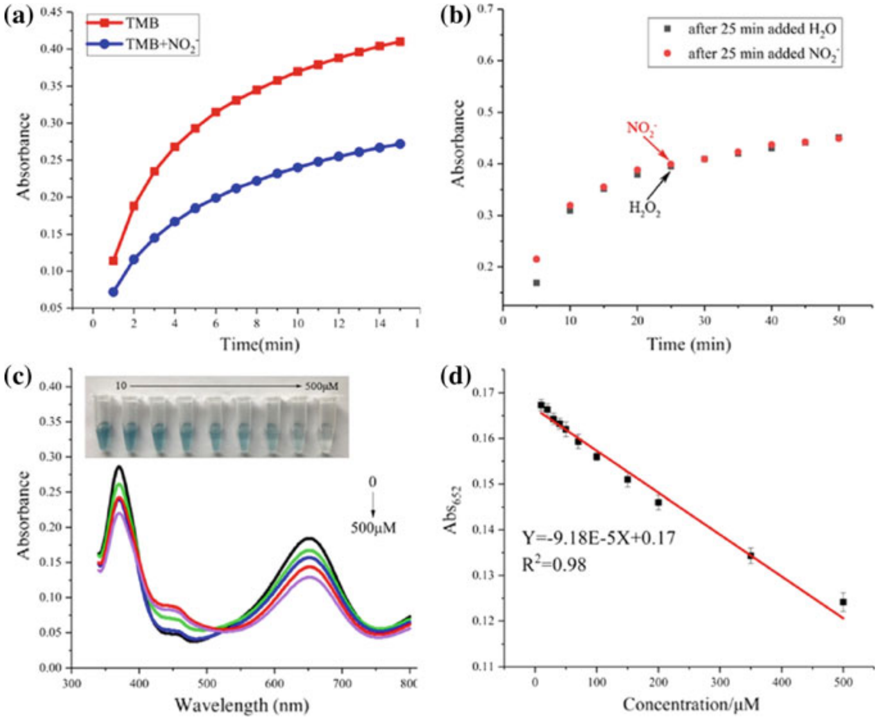


Fig. 20 **a** Variation of UV-vis absorbance of TMB and TMB with NO^{2-} in 0.05 M PBS (pH 5.0) at 652 nm wavelength in presence of His@AuNCs/RGO at different time, **b** chromogenic reaction of nitrite in time-dependent absorbance at 652 nm, **c** UV–visible absorption spectra of different NO^{2-} concentrations in the presence of TMB, **d** Linear plot of the concentration of nitrite (reproduced with permission from Ref. [88])

6 Conclusions and Future Prospective

In this chapter, different plasmonic nanoparticles decorated graphene/functionalized graphene nanocomposites for detection of water, pollutants is discussed. Three detection techniques have been considered throughout this chapter, namely colorimetric, fluorometry, and electrochemical sensing methods. The electrochemical detection technique possesses maximum sensitivity and detection limit is found low in comparison with the other two methods. Compared to other sensing methods, these three methods are very simple, easy operation, inexpensive, and no need highly skilled manpower. As all the sensing experiments are performed in the laboratory condition for real-time analysis, it is necessary to devise some large-scale synthesis method to use in some device fabrication in the near future.

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Materials for Electrical Detection of Water Pollutants

Chhavi Sharma, Sauraj and Yuvraj Singh Negi

Abstract Water pollution has become one of the irresistible problems worldwide. FETs and AlGaN/GaN HEMTs (High Electron Mobility Transistors) are the forthcoming hopeful tools for real-time, ultrasensitive recognition of analyte. They are taking attention over other techniques because of its exceptional properties like fast response, high sensitivity, low toxicity, superior biocompatibility and excellent chemical stability. Precision of FET sensors depend upon concentration of ions and inherent properties of the material i.e. band gap & carriers effective mass. 2D layered nanostructures such as graphene and its analogues, black phosphorous (called phosphorene), conducting polymers are attracting the researchers due to their in numerous novel properties over conventional bulk semiconducting materials; such as tuneable band gap, high carrier mobility ($\sim 10^2$–10^5 cm^2/V/s), good electrical and magnetic properties etc. This chapter will cover all the basic and comprehensive analysis of technique reported materials and will include the future prospective and applications.

Keywords Water pollutants · FETs · MOSFETs · 2D layered structures · Graphene · Conducting polymer

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1 Introduction

Fresh water is an essential life support, but due to rapid industrialization and/or urbanization resulting in the confinement of clean and drinkable water resources all over the world and converted to a challenging global threat. From various printed media and surveys reports, over one-sixth of the world's population is suffering from drinkable water crisis [1, 2].

As we all are aware about the sources of contamination, i.e. natural and man-made or sometimes referred as geological and anthropogenic sources. Geological sources dependents upon the geological strata i.e. route of flow of water and from what kind of rocks it is passing by. The continuous flow of water through rocks results in its weathering and constituent's e.g., calcium, magnesium, arsenic, fluoride, chlorine, nitrates, iron, soil and others get dissolved. Clean and drinkable water is always enriched with minerals because they are essential for our proper body functioning, but when the concentration levels rises above the bearing limits then it will be considered to be polluted water and becomes a cause for water borne diseases [3].

Sources including pesticides, insecticides used in agriculture, manufacturing industrial discharge which contain concentrated amounts of heavy metals, chemicals, dyes, solvents, improper disposal of household waste containing synthetic detergents, paints, gasoline and diesel fuels, pool chemicals, disinfectants, medicines comes under anthropogenic contamination resulting in ground water deterioration. According to UN report 2003 [4], about 2 billion tons of sewage per day, are discharged into the biosphere's water where sewage includes both industrial and agricultural waste [5].

2 Classification of Types of Contaminants

(i) Inorganic contaminants
(ii) Organic contaminants
(iii) Biological contaminants
(iv) Radioactive contamination

(i) **Inorganic contaminants**, is a group of contaminant, which incorporates inorganic species such as fluorine, Heavy metals, nitrides etc. They get added to the water bodies due to geological and anthropogenic causes (as discussed above [6]. *Heavy metals (HM)*, are defined as those who has density more than 5 g/cm^3. Table 1 is representing only significant to environmental perspective. Usually, Arsenic amongst all is considered to be significantly hazardous [7]. HMs possesses severe health issues e.g. reduced physical and mental among children, cancer, organ impairment, nervous system mutilation, and in extreme cases, death. Hg (II) and Pb (II) may cause autoimmunity disorder, kidney malfunctioning, rheumatoid arthritis

Table 1 Includes heavy metals with their toxicity and MCL limits based on the MCL standards (established by USEPA) [8]

Heavy metals	Reported adverse effects	Conc. (mg/L)
Arsenic (III)	Skin appearances, cancer, vascular syndrome	0.050
Cadmium (II)	Kidney destruction, renal ailment, human cancer-causing agent	0.01
Chromium (IV)	Headache, diarrhea, motion sickness, vomit, malignancy causing	0.05
Copper (II)	Liver mutilation, Wilson ailment, sleeplessness	0.25
Nickel (II)	Dermatitis, unsettled stomach, chronic asthma, carcinogenic	0.20
Zinc (II)	Despair, laziness, nervous breakdown and greater than before thirst	0.80
Lead (II)	Impairment to the fetus, kidneys impairment, circulatory and nervous system	0.006
Mercury (II)	Rheumatoid arthritis, ailments related to kidney, neurological disorders	0.00003

cardiovascular system. HMs when accumulate in the body than the permissible limit they may result in permanent damage to brain, liver and kidney [6, 8].
Fluoride, does not occur in the fundamental state in environment since it is highly reactive. It exists as mineral fluoride with mass of about 0.3 g/kg of the Earth's crust [9]. In groundwater, fluoride concentrations differ with the kind of rock bed the water drifts through but then again do not surpass 10 mg/L [10]. Various fluorides containing compounds are extensively used in various industrial sector of aluminum processing, glass fiber, steel, pharmaceutical, fertilizer and others. When fluoride is up taken orally (in the form of water or medicines or in food products) the solvable fluorides are entirely get immersed in the GI tract. Immersed fluoride is then circulate via the blood; and when it enters brain, resulting in increased risk for diseases like Alzheimer's disease and various other memory related issues collectively termed as dementia [11–14]. It is also accountable for fluorosis. As per the survey conducted, across many countries including India has more than 15 states are affected by acute fluorosis [15].

Selenium (Se) is existent in the earth's crust, bonded with minerals containing Sulphur. Selenium occurs in numerous forms, such as selenides (Se^{2-}), selenium (Se^0), selenites (Se^{4+}) and selenates (Se^{6+}) [16, 17]. The level of selenium in water arrays 0.06–400 μg/L [18–20]. In seleniferous areas, gastrointestinal disorders, skin discoloration and rotten teethes were reported in common [21].
Cyanide is highly toxic and dangerous contaminant. Major source of cyanide addition to water cycle are anthropogenic sources such as industrial waste from electroplating, gold and silver extraction, base metal flotation; coal gasification; and the decontamination of ships, buildings, grain silos, seeds in vacuum cavities. During, drinking water chlorination, cyanogen chloride might be a by-product and

in the in situ making of chloramines as a remaining sterilizer to uphold the sterile condition of supply arrangements. Prolonged exposure to cyanide above MCL value (0.2 mg/L) may cause weight loss, thyroid and nerve impairment [22].
Nitride (MCL 10 mg/L) is found in sewage from humans and/or farmhouse and commonly overflows into water sources. Extreme intake of nitrate can cause serious ailments such as methaemoglobinaemia, or blue-baby syndrome in infants, because of interfering oxygen transport in the blood [23, 24].

(ii) Organic Contaminants may include pesticides, gas or liquid-phase volatile organic compounds (VOCs), slurry's, gums, chemicals, crude wax, paper, plastic, timber etc. Contamination through organic materials may leads to severe diseases such as cancers, hormonal disturbances, and nervous system ailment [25–28].
Pesticides embrace all substances that are used to abolish or regulate pests such as insects, weeds, fungi, and others. They also play a significant role in food production or increase yields and facilitates cropping several times a year. In farming, herbicides (weeds), insecticides (insects), fungicides (fungi) and rodenticides (vertebrate poisons) are commonly used which imparts chronic health issues, depending on the amount. For instance, let's take an example for commonly used pesticides namely, organophosphates and carbamates, causes partial or permanent damage to the nervous system and endocrine system, skin or eye irritation, and it is cancer causing too [29].

(iii) Biological Contamination is produced through the existence of active living entities, such as algae, bacteria, protozoan or viruses. *E. coli* is the most commonly occurring coliform in intestines. It yields toxins that harm the intestinal lining, cause anemia, stomach pains, and bloody diarrhea [30]. Another abundantly existing microscopic species is Algae which are reliant on water nutrients such as phosphorus. Excessive algae growing imparts bad odor problem and clogs filters, and yields slime growths. Similarly, bacteria, viruses and protozoa are also the pathogens causing water contamination resulting in water borne diseases such as dysentery, cholera and gastroenteritis [28, 30].

(iv) Radiological Contaminants are unwanted radionuclides which enter into water sources. In drinking water, naturally occurring radiological isotopes of radium, uranium and radon were reported. They added up in groundwater due to weathering of granitic rocks and other minerals. Sometimes human activity changes and spreads naturally-occurring radiological, resulting increased potential levels. Referred to as Technologically Enhanced Radioactive Material (TENORM), and are originated as industrial wastes from industries like coal (mining and combustion), oil and gas industry, Fertilizer (phosphate) and recycling industries. Commonly found radiological element in drinking water is Uranium. It is kidney venom and has been linked with an rise in trivial calcium release and increased microglobulinemia [6, 31].

3 All About Transistor Family

3.1 Introduction

In the field of Integrated circuits (IC), the world famous observation acknowledged as Moore's law, and it states that amount of components per IC leading to lowest manufacturing cost every year. These days this law is used to designate high speed processing devices in the field of electronics and computation [32–34] (Fig. 1).

4 Quick Overview of the Technology with Terminology

4.1 Transistor's Working Principle

Current or voltage between two terminals is controlled by slight quantity of current or voltage through the third one. Transistors are being classified as (i) BJT and (ii) FET.

(i) *Bipolar Junction Transistor (BJT)* is a current variable device that controls the amount of current passing through the Emitter to the Collector terminals in proportion to the amount of applied biasing voltage on the base terminal. On the basis of type of majority charge carriers involved it can be further classified as **NPN** and **PNP** type transistors [35].

(ii) *Field Effect Transistor (FET)* is a three terminal device in which current conduction takes place through "channel" sandwiched between Source & Drain terminals and width of channel varies as a function of applied gate

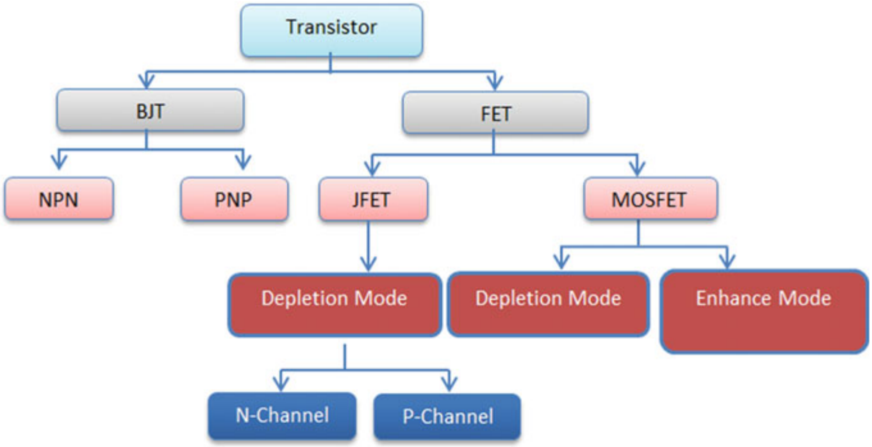

Fig. 1 Classification of transistor family

voltage. Hence, function of Drain, Gate and Source terminals can be correlated to Emitter, Base and collector terminals of BJTs. It can be classified as JFET and MOSFET (or IGFET) [36].

- *Junction Field-Effect Transistor (JFET)* is a three terminal voltage controlled unipolar device having N-channel and P-channel configurations. It is typically used in high frequency or high current systems e.g. microwave amplifiers [36].
- *Metal oxide FET (MOSFET) or IGFET (Insulated Gate FET)*, is a voltage controlled FET having thin layer of "Metal Oxide" to form insulated Gate electrode [36].

5 Metal Oxide Semiconductor Field Effect Transistors

As compared to BJTs, MOSFETs occupy very small space on an IC and hence VLSI integration can be realized by using MOSFETs. Using VLSI, some electronic circuits are designed by using only MOSFETs and essentially not using any resistor and/or diodes. This can fabrication is used in forming microprocessors, high density memory devices.

5.1 Principle of Working

the current flow is attained by put on electric field perpendicular to drain and source terminals and in the direction of flow of electric current. The phenomenon of controlling conductance of semiconductor using electric field is known as ***Field Effect or gating effect*** [35].

5.2 Physics Involved in Working of MOSFETs

In order to understand it, let's consider a parallel plate capacitor in which, two charged plates are separated by an insulating material substrate. At the top of the metal plate, a negatively biased voltage is applied and hence, other plate will be positively charged and an upwards electric field will be generated into the substrate. In influence of induced electric field and the type of substrate material (p-type or n-type) will result in the formation of a region of charge accumulation known as inversion layer. For illustrating it, let's consider an example that, lets we have taken a p-type substrate and a negatively biased voltage (with respect to the type of substrate) For simplifying the explanation, let's consider the MOSFET as simple parallel plate capacitor which is separated by a semiconducting material and an

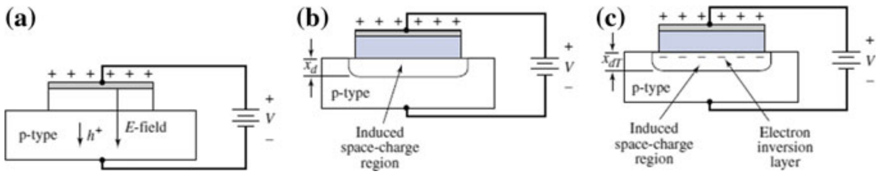

Fig. 2 The MOS capacitor with p-type substrate: **a** effect of positive gate bias, showing the electric field and charge flow, **b** the MOS capacitor with an induced space-charge charge due to a moderate gate bias, and **c** the MOS capacitor with an induced space-charge region and electron inversion layer due to larger gate bias [36]

alternating bias voltage is applied to it. Hence, upper plate is now negatively charges and respective bottom plate becomes positively charged; and an electric field is setup between the two.

For p-type semiconductor substrate, when a negatively biased voltage is applied at the top (also known as gate terminal) plates get charged and an upward electric field is being created in the space within the two. Now, due to this electric field the holes will start accumulating at semiconductor and oxide layer interface. Now, when the polarity of the bias voltage changes (negative to positive) then the polarity of the plates also changes (upper becomes positive and bottom plate becomes negatively charged) and in this case now, the accumulated holes will experience electric field in opposite direction and start to leave and results in a charged region induced because of minority carrier electrons forming a region called as **electron inversion region**. In the similar fashion if we take n-type substrate then positive biased gate voltage is applied and results in forming **hole inversion region**. The magnitude of current flow in the MOSFET is a function of width of inversion layer and width of inversion layer formed at the oxide-substrate interface is a function of gate voltage applied [36] (Fig. 2).

Modes of operation: (1) Enhancement mode and (2) Depletion mode.

In enhancement mode, positive bias voltage is applied to p-type substrate and negative bias voltage for n-type substrate to for charge inversion region and vice versa is for depletion mode.

5.3 n-Channel Enhancement Mode MOSFET

5.3.1 Simplified MOSFET Structure

Simplified MOSFET Structure is shown in Fig. 4. here we have two additional n+-regions (+ sign indicates heavily doped) present creating **source terminal** and

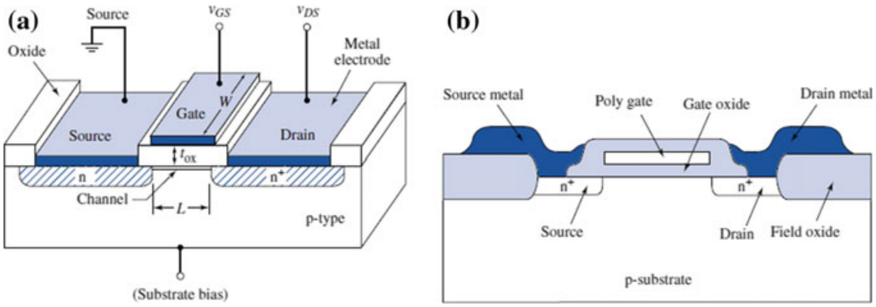

Fig. 3 **a** Schematic diagram of an n-channel enhancement mode MOSFET and, **b** an n-channel MOSFET, showing the field oxide polysilicon gate [35]

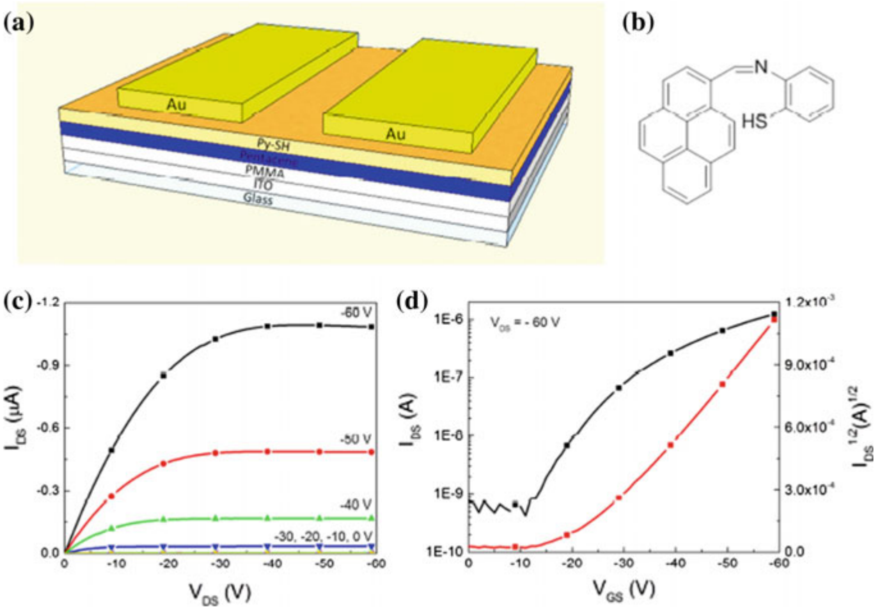

Fig. 4 **a** Schematic structures of the OTFT sensor incorporating py-SH as receptor layer for Hg^{2+} ion, **b** chemical structure of py-SH receptor layer, typical **c** output and, **d** transfer characteristics of fabricated OTFT sensor [44]

drain terminal. The current flow through inversion layer is termed as **channel region.** The more detailed diagram is shown in Fig. 4, as the actual structure of MOSFET is fairly complex, here it is a simplified version to make an understanding about the device (Fig. 3).

5.3.2 Basic Transistor Working

Case I: *When no bias voltage applied:* the current between source and drain must be zero.
Case II*: When large positive bias voltage is applied:* then a carrier region is formed between two n-terminals (i.e. n-drain terminal and n-source terminal) allowing current from source to drain. The source terminal supplied the carriers that flow through the channel and drain terminal allows carriers to drain from the channel. So, we can say that when V_{DS} (voltage drain to source) is applied then charge carriers start flowing from source to drain terminals. By convention, current is flowing in opposite fashion i.e. from drain to source terminal. As used biasing gate voltage is positive, it form electron inversion region, termed as **enhancement n-channel MOSFET** or **NMOS.**

5.3.3 Ideal MOSFET V-I Characteristics

Threshold voltage ($V_{TN)}$ is nothing but applied “turn on” voltage for the transistor.

Case I: $V_{GS} < V_{TN}$: Drain current (I_D) = 0 and is said to be in “turn-off” state because there is no inversion layer formation taking place.
Case II: $V_{GS} > V_{TN}$ and small V_{DS} is applied: It is a transistor “turn-on” state. The I_D increases with increase in V_{GS}.

(a) $V_{DS} > V_{DS\ (sat)}$: I_D becomes constant and independent of V_{DS} (Drain to source voltage) and the region is known as **saturation region**.
(b) $V_{DS} < V_{DS\ (sat)}$: The region is known as **unsaturated state**.

6 Designing of FET Based Sensors

In relevance to the above discussion, we can easily understand that, current flowing through FETs is a function of biased gate voltage applied to it. Therefore, sensing of organic and/or inorganic species is performed by adjusting gate material or by placing a selective membrane or by using (bio/chemical)-recognition component onto it. The resulting sensor is known as CHEMFET. When ion selective material is used then it is known as ISFET. When organic sensing platform is used as sensing material then it is known as OFET [37]. ISFET based sensors have numerous possible applications in diversified fields of chemistry, sensor designing and development, microbiology, flexible and wearable electronic devices and many more [38]. As of now, we are assuming that, readers got the clear picture of how a MOSFET based devices works. In the next section we will include the various nanomaterials reported in the literature towards water pollutants.

7 Overview About the Existing Materials Related to Water Contaminants in Literature

7.1 Supramolecule with Polymer Membrane

Supramolecular chemistry is the study of objects having larger complexity than distinct fragments assemblies of molecules that bond and unify over intermolecular interconnects. The design and synthesis of supramolecular systems comprises of exchanges beyond the covalent linkage, e.g. hydrogen bonding, metal coordinate bonds and π-interactions to fetch distinct building blocks together [39]. Therefore, best fitting tailoring of molecules for desired host-guest interaction is possible and when supra is embedded into polymers, and then it will enhance sensitivity and selectivity to many folds.

Among various supramolecules, in order to sense heavy metals, calixarenes have been found appropriate because they provides a route to fragments with well-defined hollows, and offers synchronized polar and non-polar features. Therefore, they can form annexation complexes with a extensive variety of guest species. Calix[4]arenes derivatives with thioether, thioamide, and dithiocarbamoyl were reported. calix[4] arene (2) with two diametrically replaced thioether ionophore with PVC membrane towards Ag (I) (selectivity 60 mV/decade); calix[4] arene, with four dithiocarbamoyl PVC membrane for Cu (II) ions (30 mV/decade); calix[4]arene, with four dimethylthiocarbamoylmethoxyethoxy substituents based PVC membrane is used for Cd(II) ions (selectivity 30 mV/decade) and oxamide and thioamide ionophores functionalised PVC membrane was reported for Pb(II) ions [40]. Another calixarene structure; 4-tert-butylcalix[4]arene (NaTPB: DBP: PVC) doped PVC based membrane is used for selective sensing towards Pb (II) with selectivity 30 mV/decade, and author acclaimed the stability of the electrode up to 6 months without change in its potential state [41].

In order to resolve the adhesion problem between polymeric membrane and the transducer, poly(vinyl chloride vinyl alcohol-vinyl acetate) (PVC-PVA-PVAc) polymer was used instead of Poly vinyl chloride (PVC). Dipropyloctadecyl Dioxadiamide was entrapped within modified polymeric membrane to make graphitic solid state sensor (CSSD or CHEMFET) and ISE towards Pb (II) & Cd (II) sensing [42]. Cutting-edge evolution in polymeric materials, as new class materials known as conducting polymers were also gained interest in order to improve the sensing application. The conducting polymers are not only hydrophilic in nature but also improve adhesion properties with the transducer. The OFETs based on this class materials reports low cost, low toxicity, enhanced conductance properties and good adhesions of the membrane spin coated high mobility polyisoindigo-based polymer with siloxane-containing solubilizing chains33 (PII2T-Si) was reported to form polymer OFET, suitable for sensing of Hg (II) ions in fresh water as well as marine water [43]. in the modification of FETs with different variants, an extended gate FETs are also getting popular to use as a solid state device. Alternative factual pentacene surface functionalised Pyrene with thiol group (py-SH) was reported towards OFET designing to increase channel sensitivity to Hg^{2+} ion. This material is capable of sensing Hg^{2+} ion as low as 0.01 μM [44].

8 1-D and 2-D Nanomaterials and Nanostructures

Class of 2-D nanomaterials contains Graphene, MoS_2, phosphorene and many more. All the 2-D structures impose best electrical and conduction properties which makes them suitable choices. Among the all, graphene is the most preferred choice of researchers.

Carbon nanostructures such as reduced graphene [45–50], CNT (single wall and multiwall) structures [47, 51] were modified or anchored with biomolecules such aptamers [52], peptides [45], DNAzyme [53, 54], nanoparticle [49, 54] and with various polymers [46] to make sensor more sensitive and selective towards Hg (II) [46, 47, 51–53], Cd (II) [48], Cu (II) [45], Ni (II) [45], Pb (II) [49, 51, 54].

In recent times, the **2D-layered transition-metal dichalcogenides (TMDs)** gained attention due to its tunable electronic properties, high swapping ratio of $\sim 10^8$, carrier freedom of movement of 200 $cm^2\ V^{-1}\ s^{-1}$ [55–57]. These exceptional features are making MoS_2 a hopeful material in future FET sensing.

Li et al. [57], has tried to explore the working and masking ability towards Schottky barrier (SC). The author also tried explore its use as an ionosphere towards As (III) with reported LOD of 0.1 ppb. Also, An and Jang [55] had designed a sensor utilizing the properties of MoS_2 and conducting polymer carboxylic polypyrrole (CPPy). As it is using two electronically conducting entities, hence it will result in extensively satisfying results. The electrode formed was named as carboxylic polypyrrole (CPPy)-coated flower-like MoS_2 Nano-spheres (CFMNSs) in order to bind As (III) with LOD: 1 pM. Zhou et al. [56] had also used MoS_2 structure decorated with Au NPs and functionalised by DNA electrode and named it hybrid FET towards sensing of Hg (II) with LOD: 9.9 nM and showed isolated behaviour towards potential interfering metal ions such as As^{5+}, Cd^{2+}, Pb^{2+} etc.

Black phosphorus (BP) is a material belongs to TMDs. Like graphene BP is also have multilayers stacked together with Vander Waal interaction and can be exfoliated to mono or multilayered systems. BP shows better carrier mobility (1000 $cm^2\ V^{-1}\ s^{-1}$) than conventional materials, larger current on/off ratio (1×10^3 to 1×10^5) than graphene and better molecule adsorption. Most fascinating feature is its high surface to volume ratio for designing an ultrasensitive sensing platform using BP. The biggest and the only limitation with BP is its physical stability [58]. Guihua Zhou et al. Had reported FET for As (III) ions, for that, BP film acts as channel material although the probe dithiothreitol (DTT) decorated on gold (Au) nanoparticles (NPs) acts as receptor for As (III). Author acclaimed the stable, sensitive and selective probe for As (III) with LOD 1 nM [59]. Li et al. [58], had

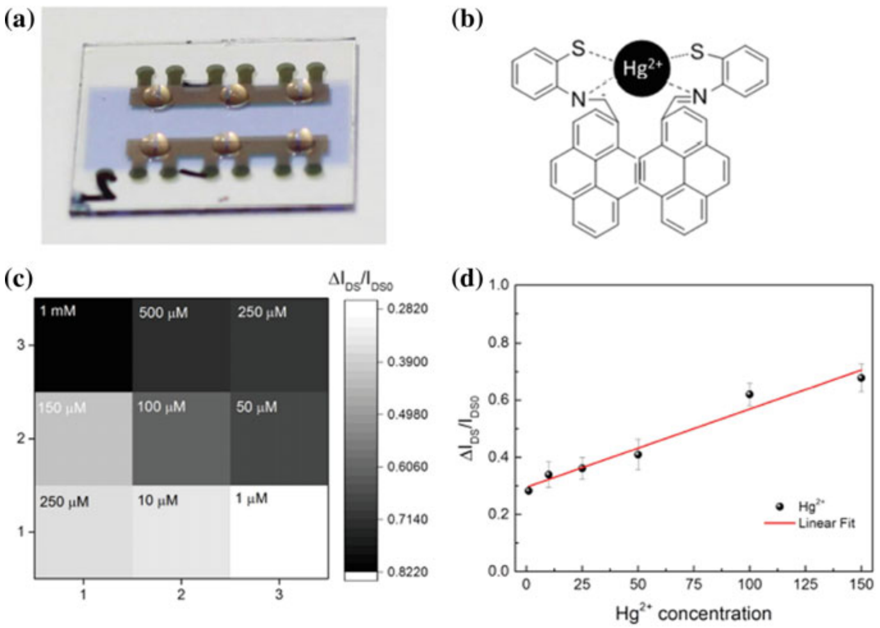

Fig. 5 **a** Photograph of OTFT sensor with 2μL Hg^{2+} ion droplet on the channel, **b** binding mechanism of Hg^{2+} to py-SH, **c** colour plot for $\Delta I_{DS}/I_{DS0}$ of Hg^{2+} ion concentrations ranging from 1 mM to 1 μM, **d** linear fitting of 150 to 1 μM concentration of Hg^{2+} [44]

reported air stable high performance BP encapsulated by ionophore coating. This layer is used as a gating material in which adsorption mechanism of Pb (II) ions were studied according to Langmuir Blogett isotherm. The author had reported the sensitivity towards Pb (II) to be 1 ppb. The paper is written so nicely that, every aspect is covered very nicely [44] (Fig. 5).

Silicon nanowires (SiNWs) are pseudo one-dimensional (1D) assemblies with a diameter of less than 100 nm resulting in larger surface to volume ratio. Hence, suitable for various electronic applications. For sensing, the small volume will excellently tolerate and respond to very small input signal making them suitable for chemical sensing and biochemical sensing [60]. The author had reported 3-mercaptopropyltriethoxysilane (MPTES) functionalized Silicon nanowires, to sense Hg^{2+} and Cd^{2+} ions. Through *I-V* characteristics, the CHEMFET demonstrated high selectivity and sensitivity with a detection limit down to 10^{-7} *M* for Hg^{2+} and 10^{-4} *M* for Cd^{2+} ions [61].

Other Materials: The HEMT (or High Electron Mobility Transistor) is a new class of high performance transistor having a combination of low noise figure and very high levels of presentation at frequencies lying in microwave region. This is a significant device for designing high speed digital and microwave circuits. It comprises of PN junction known as Metal semiconductor junction (MESFET) or Schottky barrier [62].

In the field of heavy metal sensing platform author [63] had reported a sensing mechanism based on Pb-ISHEMT (i.e. lead-ion selective HEMT). The gating material was made by ion selective membrane (ISM) incorporated with electrical double layer (EDL). Using this material Pb was sensed up to 10^{-10} M and detection time <10 min. K. H. Chen et al. had reported HEMT towards Hg(II) using Thioglycolic acid functionalized Au-gated AlGaN/GaN HEMT [62]. The outcomes propose that handy, fast response, and wireless technology based heavy metal ion sensors.

In extended gate FETs, the gate terminal is extended and connected to ITO, this won't add too cost to the device but provides flexibility of easy functionalization of the gate terminal. In the series of heavy metal sensing, OFET with an L-cysteine-immobilized extended gate electrode was designed for Hg (II) ion sensing [64]. To improve the stability of the membrane towards acidic nature, chalcogenide type of glass is commonly used in pH sensitive meter/probe. Author here used $Ge_{28}Se_{60}Sb_{12}$ chalcogenide glass and metal copper was deposited to make Cu-Ge-Se-Sb pattern to form a Cu (II) ion sensitive membrane over the gate terminal was deposited and the analysis resulted in 10^{-6} mol/L limit of detection [65].

Detection using enzymes/inorganic species entrapped polymeric membranes:

Electrode developed by single-crystal lanthanum fluoride (LaF3) for fluorine detection, named as Fluoride ion-sensitive electrode (FISE) by Frat and Ross in 1966. It has various features like good selectivity, stability, and rapid response [66]. The only limiting factor was its high cost. Later, in 1970 when Bergverd introduced the concept of ISFET, then fluoride will be sensed by the combination of single crystal LaF3 and ISFET. Later, some of the papers were reported towards fluoride sensitive ISFET using polycrystalline LaF_3 and the membrane formed was deposited with structure (Si-SiO_2-Si_3N_4,-LaF_3). This gate membrane will detect the behaviour of the electrolyte in contact with it [67]. Similarly, buffer β-alanine (2-aminopropionic acid) and HCl with and without CDTA (1,2-cyclohexanediamine tetraacetic acid) [68] and Storensen's buffer (a mixture of glycine and hydrochloric acid, pH 2.8) [69] was testified to govern free and total fluoride concentrations. Sensing of fluoride completes when we get the complete information about concentration of free fluorine and total fluorine. Therefore, concept of pF-ISFET and pH-ISFET were introduced in which pH-ISFET is taken as reference electrode and pF-ISFET is used to calculate concentration of fluorine even at very low level [70]. In order to replace LaF_3 electrode constantly various other materials were being reported. Some authors used plasticized uranyl salophen supramolecular complex [71]. Further, LAPS (Light Addressable Potentiometric Sensor) heterostructure (Au/Si/LaF_3) were investigated for sensitive fluoride detection [72]. Polydimethylsiloxane (PDMS) functionalized the gold surface with self-assembled monolayers (SAMs) of fluoride-sensitive ligands were also used towards sensing of fluoride and sodium [73]. EIS based electrode using poly LaF_3 were also reported with 1.9 ppb detection limit. The device is accomplished by sensitivity, detection limit, lesser hysteresis voltage, and slight drift ratio [74].

Organophosphate is a well known toxic compound. Organophosphate has various derivative to act as pesticide, insecticide, weedicide etc. Commonly known method for electrode designing in ISFET towards pesticides is incorporating enzyme into the polymeric membrane to immobalise the analyte of interset. Membrane A: Polymethylmethacrylate with monomer bisphenol-A-bis(2-hydroxypropyl methacrylate) For Pesticide and Membrane B: polyacrylamide with monomer bifunctional bisacrylamide for Cu (II) with enzyme urease and AChE was reported.

9 Conclusion and Prospective

As per the complete discussion, sensing through potentiometric technique is a good alternative to many lab based detection techniques such as optical detection, electrochemical detection techniques and others, because of the ability to miniaturization and easy commercial bulk production of the sensing electrode. But, still there is a great room for research to investigate materials to make fast response devices such as HEMTs (High Electron Mobility Transistors) in lower the response time and enhancement in sensitivity many folds.

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Materials in Colorimetric Detection of Water Pollutants

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Abstract Evolution in the sensor design and their potential usage in water quality monitoring has revealed the aptitude of material science in the environment protection practices. Consequently, the progress in scientific literature is rising to tail consistent and sophisticated sensory platforms. In this context, colorimetric sensors are categorised as benchmarked sensor models, owing to their cost effectiveness in sensor design, ease of analysis, on-site pollutant monitoring capability, circumvents the use of multifaceted instrumentation and most importantly, user-friendliness. This chapter is focussed on the potential use of colorimetric sensors for the water-pollutant sensing and discusses the promising prospects of sensor developments (from choice of material to read-out tools) to assist nascent researchers to review the principles, mechanistic and advancements in existing trends in colorimetric sensory probes.

1 Introduction: Colorimetric Sensors for Water Pollutants

Water is one of the most important elements essential for the survival of life on the planet and so the monitoring of its quality. In the present scenario, colorimetric sensors are being used for the detection of various analytes such as proteins, organic compound, peptides, nucleic acids, toxic gases, humidity sensors and water pollutants. Water pollutants are broadly classified into four categories i.e. pathogens, inorganic materials, organic materials and macroscopic pollutants. Of them,

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Fig. 1 Common heavy metals with their permissible WHO limits and the health effects caused due to their overdose

Inorganic materials like heavy metals in particular mercury, arsenic, lead, cadmium, and other metals having high de is wide spread concern of the society when present in high concentrations and can have lethal effects to ecosystem as well as human health as shown in Fig. 1. Their accumulation can be due to leaching from waste disposal, industrial wastes, burning of fossil fuels, mining and other human activities. Further, in worst case, their exposure may even lead to death of humans or animals. Due to these reasons development of water monitoring technologies is the prominent area of research these days. The colorimetric technique is one of the preferred methods for the onsite detection of water pollutants because of the usage simplicity and affordability i.e. in most cases observations can be made by naked eyes without need of any expensive instrumentation for analysis. It does not require any skilled manpower for the analysis and can be used by the general public. Despite these advantages, the colorimetric techniques lack in accuracy and may not be able to fulfil the criteria of low detection limits, as compared to other spectroscopic and chromatographic techniques. These disadvantages is usually due to high background noise and in case of naked eye observation, color perception can vary person to person. In order to increase the accuracy and achieve the low limit of detection by colorimetric techniques, many research groups today combining these methods with digital imaging techniques.

This chapter intends to provide an overview of the design of colorimetric sensors which includes principle of colorimetry and various sensing mechanisms on which sensors are based Also, the recent developments in the materials utilized for the colorimetric sensing of the water pollutants. Nevertheless, a discussion on the commercially available colorimetric sensors.

2 Principles, and Sensing Mechanisms of Colorimetric Sensors

2.1 Principle of Colorimetric Sensors

In order to design the colorimetric sensors for the detection of analyte, there are two major principle factors which are considered i.e. the change in absorbance value at particular wavelength and second is the shift in maximum absorption wavelength. These two factors can be studied and confirmed with the help of UV/Vis spectroscopy and observed by naked eyes. The sensors based upon the first principle, appears to fade or darken when the analyte is introduced based upon its concentration and in second case, the change of color to the new color is observed. There are times, when color changes are not observed by naked eyes, even when these changes are observed with the help of UV/Vis spectroscopy. The rhodamine based copolymer poly(2, 3-dihydroxybutylene-alt-2,3-dihydroxybutylenedithioether) [P(DHB-a-DHBDT)] self-assembled onto 2-(5-bromopyridine-2-yl)-3′,6′-bis (diethylamino)spiro-[isoindoline-1,9′-xanthene]-3-thione shows the sensitivity towards the Hg(II) ions, in which color change from colourless to pink color observed by naked eyes as shown in Fig. 2. The said probe utilizes the second principle of colorimetry and its sensing mechanism is based upon the shifting of aromatic protons in the presence of metal ions [1].

Apart from these above-mentioned principles there are practical considerations which needs to be considered i.e. solubility of the sensor and matrix of the analyte, pH of the medium and behaviour of analyte in that pH, and medium does not have spectral overlap with the analyte to avoid interference while analysis.

Further, there are four major transduction methods or parameters which are considered or evaluated while designing colorimetric sensors i.e. aggregation observed while using metal nanoparticles, pH in case of organic dyes, in case of polymers conjugation geometry, and analyte induced reactions when dependent on irreversible chemical change. These transduction parameters cause the color changes upon the addition of the analyte to the matrix.

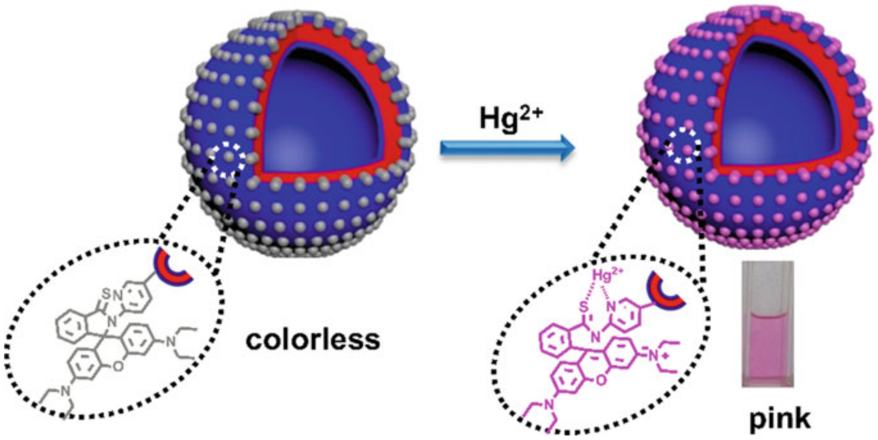

Fig. 2 Behaviour of Probe in the presence of Hg(II) (adapted from Ref. [1])

2.2 *Sensing Mechanisms of Colorimetric Sensors*

There are different sensing mechanisms based upon which colorimetric sensors can be designed i.e. Intramolecular Charge Transfer, Forster Resonance Energy Transfer, aggregation, pH, indicator formation,

2.2.1 Intramolecular Charge Transfer (ICT)

ICT refers to the charge transfer to the electron deficient acceptor from election rich moiety within the same molecule. It generally occurs when the molecule is in the photoexcited state by absorbing the light of specific wavelength which facilitates the transfer of electron from one part of molecules to the another. This forms a π-bridge which connects the donor and acceptor groups. Utilizing this sensing mechanism, the receptor molecule aminonaphthoquinones is utilized to design the colorimetric detection of Cu(II) where pyridine N-atom and amine N-atom forms square planar complex with Cu(II) shown in inset of Fig. 3. This results in blue shift of ICT band and increase in d-d transitions upon the increase in concentration of Cu(II) ions. These results in change in color of receptor from yellow to blue instantaneously, which indicates the selectivity of Cu(II) towards the synthesized receptor as shown in Fig. 3 [2]. Similarly, hemicyanine is reported as colorimetric sensing agent for Hg(II) ions which changes its color from red to colourless, which is also confirmed by the changes in UV/Vis spectra [3].

The concept of ICT has been utilized in several for colorimetric sensing applications, but there are challenges which still exist to utilize its full potentials.

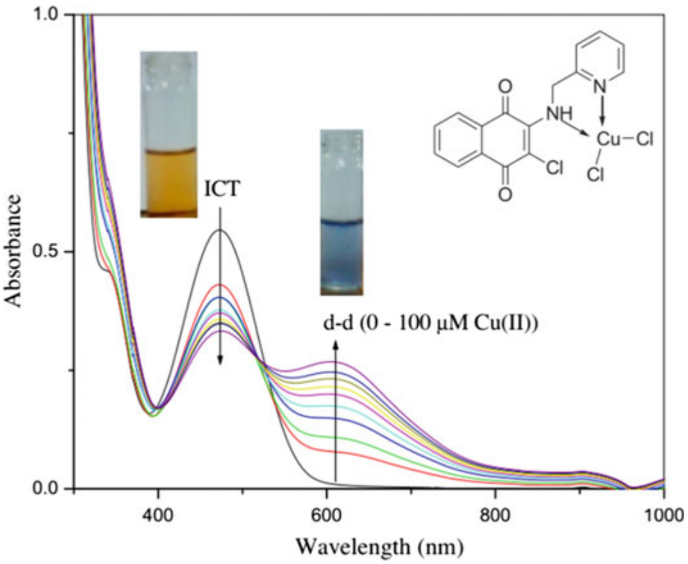

Fig. 3 Effect on receptor upon the addition of Cu(II) ions observed by UV/Vis Spectra and naked eye (inset: square planar complex formation upon the addition of Cu(II) (adapted from Ref. [2])

2.2.2 Forster Resonance Energy Transfer (FRET)

FRET occurs when there is transfer of energy from the donor fluorophore to acceptor fluorophore which are in close proximity between 1 and 10 nm in the absence of radiation through dipole-dipole interactions. For the FRET to occur, there should be a spectral overlap between the absorption of acceptor and emission of receptor and high quantum yield as shown with the help of example in Fig. 4a.

Recently Wanichacheva and his co-workers developed a FRET based Hg(II) sensor where helicene dyes used as energy donor fluorophores and exhibits high quantum yield and rhodamine 6G dyes as energy acceptor as it has absorption and emission wavelengths in the visible region, large molar extinction coefficient and high quantum yield as well [4]. Further, large stokes shifts of donor minimizes interference and small stokes shifts of the acceptor fluorophores which could leads to self-absorption. This small stokes shift of the rhodamine 6G dyes also changes the ring structure of the amide, which produces a fluorescent enhancement and colorimetric change. The both donor and acceptor molecules connected to each other by hydrazine moiety and upon the addition of Hg(II) to the sensor, the color change from greenish yellow to orange is observed by the naked eyes and also confirmed by UV/Vis Spectroscopy as shown in Fig. 4b [4].

Further, rhodamine-6G in another work is appended with benzothiazole conjugated quinoline derivative and used as a ratiometric probe for the detection of Fe (III) using FRET mechanism. Here, color change to yellowish orange from

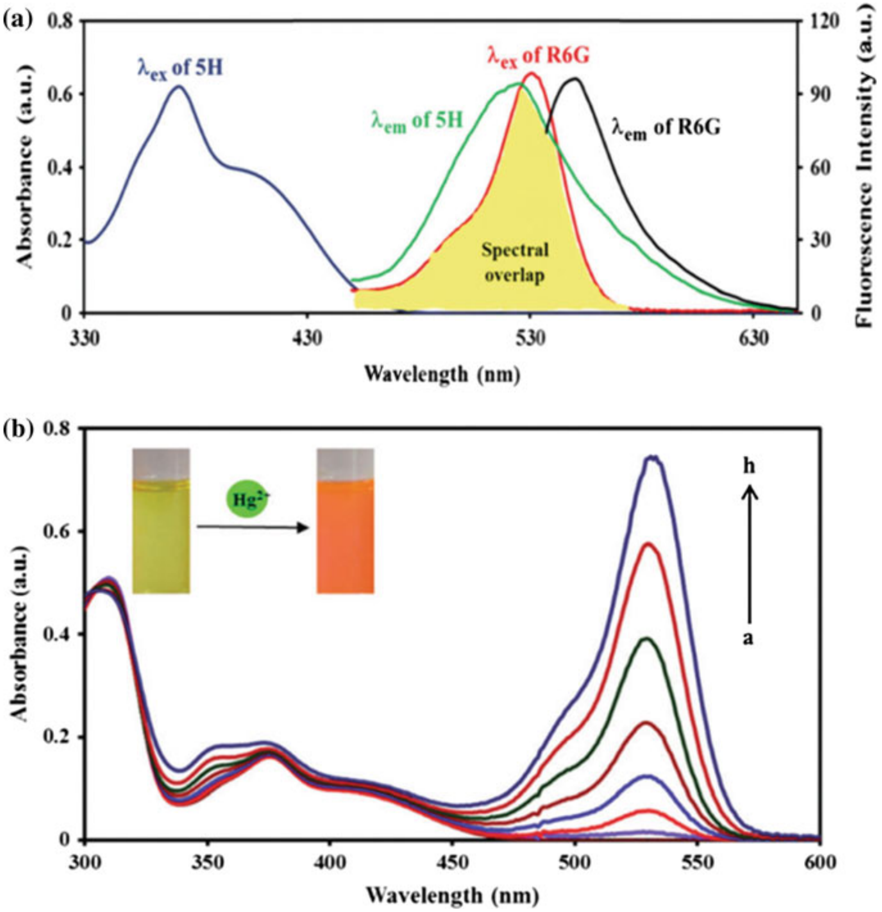

Fig. 4 **a** Overlap of emission and absorption of rhodamine 6G (R6G) and Helicene(5H). **b** Effect on UV/Vis spectra of sensor as function of Hg(II) concentration (a) 0 mM, (b) 10.0 mM, (c) 16.7 mM, (d) 23.3 mM, (e) 36.7 mM, (f) 50.0 mM, (g) 63.3 mM, (h) 83.3 mM (adapted from Ref. [4])

colourless is observed upon the addition of Fe(III) and their absorption spectra is also studied using UV/Vis spectroscopy for the different concentrations of the Fe(III) [5].

2.2.3 Aggregation Based Approaches

In colorimetric sensing, in most of the cases these approaches are utilized by the metal NPs such gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and others like platinum nanoparticles (PtNPs) or their complex as they are having the characteristic property of localized surface plasmon resonance (LSPR). This

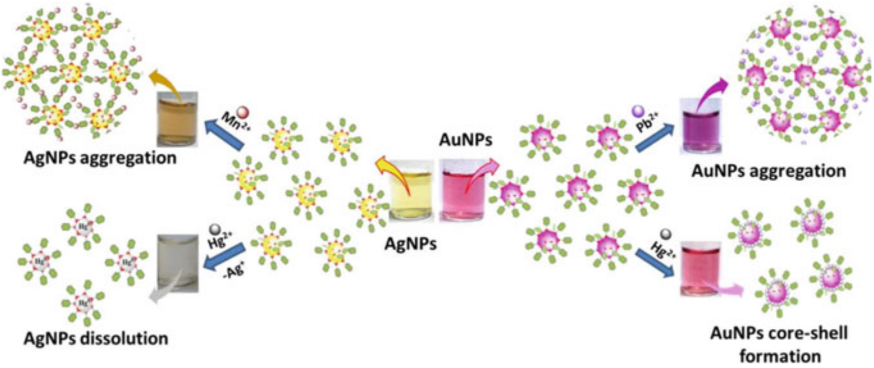

Fig. 5 Effect of aggregation on the color on nanoparticles (adapted from Ref. [6])

property exhibits its effect, when the frequency of conducting electrons matches with the incident electromagnetic radiations. LSPR effect is dependent upon the morphology i.e. shape, size, and interparticle distance, composition, and optical properties like refractive index of the nanoparticles. For example, when there is a decrease in interparticle distance, strong overlap between plasmon fields occurs which causes the red shift in LSPR and can result in change in intensity and observable color change that can be noticed by naked eyes. The aggregation-based approaches are usually simple in design in comparative to other mention approaches. In case of quantum dots, these approaches, when results in the increase of emission intensity then refer as aggregation induced emission and decrease in intensity refer as aggregation induced quenching.

Considering these approaches, Rajendiran and his co-workers synthesized the AuNPs and AgNPs stabilised by L-tyrosine for the detection of Pb(II), Hg(II) and Mn(II). When Hg(II) is added to the solution of as synthesized AgNPs, then color changes from yellow to colorless and changes to brown in case of Mn(II). Similarly, the color change is observed in case of AuNPs due to aggregation upon the addition of Pb(II) and Hg(II) as shown in Fig. 5. There is no color change is observed when other ions apart from these are added to the solution [6].

3 Advances in Materials Used as Colorimetric Sensors

In the recent years, various chromogenic materials have been reconnoitred for the colorimetric based quantification of heavy metal ions, especially in water matrix. Here, in this section, we have categorized the materials into three kinds based upon the molecular assembly and properties, i.e., organically tailored linkers, nanomaterials/quantum dots, and other polymeric, MOF etc. materials as tabularized in Table 1.

Table 1 Recent materials for colorimetric sensing of inorganic water pollutions

Material	Heavy metals	Analytical details	Water matrix
Organic tailored linkers			
P(DHB-a-DHBDT) grafted with PST probes [1]	Hg(II)	LOD: 10.6 ppb	River water; Distilled water
sulfo-rhodamine 101 with cuprizone [19]	Cu(II)	LOD: 0.1 ppb	Groundwater; Distilled water
HCFI [20]	Cu(II)	LOD: 1 ppm; LR: 0.1–10 ppm	Waste water
Heptamethine cyanine dye [9]	Ag(I)	LOD: 3 ppb	Lake water; Tap water; River water
MPA derivatized RS [8]	Hg(II)	LOD: 0.29 ppb	Waste water; Tap water; Drinking water
Nitro-functionalized Co(II) based MOF [11]	Hg(II), MnO_4^-	LOD: 800 ppb for Hg(II)	Distilled water
PyDPP [21]	Hg(II), Cu (II)	LOD: 5 ppb	Distilled water
Tpy-QL; Tpy-BZ [7]	Fe(II), Fe (III), Co(II) and Hg(II)	LOD: Hg(II), Co(II), Fe(II), and Fe(III) are calculated to be 6.51, 0.34, 0.49, and 1.01 ppb; Naked eye limit: 10, 25, 10, and 200 ppb for Fe(II), Fe(III), Co (II), and Hg(II)	Tap water; River water; Ground water
Nanomaterials based platforms			
$HS\text{-}CH_2$-6-GGGTGGGTGGGTGG aptamer modified oligonucleotide [22]	Pb(II); Hg (II)	LOD: 100 ppb for Pb(II); 500 ppb for Hg(II)	Lake water; Distilled water
BSA-AuNCs and L-Cys-AuNCs [17]	Hg(II)	LOD: 1.8 ppb	Distilled water
PEG functionalized AgNPs [15]	As(III)	LOD: 1 ppb	Distilled water
Glucose capped CuNPs [16]	Ag(I)	LOD: 10 ppm; LR: 10–60 ppm	River water
amino-carbon dots and AuNCs [23]	Cu(II); Pb (II)	LOD: 100 ppb for Pb(II); 9.5 ppb for Cu(II)	Distilled water
Nitrogen-doped graphene QDs [13]	Fe(III)	LOD = 132 ppb; LR = 88–132 ppm	Distilled water
captopril modified HgS/ZnS core/shell QDs [14]	Cr(III)	LOD: 51 ppb	Distilled water

(continued)

Table 1 (continued)

Material	Heavy metals	Analytical details	Water matrix
Other chromogenic materials			
ZIF-8/GO [24]	Ag(I)	LOD = 153 ppt	River water; Human serum
PAN fibre [25]	Hg(II), Cu (II)	Screening only	Distilled water
Curcumin based NFs [26]	Pb(II)	LOD: 207 ppm	Distilled water
PAR onto PAN fibre [27]	Hg(II)	LOD = 35 ppb	Distilled water

BSA bovine serum albumin, *Cys* cysteine, *GO* graphene oxide, *HCFI* 3-(5-hydroxy-4-carboxyphenylimino)-5-fluoro indol-2(H)one reagent, *LOD* limit of detection *LR* linear range, *MOF* metal-organic framework, *MPA* mercapto-propanoic acid, *NC* nanocluster, *NF* nanofiber, *NP* nanoparticle, *PAR* 4-(2-pyridylazo)-resorcinol, *PAN* polyacrylonitrile, *PEG* polyethylene glycol, *P(DHB-a-DHBDT)* poly(2, 3-dihydroxybutylene-alt-2,3-dihydroxy-butylenedithioether), *PST* 2-(5-bromopyridine-2-yl)-3′,6′-bis(diethylamino)-spiro[isoindoline-1,9′-xanthene]-3-thione, *PyDPP* 2-(2-(2-methoxyethoxy)-ethyl)-3,6-di(pyridin-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, *QD* quantum dots, *RS* rhodamine hydrazide, *Tpy-BZ* terpyridine benzo thiazolium iodide, *Tpy-QL* terpyridine quinolinium iodide, *ZIF* zeolite imidazolate frameworks

3.1 Organic Linkers

Organic Linkers refers to category of complexes which are organic ligands, for example, polyacrylonitrile (PAN) or coordinated to organic ligands like metal organic frameworks (MOFs). These organic ligands are defined as molecules that can bind to, and form a stable complex with, trace metals in the aquatic dissolved (typically <0.2 µm) phase. They have always been an attractive complexing agent in trace metals detection by virtue of the selective chelating ability of their heteroatoms such as oxygen, sulphur, nitrogen, etc. In general, the formed selective complex is either a chelate or a ring. They often used in conjugation with metallic nanoparticles and quantum dots. Further, previously discussed sensing mechanisms can be employed for the detection of desired analytes. Here, recently discovered or utilized organic linkers in the area of colorimetric sensing of inorganic water pollutants are discussed.

Recently Tian et al. recognises the potential of small organic molecules in field of colorimetric detection of multiple inorganic metals ions and utilized them for the detection of Hg(II), Co(II), Fe(II), and Fe(III) well below the prescribed WHO limits [7]. To achieve this, Terpyridine (Tpy), a heterocyclic compound having three nitrogen elements results in strong chelating effects and ability to shows color changes and change in absorption spectra on interacting with metal ions. To improve the hydrophobicity of Tpy molecule quinolinium iodide (QL) and

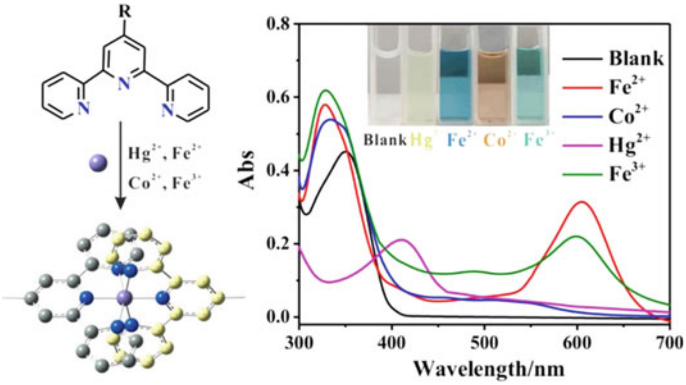

Fig. 6 Schematics of complex formed after interaction with metal ions and their effect on absorption spectra (inset: change in color w.r.t. metal ions) (adapted from Ref. [7])

benzothiazolium iodide (BZ) is introduced. The color changes from colourless to pale yellow in case of Hg(II), pink with Co(II), dark blue for Fe(III), and light blue for Fe(II), which can be observed by the naked eyes. Further, the change in absorption spectra is also studied as shown in Fig. 6 [7].

Likewise, organic dye is another class of organic molecule, which are emerging these days as new fluorophore because of their interesting properties i.e. absorption of visible light, presence of chromophore, resonating electrons, and conjugated system. These properties makes them a good candidate in the field of colorimetric sensing. Of them rhodamine 6G, is one of the most popular dye used while designing the colorimetric sensor. Recently it has been used for the detection of Hg (II) ions after its modification with mercaptopropanoic acid (MPA) which provides thio functionality to the sensor so as to increase its sensitivity towards Hg(II). In the presence of Hg(II), color of sensor changes to pink from colourless [8]. Some examples of rhodamine 6G dye also discussed in Sect. 2. Apart from this, other dyes like heptamethine cyanine-based dye is used for the detection of the Ag(I) ions, where it changes its color to red from blue, which can easily notice by the naked eyes. Further, gradual change in UV/Spectra is observed upon increasing the concentration of Ag(I) ions [9]. Further boron-based dyes like boron–dipyrromethene are also gaining potential in this field. This particular dye is having thia-aza crown ether as metal ion receptor and is used for the uv-based colorimetric detection of Hg(II) ions, here color changes from colourless to green under the UV light [10].

Metal organic frameworks (MOFs) are another promising candidate used for the colorimetric detection. MOFs consists of coordination bonds between organic linkers and transition metal cations, offers many active sites for the detection of inorganic ions and have high surface are attributed to their high porosity. MOFs are having void spaces in between, which are utilized to capture the desired analyte and hence can have high selectivity. Recently, Sun et al. synthesized a nitro functionalised Co(II) based MOF for the detection of Hg(II) and MnO_4(-I) ions. The MOFs contains a nitro-functionalised ligand (NPDC) which is synthesized by solvothermal method. The 3D structure of MOF consists of bipyridine linkers and NPDC ligand coordinated to Co(II). Upon the addition of ions to the MOF containing solution, change in intensity of color can easily be observed by naked eyes [11].

3.2 Nanomaterials Based Platforms

Nanomaterials such as quantum dots, and metallic nanoparticles offers large surface area and simplicity in sensor design which makes them suitable for the sensing applications. Quantum dots (QDs) are the zero-dimensional semiconductor nanocrystals with the size usually less than 12 nm. Due to this, they have substantial advantages in the field of sensing process as an outcome of their exceptional optical and electronic properties. These properties include high fluorescence quantum yield, broad absorption spectra, tuneable composition, high photostability, etc. Also, QDs can overcome issues including pH dependence, self-quenching at high concentrations, and photobleaching with the traditional fluorescent probes [12]. Upon realizing these advantages, Zhou et al., synthesized nitrogen doped graphene quantum dots for the colorimetric sensing of Fe(III). Here, these QDs prepared by hydrothermal treatment and ethylenediamine (EDA) is used as nitrogen source change in intensity of blue color w.r.t. change in concentration Fe(III) ions is observed by naked eyes under the UV light [13]. Further, Wang et al. developed a HgS/ZnS core/shell quantum dots for the visual sensing of Cr(III) ions [14].

Metallic nanoparticles are like gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles(CuNPs) are another promising candidates which are used to described nanosized metals with dimensions (length, width or thickness) within the size range 1–100 nm. The main characteristics of these particles are large surface-area-to-volume ratio as compared to the bulk equivalents, large surface energies the transition between molecular and metallic states providing specific electronic structure (local density of states LDOS), plasmon excitation, quantum confinement, short-range ordering, increased number of kinks, a large number of low-coordination sites such as corners and edges, having a large number of ″dangling bonds″ and consequently specific and chemical properties and the ability to store excess electrons. Using these benefits, Biswas et al. reported the use of polyethylene glycol (PEG) functionalised AgNPs for the colorimetric detection of arsenic with the detection limit of 1 ppb [15]. PEG is a biocompatible polymer contains various hydroxyl groups which acts as the binding sites for the As (III) and AgNPs are having its characteristic property of Localized surface plasmon resonance which depends upon the dielectric constant of the surrounding environment. Here, red shift in localized surface plasmon resonance and color change from pale yellow to bluish color is observed upon the addition of arsenic(III). Further schematic representation of sensing of As(III) is shown in Fig. 7 [15].

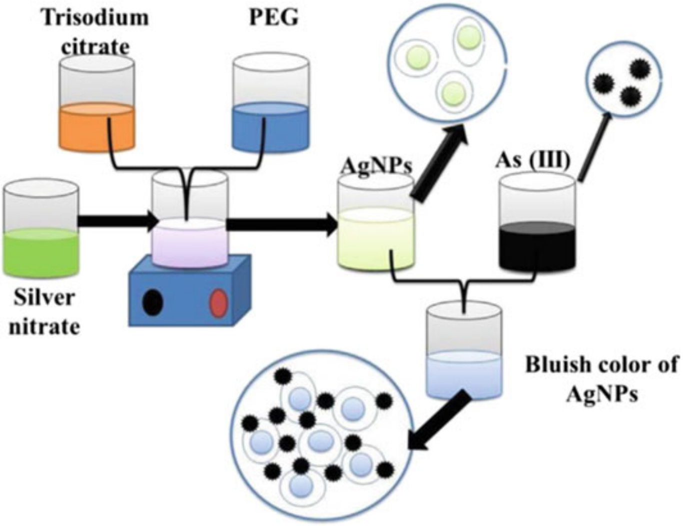

Fig. 7 Schematics of formation of AgNPs for the colorimetric detection of As(III) (adapted from Ref. [15])

Similarly, the use of glucose modified copper nanoparticles (Glc-CuNPs) having high fluorescence is reported for the visual detection of Ag(I). Upon the addition of Ag(I) ions to the sensor assay, aggregation of Glc-CuNPs occurs, which results decay of fluorescence and gradual change in intensity of color on increasing the concentration of Ag(I) is observed [16].

Further, Zhao et al. reported a ratiometric probe having blue colored L-cysteine-Au NCs as internal standard probe and red colored bovine serum albumin-Au nanocluster as detection probes for the sensing of Hg(II) ions. In presence of Hg(II) ions detection probe shows the fluorescence quenching but no effect on the fluorescent signals of internal standard probe i.e. AuNCs. This causes color variations from red to blue, and thereby enabling the visual detection of Hg(II) ions by naked eyes as shown in Fig. 8 [17].

3.3 Other Chromogenic Materials

Apart from organic linkers, metal nanoparticles, quantum dots, there are other materials deliberated here. Li F. et al. reported a two-fold metal-organic framework (MOF), [Co (NPDC) (bpee)]·DMF·$2H_2O$ (1) (NPDC = 2-nitro phenylenedicarboxylate, bpee = 1,2-bis(4-bipyridyl) ethylene) nitro functionalized ligand (NPDC) and bipyridine type linkers (bpee) coordinated to Co(II). The complex consists of a 3D structure which exhibits high selectivity for the sensing of MnO_4^- and heavy metal ion Hg^{2+} in water by quenching or enhancing luminous intensity [11]. Similarly, Deng et al. reported a

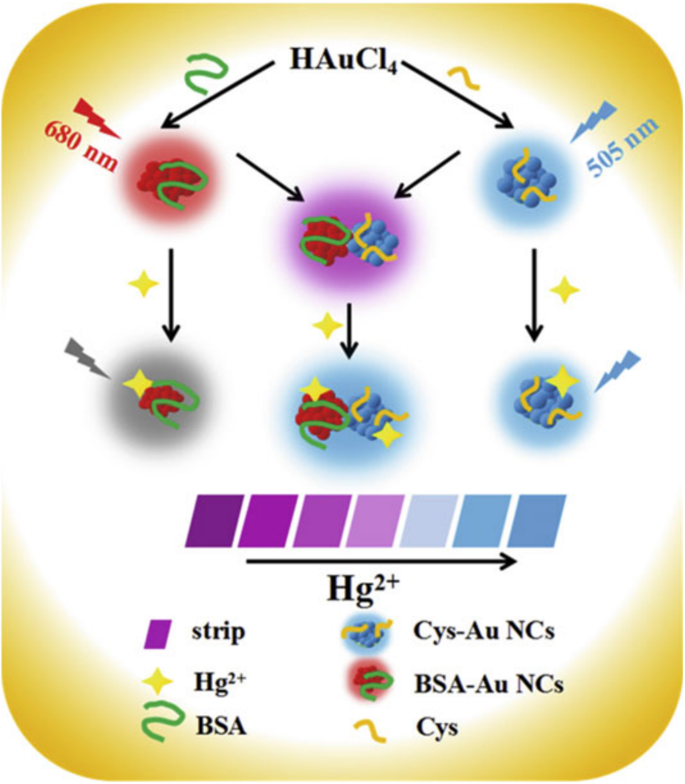

Fig. 8 Schematic for determination of Hg(II) ions (adapted from Ref. [17])

dual functionalized material by incorporating a chromophore, 4-(2-pyridylazo)-resorcinol (PAR), onto polyacrylonitrile (PAN) fiber for the detection and removal ability for heavy metal ions, including Hg^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+} [18].

4 Perspectives and Strategies in Colorimetric Sensor Development "Lab-to-Market"

4.1 Colorimetric Sensors on Solid Supports

The effectiveness of any colorimetric sensor is inclined not only by the choice of materials (e.g., chemo responsive dyes, organic ligands, metal nanoparticles quantum dots,) but also by the selection of substrate type and materials (e.g., geometry of flow path and immobilization technique) [28]. The vital characteristics of substrates include optical transparency (owing to high reflectivity), regular structure, stability, and chemical compatibility. Mostly, opted substrates are based upon cellulose derivatives like cellulose paper, chromatography paper, printer paper, etc., polymeric membranes like polyvinylidene difluoride (PVDF), polypropylene (PP), and polyethylene terephthalate (PET). Like as, Zhou et al. reported a quenching paper based sensor using Fluorescent Nitrogen-Doped Graphene Quantum Dots for the detection of Fe(III) and fabricated a paper strip using inkjet printing technology by HP inkjet printer 2050 onto bond paper. Te printed patterns were observed and photographed under 365 nm ultraviolet lamp, and the fluorescence intensity of the paper was scanned by fluorescence spectrometer [29].

4.2 Read-Out Signalling Approaches

The advancements in colorimetric sensing with the aid of ubiquitous consumer electronic products (like scanners, computers, mobile phones, etc.) as read-outs is a moderately new research arena. On the basis of reviewed literature, we have further analysed these consumer electronic products as read-out signalling approaches on the basis of commercial parameters such as market growth and user-friendliness as shown in Fig. 9.

Smartphones/mobiles (such as Apple, Samsung, OnePlus, and Nokia) have distinguished features of onboard processing potential similar to the hand-held reader. Furthermore, their worthy assets namely portability, user friendliness, and onboard image processing capability makes them a suitable candidate in this field. Like as, camera are also equipped with higher bandwidth data transfer methods to acquire images in a fraction of seconds. However, images acquired by the digital camera/camera can be affected by the improper focusing, alignment, lighting conditions, and many other factors. Furthermore, the high cost of digital cameras

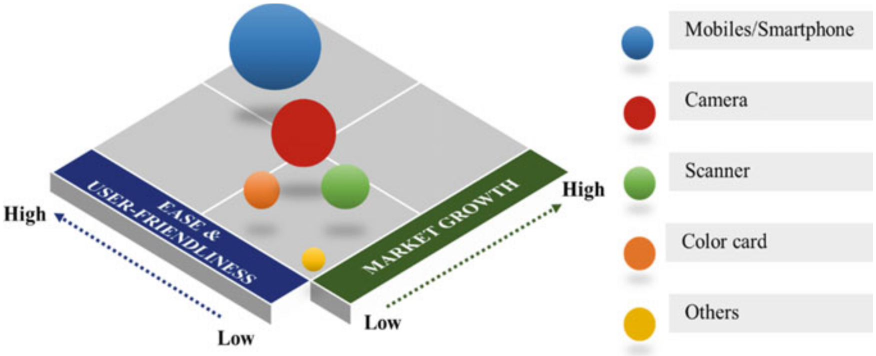

Fig. 9 Consumer electronic products as read-out signalling approaches: market potential and user-friendliness

and associated accessories for image capturing is a fall back for their frequent use in colorimetric sensors. Scanners has some benefits over digital cameras and smartphones i.e. problems like focusing, blurry corners, movement, alignment, lighting, etc. which will affect the image quality and can cause variations in sensor data does not comes into existence while using scanners. But they suffer due to certain demerits like as lack of instant scanning of image, portability and extended scanning time for the acquisition of high-resolution image. Additionally, colour card are the physical colour reference for comparisons and measurements in colorimetric sensors. These are widely used in textile industry, food industry, photography etc. Although this approach is easy to implement and requires negligible instrumentation for the analysis but this method is largely affected by the intensity of light and error while color interpretation. Other devices like membrane strip reader which are type of microplate reader, fiber optic devices, etc. are also investigated in colorimetric imaging, but these devices suffer from user friendliness and portability, as they are not popular in comparison to the other available devices.

5 Case Study: Commercial Accomplishments of Existing Colorimetric Sensor Platforms for Water Pollutants

Knowingly, water pollution has turn out to be one of the utmost tenacious ecological glitch in the world today. Although a limited effort to commercialize the technology of colorimetric sensory platforms for the real-world water pollutant monitoring application have been known and now exists in global market. Some companies like *Thermo Fisher Scientific*, *Merck, Sigma-Aldrich, Hanna Instruments*, *Elabscience*, *Libelium, Cole Parmer, CHEMetrics, Appealing Products, Inc., MicroWaterman, Appealing Products, Inc., Industrial Test Systems, Vitality Plus Australia, Inc., Industrial water systems*, have also fruitfully commercialized their kits for online water quality monitoring as portrayed in Fig. 10. In this section, case study on recent progress in existing colorimetric sensor platforms is described with an emphasis on the various water pollutants i.e. chemical, microbiological, and other ecological contaminants. Furthermore, we highlight the available commercial kits and deliberate their market-potential to water research. *Thermo Fisher Scientific* launched *Orion*™ *AQUAfast AQ4000* Colorimeter to measure water and wastewater pollutants with 65 pre-programmed methods, automatic selection of four wavelengths and timer [30]. The water quality parameters measured include dissolved ions like as cyanide, fluoride, nitrite, nitrate, chloride, iodide, bromide, sulphide, ammonia, zinc, phosphate and sulphate. The company provides auto-test ampoules reagent with *Orion*™ *AQUAfast AQ4000* colorimeter to abridge sample preparation and tests. The auto-test ampoules enclose a pre-measured quantity of liquid colorimetric reagent and effortlessly fill with the precise volume of sample to be tested for reagent mixing. Respectively, every

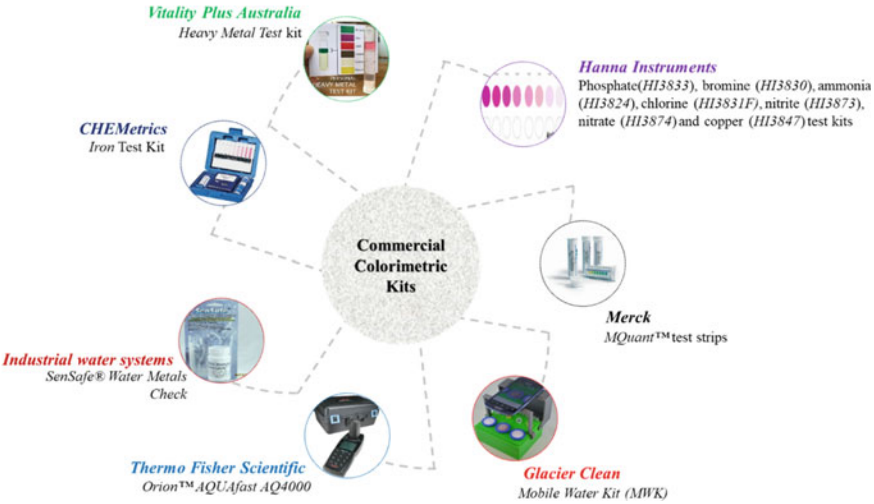

Fig. 10 Commercial colorimetric sensory platforms for the real-world water pollutant monitoring applications

ampoule contains an auto-ID barcode that is read by the *AQ4000* colorimeter and used to spontaneously recognize the test water pollutant parameter [30].

In addition, *Glacier Clean* launched *Mobile Water Kit (MWK)* to measure contamination of water resources with *Escherichia coli (E. coli)* bacteria [31]. It contains a plunger-tube assembly with an in-built filter. The plunger-tube assembly comprises of a hydrogel encapsulating the explicitly developed colorimetric substrates selective towards *E. coli* and can facilitate the colorimetric detection of bacteria and identification of their concentration. The presence of *E. coli* will craft a colour change on the substrate. Besides, the kit is handy and can be used at the point of source itself thereby eradicating the need for transport of the water samples. This test kit also allow the user to map the location data with the help of a custom built smart phone application (m-Water), which is then automatically uploaded to a central server [31].

Similarly, *MQuant*™ test strips, from *Merck*, are pocket-sized laboratories for quick analysis and give the user a quick summary of substance concentrations present in the sample. By providing a means of pre-selection, they can contribute significantly to the lowering of the time and costs for laboratory analyses. The reaction zones are wetted by simple dipping into the solution being tested. After the given reaction time has elapsed (e.g., a maximum of two minutes), the colouring of the reaction zone is compared with the colour scale on the package to determine the concentration [32]. There is *MQuant*® *StripScan* app, by *Sigma-Aldrich*, to determine pH or concentrations of chemicals in aqueous solutions. This easy-to-use mobile analytical detection platform provides reliable quantification of water, food & beverage samples for customers from research, industry, environment and diagnostics. The *MQuant*® test strips are employed with contain all necessary reagents, including those required for sample pre-treatment [33]. Additionally, *Merck's* colorimetric and titrimetric test kits are especially suited for the analysis of drinking water, ground water, clean water and mineral water as well as in water production. Each test kit pack contains all reagents necessary for the test with high-quality and brilliant colour cards decisively simplify the allocation of the samples to the stated values. In the titration tests the sample is titrated until the colour changes. The concentration of the tested parameter is determined by the number of drops consumed to the turning point or the scalar value read off from a pipette. For performing the colorimetric tests a colour reaction is produced by adding reagents to the sample solution. The special feature of these test kits range lies in the measurement of low concentrations down to the ppb range [34].

Likewise, *Hanna Instruments* launched colorimetric chemical (CC) test kits namely, phosphate test kit (*HI3833*), bromine test kit (*HI3830*), ammonia test kit (*HI3824*), chlorine test kit (*HI3831F)*, nitrite test kit (*HI3873*), nitrate test kit (*HI3874*) and copper test kit (*HI3847*) [35]. The *HI3833* is a CC test kit that uses the ascorbic acid method to measure phosphate in water. The colour change determines the presence of phosphate. The *HI3830* is a CC test kit that determines the bromine concentration in samples within a 0 to 3 ppm bromine range. The *HI3830* is supplied with all of the necessary reagents and equipment to perform the analysis. The *HI3824* is a CC test kit that uses Nessler reagent to measure ammonia in fresh water within a 0.0 to 2.5 ppm range. The *HI3831F* determines the free chlorine concentration within a 0.0 to 2.5 ppm range by employing the DPD method. The *HI3873* uses the chromotropic acid method to measure nitrite within a 0.0 to 1.0 ppm range. The *HI3874* uses the cadmium reduction method to measure nitrate within a 0 to 50 ppm range. The *HI3847* uses the bicinchoninate method to measure copper within a 0–2.5 ppm range [35].

Similarly, *Elabscience* launched *Urea Colorimetric Assay* Kit to measure the concentration of main water-pollutant, urea, in water resources, serum, plasma and urine [36]. This kit uses the strong diacetyl oxime-urea chemistry. In the presence of urea, diacetyl oxime form red diazine compound. The gradient of red diazine colour is relational to the concentration of urea [36].

Also, *Heavy Metal Test* kit, from *Vitality Plus Australia*, is a home testing kit for checking heavy metals in both urine, saliva, and liquids. Easy to use it will detect the presence of ionic metals in the liquid solutions tested. This is an economical way to see what under the naked eye cannot see from water (bore water, tap water, and tank water), urine, and saliva. The testing kit can also be used to detect the presence of heavy metals (mercury, lead, cadmium, chromium and thallium) in other complicated media like paint, foods, makeup, skin care, etc. [37].

Likewise, *Libelium*, a reputed company of Spain, launched *Waspmote Smart Water*, a smart water wireless sensor platform to abridge remote water quality monitoring [38]. Furnished with multiple sensors that measure the most relevant water quality parameters, *Waspmote Smart Water* is the water quality-sensing platform to feature autonomous nodes that connect to the cloud for real-time water control. This platform is an ultra-low-power water-pollutant sensor designed for use in rugged environments to detect changes and potential risk to public health in real time. It is suitable for potable water monitoring, chemical leakage detection in rivers, remote measurement of swimming pools and spas, and levels of seawater pollution. The water quality parameters measured include pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), conductivity (salinity), turbidity, temperature and dissolved ions (fluoride, calcium, nitrate, chloride, iodide, cupric, bromide, silver, fluoroborate, ammonia, lithium, magnesium, nitrite, perchlorate, potassium and sodium [38].

Likewise, *SenSafe*® *Water Metals Check*, from *Industrial water systems*, determines the presence of heavy metals (cadmium, cobalt, copper, iron, lead, mercury, nickel and zinc) present in water. This quick test uses a very sensitive non-specific indicator that detects many common heavy metals with detection limits to <10 ppb. This test is a screening tool and does not specify levels of each metal present [39].

Additionally, *Cole Parmer* launched *NECi Colorimetric Nitrate Water* Test Kit, for nitrate testing without the use of cadmium, a toxic heavy metal and known carcinogen. This kit uses the naturally occurring enzyme called nitrate reductase which safely measures nitrate within 0.5–10.0 ppm range by giving a colorimetric change in water samples [40].

Likewise, *TotalCARE Heavy Metal* Screen Test, from *MicroWaterman*, is a semi-quantitative, rapid, and user friendly test kit for the analysis of free zinc, copper, lead, mercury, cadmium, nickel, cobalt and manganese ions in the urine, saliva, water, etc. Any color change deviating from green to purple, pink, beige, red determines high heavy metal concentration (3–5 ppm) viewed directly below the surface level of the test tube represents the presence of heavy metal ions [41].

Furthermore, *CHEMetrics* launched *Iron* Test Kit, to measure the concentration of iron in water samples by using phenanthroline-colorimetric method. This kit uses 1,10-phenanthroline which securely measures iron within 1–10.0 ppm range by giving a colorimetric change in water samples. In the presence of iron, the reagent 1,10-phenanthroline forms an orange-coloured chelate [42].

An another kit namely, *Generic Heavy Metal Detector*, (GHM-01), from *Appealing Products, Inc.*, is developed to easily and rapidly detect common heavy metals (lead, thallium, mercury, cadmium, iron, nickel and zinc) in water and urine samples. The test kit consists of detection tube, testing paper and colour charts. A reference color chart is provided for interpreting the test results. The operating procedural steps include to simply add the detection tube to the vial, then add sample, shake for 30–40 s and allow the liquid to separate. Once the liquid gets separated into two phases, observe at the color formed on the top phase and compare it to the reference color chart [43].

The *eXact iDip*® *Smart Photometer System*®, from *Industrial Test Systems, Inc.*, is the first patented and handheld photometer to provide 2–way communication with a Bluetooth® Smart (4.0) ready Apple or Android smartphone/tablet for the detection of cadmium, cobalt, copper, iron, lead, mercury, nickel, and zinc in water. The *eXact iDip*® photometer is waterproof (IP67) and has a permanent built-in sample cell. This eliminates the separate cell and simplifies the test procedure, which improves accuracy. The multilingual *eXact iDip® app* system also allows for instantaneous software updates/upgrades, test customization, and mobile sharing of results with spreadsheet [44].

6 Summary

In summary, this chapter focussed on the potential use of colorimetric sensors for the water-pollutant sensing and discusses the promising prospects of sensor developments (from choice of material to read-out tools) to assist nascent researchers to review the principles, mechanistic and advancements in existing trends in colorimetric sensory probes. In this direction, smartphone-based colorimetric sensor platforms aim to empower easier and more resourceful water-pollutant testing in resource-limited locales, which accords with the important goal of field-deployable sensory systems. The adept features of smartphones namely, concept of miniaturization, ease-of-operation and portability recommend great prospective for their operative integration with sensory probes in the direction of facilitating a wide range of new mobile-based pollutant sensing applications.

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Fluorescent Chemosensor for Detection of Water Pollutants

Annasamy Gowri and Arunkumar Kathiravan

Abstract Fluorescent chemosensors for detection of water pollutants (organic, inorganic and biological) are of primary importance due to the pressing need for safe drinking water. This chapter focuses on the application of fluorescence spectroscopy, an excellent analytical technique for sensing various water pollutants due to its improved sensitivity and operational simplicity. The recent advances in the development of fluorophores and the respective photophysical phenomena involved for selective detection of water pollutants including toxic metal ions and pathogens are discussed in detail. Furthermore, the future prospects of fluorescent sensors for rapid and on-site detection of water pollutants are presented.

Keywords Fluorescence · Chemosensor · Water pollutants · Photophysical process

1 Introduction

Water is one of the most valuable natural resources indispensable for the basis of life. There is a huge demand for safe drinking water as the natural aquifers are becoming depleted due to the growing human population. Natural calamities and anthropogenic activities (such as climate change, weathering of soil and rock, agricultural runoff, advances in farming technology, industrialization and improper disposal of sewage) alter the physical, chemical and biological quality of water making it unsuitable for drinking [1–4]. According to the recent report by world health organization (WHO), more than 1.2 billion people lack access to clean drinking water. This eventually resulted in increased mortality rate especially children due to the outbreak of waterborne diseases [5–10]. The list of emerging water pollutants is expanding at a faster pace and not limited to nitroaromatics,

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nitrates, heavy metal ions, anions, microplastics, polychlorobiphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pathogenic microorganisms and so on [11–13].

Water conservation measures and wastewater treatment processes are given importance to mitigate the adverse societal impact of water pollution [14, 15]. The quality of water is basically evaluated by measuring the universal parameters such as pH, total dissolved solids (TDS), biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). The existing analytical techniques for water quality monitoring require sophisticated laboratory, expensive equipment with frequent maintenance, skilled personnel, laborious sampling procedures and long assay time [16]. However, there is a pressing need in the real time monitoring of water pollutants to address the timely delivery of potable water to the consumers. In this context, fluorescent spectroscopy is considered to be the most dominant analytical tool due to its operational simplicity, improved sensitivity, rapid and real-time response. Moreover, the acquisition of fluorescence spectra is relatively straightforward and facilitates simpler detection of water pollutants from their characteristic fluorescence fingerprint. In addition, the dissolved organic matter (DOM) in water exhibits fluorescence which is exploited as a useful measure to correlate well with the TOC and BOD of water samples. The corresponding excitation-emission matrix of aromatic structures present in naturally occurring organic substances is listed below in Table 1 [17].

Table 1 Characteristic fluorescence peaks of organic compounds (reproduced with permission from [18])

Peak	Ex/Em wavelengths	Description
A[a]	(Ex260, Em (380:460))	Terrestrial humic-like, high molecular weight, aromatic humic, hydrophobic acid fraction (HPOA); always high in wetlands and forested environments
B	(Ex275, Em310)	Tyrosine-like organic compounds, associated with amino acids and hydrophobic neutral fraction(HPON); indicates more degraded peptide material
T	(Ex275, Em340)	Tryptophan-like organic compounds, associated with amino acids, hydrophobic base fraction (HPOB), and hydrophilic acid fraction (HPIA); indicates less degraded peptide material
C[a]	(Ex350, Em (420:480))	High molecular weight, humic-like compounds; high in terrestrial environments
M[a]	(Ex312, Em (380:420))	Low molecular weight, marine humic-like compounds
I	(Ex 260, Em 290)	Due to ibuprofen

[a] consolidated as humic-like peak in the manuscript: Indicates a range

2 Fluorescent Chemosensors

Fluorescent chemosensor has been widely explored as a rapid and sensitive analytical tool for detection of pollutants in natural water resources, sewage and industrial wastewater treatment plants compared to chromatographic techniques [18, 19]. Fluorescent chemosensors offer selective detection of water pollutants by monitoring the fluorescence of dissolved organic matter and humic-like fluorescence peaks. In this chapter, the fundamentals, sensing mechanisms and advances of fluorescent chemosensors and their application for sensing water pollutants are discussed in detail. Fluorescence is defined as light-matter interaction phenomenon in which the electronically excited molecule upon absorption of the incident light emits light in longer wavelengths. The emission of light is dependent on the interaction of the molecule with the medium and the molecule is termed as fluorophore. The emission of fluorescence could be tuned from visible to NIR wavelengths based on the energy gap of the individual fluorophores [20, 21]. Fluorophore (signaling moiety) and receptor (recognition moiety) [22] are the basic building blocks of fluorescent chemosensor. They are usually connected to each other by means of spacer through chemical bonding or integrated together.

2.1 *Fluorescence Sensing Mechanisms*

Modulation of the photophysical properties of a fluorophore (such as emission wavelength, lifetime (τ), quantum yield (φ) and quenching) upon interaction with the analyte of interest is exploited for sensing applications. The interaction of an analyte with the fluorophore is influenced by various mechanisms such as electron transfer, charge transfer, energy transfer, excimer/exciplex formation and aggregation induced quenching/emission [23, 24] as shown in Fig. 1.

In photoinduced electron transfer (PET) process, the electron transfer occurs between fluorophore and acceptor site (receptor), resulting in non-radiative dissipation of excited-state which can quench the fluorescence. Due to PET, a charge separation is generated and the species relaxes to the ground state via charge recombination (Fig. 1). Upon interaction of PET probes with the analyte, fluorescence signal change was large enough to be considered as 'off–on' or 'on–off' through inhibition of PET process [25, 26]. On the other hand, colorimetric based intramolecular charge transfer (ICT) probes have been effectively utilized for sensing. This involves the interaction between analyte and the receptor, resulting in the distinct color change. Therefore, both PET and ICT probes are recognized as good candidates for the development of highly sensitive fluorescent chemosensors.

Fluorescence resonance energy transfer (FRET) is the interaction between donor and acceptor with the distance between them range from 10 to 100 Å resulting in

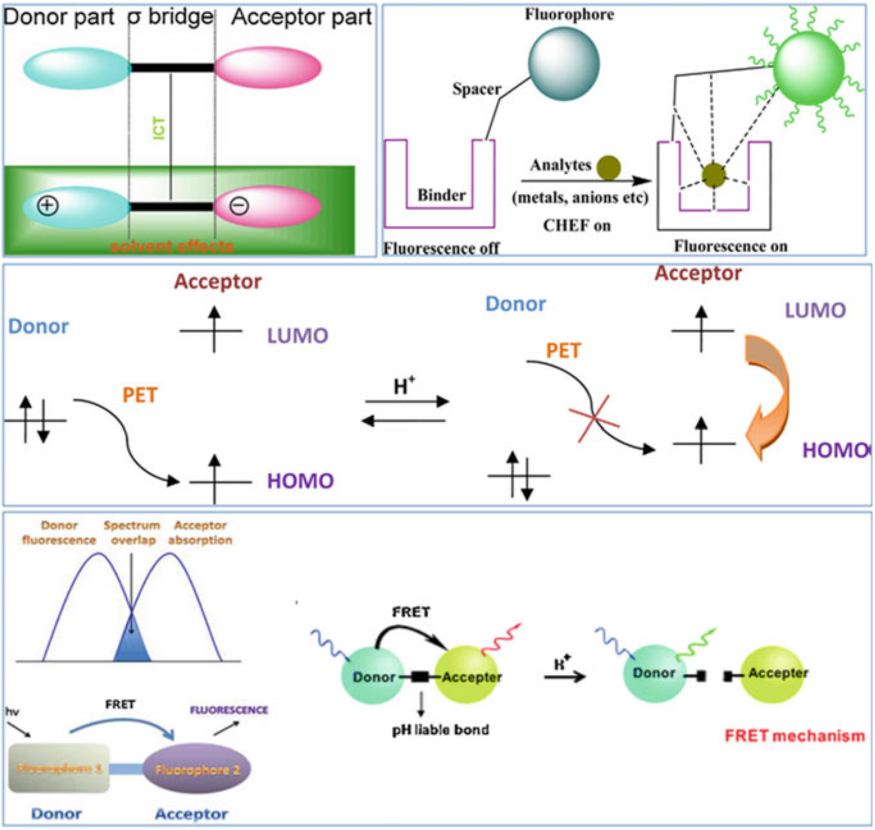

Fig. 1 Schematic representation of the conventional fluorescence sensing mechanisms (Reproduced with permission from [23])

the transfer of excitation energy. The FRET process is influenced by several factors between the donor and acceptor including distance, spectral overlap and dipole moment. The fluorescence of organic fluorophores tends to quench in its aggregated form resulting in aggregation caused quenching (ACQ) limiting the application of fluorophores in solid state sensor development. To overcome the challenges associated with ACQ, an abnormal phenomenon termed aggregation induced emission (AIE) was introduced by Tang and his co-workers [27]. Some of the organic molecules tend to be non-fluorescent in solution and exhibit enhanced fluorescence in their aggregated form. The modulation of fluorescence intensity due to photoinduced electron transfer (PET), intramolecular charge transfer (ICT), chelation enhanced fluorescence (CHEF), aggregation induced emission (AIE) or aggregation caused quenching (ACQ) mechanism is utilized to devise turn-on/-off fluorescent chemosensors [28–30]. The above mentioned mechanisms require interaction between the fluorophore and absorber (analyte). Moreover, those mechanisms involve no overlap between the absorption spectrum of analyte and the emission spectrum of the fluorophore with alterations in the fluorescence lifetime upon interaction with the analyte.

2.2 Inner Filter Effect (IFE)

On the contrary, fluorescence sensing mechanism based on inner filter effect (IFE) does not require any interaction which led to minimal intervention during detection (Fig. 2). Hence, fluorescence chemosensor employing IFE offers flexibility and ease in implementation as it does not involve any specific complexation and covalent linking of fluorophore and analyte [31–35]. Inner filter effect is defined as the reabsorption of excited/emitted light of the fluorophore by the analyte of interest. The efficiency of IFE depends on the following conditions [31] (a) the extent of spectral overlap between excitation/emission spectrum of fluorophore and excitation spectrum of analyte (b) variation of analyte concentration leads to hyperchromic effect in the absorption spectrum of fluorophore (c) the absorption and fluorescence spectra of the respective analyte and fluorophore should not be influenced by other interferences. There will not be any alterations in the fluorescence lifetime of the fluorophore and analyte since there is not any interactions between them.

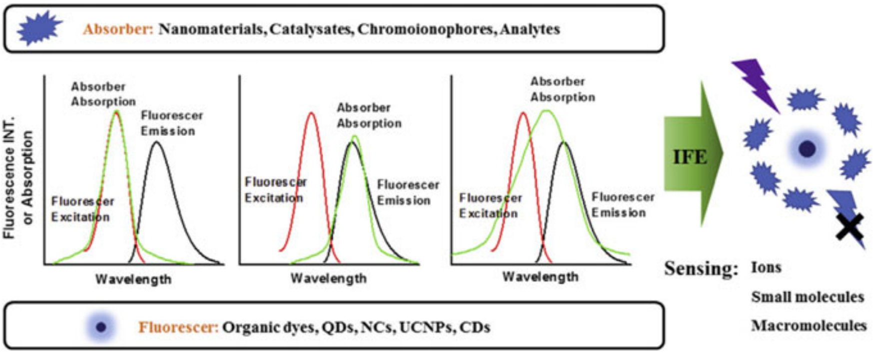

Fig. 2 Schematic showing the mechanism of inner filter effect (Reproduced with permission from [34])

3 Fluorophores Reported for Detection of Water Pollutants

There are various fluorophores reported in literature including organic dyes, inorganic complexes, metal organic frameworks, quantum dots and noble metal nanoclusters [36–40]. However, the main challenge in the design of IFE based sensing lies in selection of the fluorophore-absorber combination with complete spectral overlap. Some of the efficient absorbers with high extinction co-efficient are listed in Table 2 suitable for IFE based sensing.

In this context, fluorescent gold nanoclusters and quantum dots gained significance due to their excellent size tunable optical properties facilitating desired spectral overlap. Also, the high extinction co-efficient and excellent photostability

Table 2 Absorbers for IFE based fluorescence sensors (Reproduced with permission from [34])

Type	Absorber	λ_{max} (nm)[a]	$(M^{-1}\ cm^{-1})$[b]
Nanomaterial	AgNPs	400	5.56×10^{8}[d]
	Ag_2S	230	–
	AuNPs	520	2.7×10^{8}[e]; 3.7×10^{9}[f]
	AuNPs-Fe_3O_4 NPs	548	–
	MnO_2 nanosheets	380	9.6×10^{3}
	DEA-GQDs-Pb^{2+}	269	–
	BPEI-CQDs-Cu^{2+}	275	–
Chromoionophore	Cu^{2+}-spiropyran		3.12×10^{4}
	Cu^{2+}-I[c]		–
	FeTMPyP		1.05×10^{5}
	Fe^{3+}-SQA		–
	Cr^{3+}-diphenylcarbazone		–
	Pb^{2+}-ETH 5418		–
	Al^{3+}-ARS		–
	Bromothymol blue		–
	CP		6.4×10^{3}
Catalysate	ox-OPD	450	–
	ox-TMB	652	–
	PNP	400	–
	NADH/FDA	345	–
Analyte	Cr (VI)	360, 380	155 ± 7[g]; 935 ± 27[h]
	TNP	356	1.048×10^{4}
	Tetracycline	370	6534

[a] Maximum absorption wavelength

[b] Molar extinction coefficient at the maximum absorption wavelength

[c] Cu^{2+} and salicylaldehyderhodamine B hydrazine complex

[d] 9.5 ± 1.5 nm AgNPs

[e] 13 nm AuNPs

[f] 30 nm AuNPs

[g] $Cr_2O_7^{2-}$

[h] CrO_4^{2-}

of these fluorescent nanoparticles compared to conventional chromophores make them the ideal candidate for development of IFE based fluorescent chemosensors [41].

Recently noble metal nanoparticles are adopted in fluorescence assays [42] to enhance the sensitivity by means of interaction between the fluorophore and metal nanoparticles. The interaction between the fluorophore and the metal nanoparticles requires the linking through covalent bonding which requires the surface functionalization and modification of the fluorophore. However, surface modification of the fluorophore without affecting the inherent properties of the fluorophore is a tedious and time consuming procedure. In this context, IFE based sensing system proves to be a better alternative to the conventional fluorescence sensing techniques as it does not require any link between the fluorophore and the absorber. Thus, noble metal nanoparticles (gold and silver) are chosen to be potential absorber in IFE based sensing system. The spectral overlap of the fluorophore and absorber is made possible by simply fine tuning the localized surface plasmon resonance peak of metal nanoparticles which is dependent on the size and shape of the nanoparticles and is highly sensitive to the local environment changes such as refractive index and pH. The sensing mechanism involves the translation of the changes in the absorbance of the metal nanoparticles into the fluorescence of the fluorophores exponentially which eventually led to the improved detection limit compared to conventional fluorescence methods. A turn on fluorescence chemosensor for detection of cyanide in drinking water was proposed by combining gold nanoparticles with a model fluorophore (Poly [2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene]MDMO-PPV) [43]. The sensing of cyanide involves initially decrement in the fluorescence of the fluorophore for the respective increase in the concentration of gold nanoparticles and the decreased fluorescence was recovered upon addition of cyanide. Cyanide is known to dissolve nanoparticles yielding gold cyanide complex and does not interfere with the fluorophore which is revealed from the control experiments. The efficiency of cyanide sensing due to inner filter effect is validated by conducting optical absorbance based sensing of cyanide by dissolution of gold nanoparticles with increasing concentration of cyanide. The enhanced sensitivity was achieved using IFE which is attributed to the intrinsic relation between the model fluorophore and the gold nanoparticles.

A fluorescent nanoswitch employing polymer carbon dots (PCDs) for detection of explosives in water samples was reported [44]. The polymer carbon dots exhibit two characteristic absorption peaks at 234 and 410 nm which is completely overlapping with the absorption spectrum of 4-nitrophenol. This resulted in the quenching of PCDs upon interaction with 4-nitrophenol. In addition, PCDs were explored as fluorescent nanoswitch based on the changes in pH. 4-nitrophenol exhibits peak absorbance at 400 nm in pH 8 whereas, the spectrum is blue shifted to 320 nm in acidic pH. Hence in acidic pH, the absorption spectrum is not overlapping with that of PCDs. Due to the failure in meeting the criteria for IFE, a significant enhancement in fluorescence was observed, thus acting as a fluorescent nanoswitch.

Fluorescence chemosensors for detection of anions, pesticides, heavy metal ions and explosives using organic dyes, inorganic metal complexes have been extensively reviewed [45–50]. However, recent advances on the exploitation of fluorescent nanoparticles using inner filter effect have not yet been widely explored. The application of noble metal nanoparticles and their combination with fluorescent molecules or quantum dots for detection of water pollutants using inner filter effect is tabulated in Table 3.

Table 3 Inner filter effect based fluorescence sensing of water pollutants

Water pollutants	Fluorophore	Samples	Sensitivity	References
Bisphenol-A	Nitrogen doped carbon dots with aptamer conjugated gold nanoparticles (AuNPs)	Spiked tap water	3.3×10^{-9} M	[50]
Methyl paraoxon	Nanoceria with carbon dots	Spiked tap water	0.05 mg/kg	[51]
Imidacloprid	Antibody conjugated upconversion nanoparticles with AuNPs	Spiked tap, river and lake water	0.79 ng/ml	[52]
Organophosphorus pesticides	Ratiometric fluorescent quantum dots with AuNPs	Tap water	0.018 ng/ml	[53]
Sulfide	Silver ion mediated carbon dots	Tap and mineral water	0.43×10^{-6} M	[54]
Cyanide	Poly(9,9-bis(40-sulfnoatobutyl) fluorene-co-alt-1,4-phenylene) sodium salt (PFS) with silver nanoparticles (AgNPs)	Spiked tap water	2.5×10^{-7} M	[55]
Chromium	Hydrophilic ionic chemosensor	Spiked tap and waste water	8.9×10^{-7} M	[56]
Iron (III)	Graphitic carbon nitride quantum dots	Spiked natural water	23 nmol. L^{-1}	[57]
Copper	Polyamine functionalized carbon quantum dots	River water	6×10^{-9} M	[58]
Metronidazole	Carbon dots		0.257 µg/ml	[58]
Lead and cadmium	Upconversion nanoparticles with dithizone	Tap water	3.7 and 8.4×10^{-9} M	[59]
Fluoride	Curcumin-upconversion nanoparticles	Tap water	5×10^{-6} M	[60]
Mercury	Black phosphor quantum dots with tetraphenylporphyrin tetrasulfonic acid (TPPS)	Pure, tap and river water	0.39×10^{-9} M	[61]
Trinitrophenol	Anthracene based AIEgen	Sea, lake, tap and pure water	93×10^{-9} M	[31]
Trinitrotoulene	MoO_x quantum dots	River water	0.12×10^{-6} M	[62]

4 Future Scope

The scope of fluorescent chemosensors for continuous water quality monitoring is expanding with the dramatic advances in the development of affordable and portable monitoring tools. In this context, paper based test strips in combination with microfluidics are promising for fabricating affordable and disposable analytical devices. The current challenges in addressing the development of portable fluorimeters for real time water quality monitoring could be potentially met by integrating the paper based sensors and the innovative advancements in wireless communication. Micro-paper based analytical devices (µPADs) integrated with smart phones (Fig. 3) for onsite detection and quantification of water contaminants have enormous potential as a rapid alerting system for improving the global health [63]. Some of the reported Lab-on-a-chip based fluorimeters along with the selection and surface modification of various paper materials have been reviewed in detail.

Submersible fluorometers have gained significant potential for real time detection of water contaminants. Bridgema et al. [64] demonstrated a portable LED based fluorimeter for detection of organic and microbial contamination in potable water samples from the fluorescence C and T peaks [64]. Flexible paper film or textile fiber based chemosensors utilizing fluorescent hydrogel were reported for selective detection of Hg^{2+} ions in real water and food samples [65]. The specific chemical reaction between Hg^{2+} ions and grafted thiourea moieties results in green-to-blue emission which was exploited to develop wearable sensing gloves. Xu et al. [66] reported a small molecule fluorescence sensor array for qualitative and quantitative detection of seven heavy metal ions. The sensing mechanism

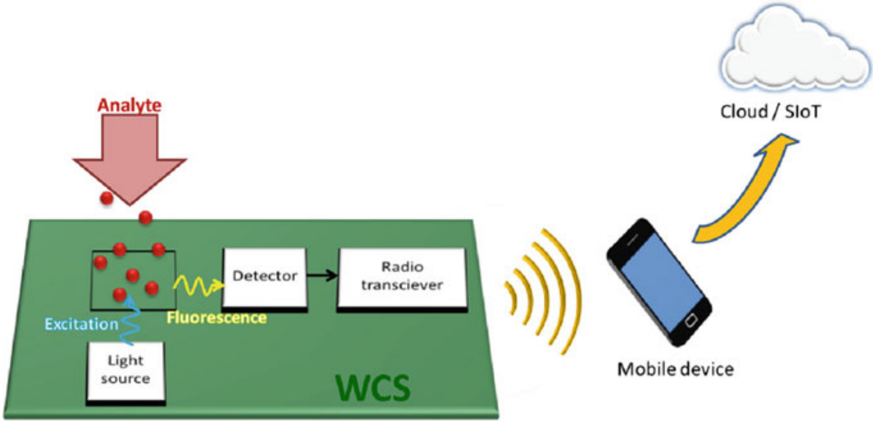

Fig. 3 Fluorescence based wireless chemical sensor (Reproduced with permission from [66])

mimics the behavior of tongue which could be exploited for on-site water quality analysis. Each of the heavy metal ions is identified from their unique fluorescence colour upon irradiation with a UV lamp. The fluorescence dyes utilized in the study include (i) picolinium dyes fluoresces between 530 and 600 nm depending on the interaction with the heavy metal ions (ii) Quinolinium dye intrinsically fluoresces at 580 nm and can be shifted between 560 and 600 nm (iii) BODIPY dye fluoresces at longer wavelengths between 600 and 630 nm. Kassal et al. [67] reported the development of a wireless fluorimeter system which finds huge scope in various fields including sensor internet of things (IoT), wearable sensors and point of care diagnostics [67]. The designed wireless fluorimeter was explored for detection of sweat chloride which is a vital parameter for the diagnosis of cystic fibrosis. The system showed a detection limit of 1.11 mM of chloride and the efficiency of the system for chloride sensing was evaluated using standard fluorimetry in solution as well as paper test strips. A Lab-on-a-chip (LOC) device for on-site water quality analysis employing electrochemical/optical dual transduction mechanism was developed [68]. The design of the LOC device involved fabricating and integrating microfluidic multi-channels, optoelectornics (consisting of OLEDs and organic photodetectors) and electrochemical microcells and optimized for on-site analysis. The LOC device was explored for detection of pesticides and in particular, effect of diuron herbicide on the photosynthesis of algae. Diuron, a model pollutant known to enhance algae fluorescence was exploited for on-site detection of pollutants in water resources.

A paper based electrochemical biosensor for the detection of E. *coli* present in water was built with a detection limit as low as 10 CFU/ml [69]. Thale et al. [70] reported the application of BTA loaded silica gel for real time detection of fluoride from the visual color changes [70]. A lateral flow immunoassay paper strips for detection of cadmium in water samples was reported with a detection limit of 0.4 ppb [71].

5 Concluding Remarks

Fluorescent chemosensors are proven to be a potent material for the detection of water pollutants. Sensitive and real time monitoring of water pollutants could be made possible by focusing on development of portable fluorimeters. Fluorescent chemosensors for sensitive detection of trace level contaminants is achieved through simple IFE based sensing assays by exploiting fluorescent nanoparticles. In combination with the advances in novel material synthesis, the challenges in selecting suitable fluorophore/absorber pair in IFE sensing for ultrasensitive detection of water pollutants could be facilitated.

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Materials in Electrochemical Detection of Water Pollutants

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Abstract Heavy metals, radioactive wastes, organic pollutants, chemical and biological wastes, pathogens and other such water contaminants have posed an acute threat to man and other living beings worldwide. Monitoring of water pollutants is a matter of serious concern and electrochemical detection is one such real-time and in-process monitoring is highly promising technique in this regard. This real-time monitoring reduces detection time as well as minimizes chemicals and reagents consumption as compared to conventional detection and analysis techniques. They hold an additional advantage on-site detection of chemical composition before discharge in water bodies. Advanced materials such as screen-printed electrodes, Ionic liquids based sensing devices, electrochemical biosensors and bioelectronics, etc. have proved to be effective innovations in detection of contaminants. Their compactness, portability and easier handling methods make them more reliable than conventional technologies. The chapter will cover an account of all such electrochemical detection techniques (including bio-sensing), their future perspectives and limitations.

Keywords Contaminants · Pollutants · Electrochemical · Sensors · Bioelectronics · Screen-printed electrodes

1 Introduction

Sustainable development is rising as a major challenge in the current era of Science and Technology. With an exponential rise in anthropogenic activities, there has been tremendous increase in global environmental issues. These activities have proved to be fatal for living systems worldwide. The passage of time is only adding obstacles in the path of attainment of clean environment (i.e. air, water and soil). Techniques are required for quick and effective monitoring of pollutants in water

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these days. Chemical pollution of water stands as a major challenge when it comes to environmental issues. Dyes, petrochemicals, pathogens, organic compounds, metallic compounds, pharmaceutical waste products etc. are a continuous source of chemical and biological pollution in water bodies. The situation is quite alarming with the continuous addition of these pollutants into the water bodies and environment. Emerging contaminants include variety of chemicals used in various industries as well as daily applications. It ranges from potential sources such as herbicides, insecticides, pesticides, fertilizers, nanomaterials, petrochemical and pharmaceutical wastes, dyes, metal ions used in various industrial wastes as well as biological contaminants. The primary route and highest contaminating source for the addition of contaminants is industrial wastewater which is directly discharged into water bodies and then carried forward [1, 2]. A wide variety of synthetic chemicals used in different industrial practices are emerging as a source of environmental contaminants. These pollutants are classified on the basis of their use, point of origin and/or effects on the living systems. Some of the potential water pollution sources include industries, agricultural, domestic sewages, small scale factories, power plants which releases variety of pollutants such as fertilizers, pesticides, herbicides, nanoparticles, petrochemicals, plastics, aromatic compounds, phenolic compounds, metal ions and metal complexes and pharmaceuticals [3]. The primary route of addition of these contaminants is industrial wastewater carrying largest concentration of pollutants.

Traditional method of environmental pollutant detection follows discrete sampling methods followed by laboratory analysis. The sampling involves natural sources which are easily perturbed by various physical, chemical and biological factors. Discrete sample methods are time consuming, expensive and need high resolution data for differentiating in aqueous systems. Current time requires robust, fast response sensors with high sensitivity and bigger lifetime so that the pollution can be continuously monitored [4]. Present day technological developments need a fast, reliable, robust and cost effective system for the detection of these pollutants. New prototypes are to be developed for rapid and on-site detection of these pollutants in terrestrial as well as aquatic ecosystems. Conventional techniques such as Chromatography as less reliable, demand sample pretreatment and are highly time taking. High detection limits and less selectivity adds to the drawbacks of conventional detection methods [5–8].

The chapter focuses on such electrochemical sensing devices which have been proved to be simple and inexpensive when it comes to detection of pollutants at traces and sometimes even at ultra-traces level. It puts light on their mechanisms and various modes of applications. Electrochemical techniques are slowly growing as one the major mode of in situ determination of pollutants in water samples. It is much reliable and sensitive method for detection and determination of pollutants.

Electrochemical sensor techniques are important subclass of chemical sensing technology that employs an electrode as transduction element designed in such a way that it is inexpensive, miniaturized and can be used for on-site detection of pollutants. These sensing systems are highly sensitive, selective, wide range, small size and require less power for operating. Electrochemical techniques hold an

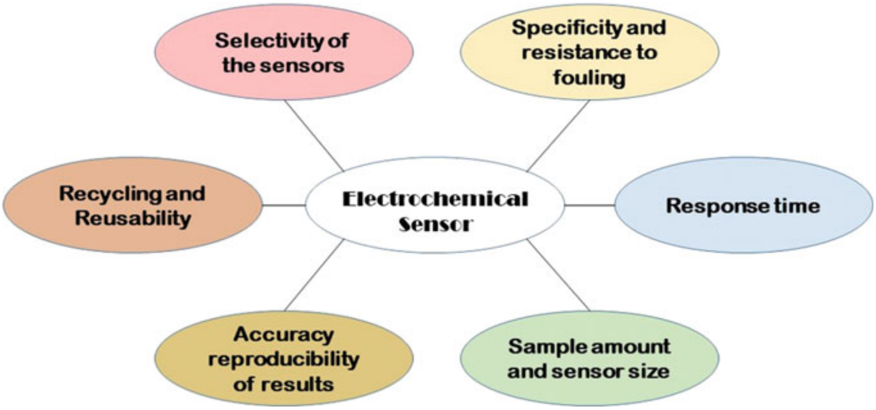

Fig. 1 Factors regulating the selection of electrochemical sensors

additional benefit of real time trace level detection of pollutants such as toxic metals or carcinogenic organic compounds in solution under analysis. Some of the key points for the advantages of these sensors over conventional detection techniques is given in Fig. 1. Electrochemical sensing techniques basically employs an electrochemical cell comprising of a two-electrode arrangement including a working electrode and a counter (or reference) electrodes or a three-electrode arrangement consisting of a working, electrode, a counter electrode and a reference electrode [9–11]. The history of these sensors holds back for application in many industries. Max Cremer invented glass electrode (1906), the first electrochemical sensor.

Electroanalytical sensors are systems interplaying between electricity and chemistry, relating the chemical parameters with factors such as current, potential or charge. They are mainly three types based on mode of measurement: Amperometric (redox current measurement based), conductrometric (measures change in resistance) and potentometric or voltammetric (depending on change or generation of potential) [12].

2 Types of Electrochemical Sensors

2.1 *Potentiometric*

Potentiometric sensors consist of a system of membrane constituting ion-exchangers, lipophilic salts (such as tetra(alkyl)ammonium-tetra(butyl or phenyl)borate) and plasticizers (such as ortho-nitrophenyloctyl ether, dibutyl phthalate), and the membrane or trans-membrane potential is used to measure the activity of analyte ion in sample solution. Potentiometric sensors are principally working on the relation between voltage of the electrochemical cell and concentration of active species in the sample. A large section of such electrochemical sensors work on the 'zero current potentiometry' mode. These sensors convert ion-recognition event into a potential signal and provides analytical information. The recognition membrane undergoes equilibrium and therefore changes in membrane potential are recorded. The potential difference between analytical electrodes and reference electrodes is used for obtaining information about the analyte. These sensors are further categorized into symmetrical devices such as ISEs and asymmetrical configurations of selective membranes in reference to sample under analysis. Asymmetrical potentiometric sensors (ASPs) hold an additional advantage of robustness and high stability over symmetrical potentiometric sensors (SPSs). The most common potentiometric sensors include Ion selective electrodes (ISEs) (Fig. 2).

ISEs of ions of metals such as Cu, Hg, Fe, Cd, Mg; anions such as CN^-, F^-, NO_2^-, $H_2PO_4^{2-}$, etc. and ions such as Ammonium, uranyl etc. have been studied widely [13]. The measurement of ion under investigation largely depends upon the potential difference across the membranes of the sample and inner electrolyte used. The concentration of ion under study is determined by the application of Nernst equation. Here the membranes potential is obtained by measuring the difference between ISE and reference electrodes at equilibrium when no current is flowing.

The membranes electrodes in ISEs are effective only when they are selective to a particular ion, attains equilibrium easily and shows linear change with ion concentration. The major categories of membranes in ISEs include glass membranes (made of ion-exchange glasses made of silicates or chalcogenides), solid state membranes (made up of inorganic salts), liquid and polymeric membranes [14]. Advancements are being made for developing techniques of potentiometric sensors

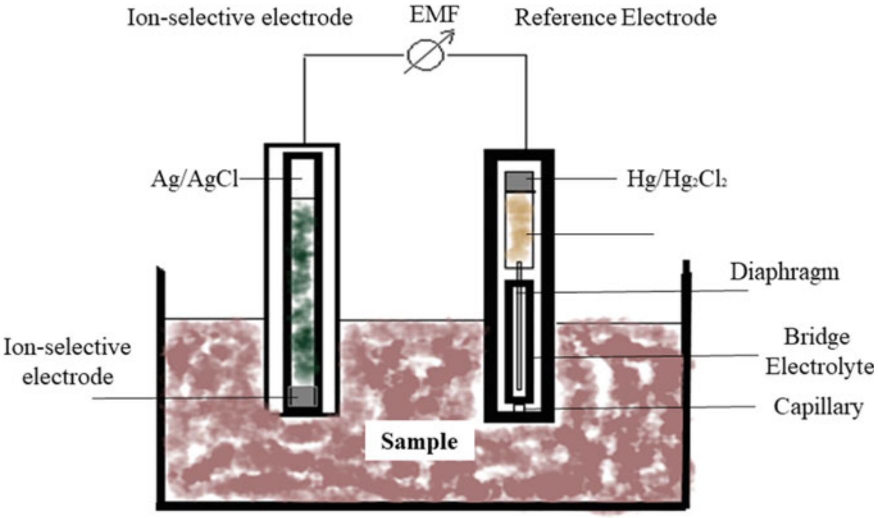

Fig. 2 Schematic representation of ISEs

which are highly robust, much reliable (easily calibrated with little potential drift), easy handling and can be used for wider range of species. One of the most conventional membrane electrodes are Glass membrane electrodes (which are highly selective, low detection limit, very stable and free from redox interferences. The selectivity of these membranes for various ions of interest largely depends upon their composition. They are not only used for measuring protons concentration but can also be applied for sensing metal ions such as alkali metals (Lithium, sodium, Potassium) or transition metals ions (copper, Lead, Cadmium, Silver). Chalcogenides based Glass membranes have been developed to detect metal ions. They can be used in combination with microactuators or microelectronics for monitoring heavy metals in waste water [15].

Solid state membranes are made up of inorganic salts. For example F^-ions can be detected by using single crystal LaF_3doped with Europium (to enhance ionic activity) based membranes [16]. Other doped atoms used are Nd, Sm, Ca etc. which are used as dopant for enhancing ionic activity [17]. Silver salts of iodide, chloride, bromide and sulphides are being used for the detection of metal ions such as Cu^{2+}, Pd^{2+}, Br^-, I^-, etc. these salts are dispersed into inert matrices such as PVC, methacrylate, epoxy resins or polycrystalline membranes [18–20]. The robustness of these solid state membranes is increased by subtracting conventional internal electrolytes and hence reducing its temperature and pressure sensitivity and increasing the chances of its miniaturization [20].

Liquid ion selective electrodes are mainly synthesized by inducing ionophores (macrocyclic ion carriers, lipid-soluble entities either natural or synthetic chemicals that transport ions across a membrane) into viscous ionic liquid membranes [21]. Ionophores can also be incorporated in PVC or other polymers to function as liquid membranes and these polymer based membranes are much selective in comparison to liquid membranes [21]. Conventional liquid electrolytes can easily be replaced by attaching conducting polymers to liquid membranes. This will lead to an enhanced ion-to-electron transduction between the electronic conductor and liquid membranes [22, 23]. Conducting polymers may also be applied as ion selective membranes by creating ion recognition sites in the polymer matrix [24]. Ca^{2+} selective electrodes have been studied widely and many organophosphoric acid based liquid membranes have been developed in past few years [25, 26].

Neutral carriers doped plasticized PVC membranes have been developed for a wide range of metal ions [21, 27]. Polymer membranes incorporated with crown ethers and bis-crown ether ionophores are used as site specific binding of metal ions with ligands. Host cavity can be tuned for recognizing of pollutant materials. Calixerenes (phenol-formaldehyde condensates) are widely used for metal ion binding recognition. Electropolymerization techniques of monomers to conducting polymer from a counter ion solution to tailor the cavity size in polymer film from the desired ion for detection. Such efforts play an important role in enhancing the selectivity of sensors with respect to interfering species using chemical recognition techniques.

2.2 Conductometric

Charge concentration is measured in terms of solution resistance in such electrochemical sensors. They lack species-selectivity and are much effective in cases where total ion concentration is below a certain permissible maximum level or can be used as detector in ion exchange chromatography after the separation of ions as online detectors. It measure the change in electrical conductivity on the surface of electrode. They are simple, cost effective and miniaturized sensors but are least selective in all the variants of electrochemical techniques. There are various kinds of resistance such as electrical, contact resistance (between electrodes and selective layer), bulk and surface resistance. This may affect the sensing activity of the selective layer of electrode and analyte and thereby creates hurdles in differentiating the ions or molecules being analyzed.

Various types of Conductometric sensors have been developed in past few years. Some of them employ ionophores based polymeric membranes for the detection of potassium, calcium, ammonium and Lithium ions with the sensitivity in micro molar concentration range and fast response time. Their stability is very high and can be used for several weeks [28]. Enzyme immobilized Conductometric sensors can be employed for toxic organic compounds such as organophosphorus pesticides and heavy metals from micro to nano molar concentration range [29]. Similarly many other biosensor based Conductometric techniques have been developed that has been discussed further in this chapter. Application of molecularly imprinted polymers (MIPs) is also broadly discussed in terms of application in case of organic pollutants and metal ions.

2.3 Voltammetric

Current is measured as a function of applied potential in these type of sensors. They provide much insight of species present and work with very low detection limits (up to Pico molar) using state-of-the-art instrumentation and analyte pre-concentration on the surface of electrodes. Separation of species are not required in these sensors and it can be combined with Amperometric or coulometric sensors once the voltammetric profile has been assigned to the mixture of analyst [4]. Keys steps for voltammetric determination of pollutants includes preconcentration and stripping of ion of the interest. These steps leads to higher selectivity and sensitivity. The ions of interest are collected in a working electrode and then they are oxidized or reduced to send back them in solution. These voltammetric sensor have been proved to be highly efficient and can be used for solution with very low detection range (nano to Pico molar concentration). This gives an extra advantage of monitoring of trace metals in water bodies. They are also proved worthy in multi-elemental analyses, speciation of trace elements and in situ detection. There are mainly two major categories of such sensors: Anodic Stripping Voltammetry (ASV) and Adsorptive Cathodic Stripping Voltammetry (ASCV).

ASV is the most common, highly reliable and well established method. It employs electrodes such as Hanging Mercury Drop Electrode (HMDE) and Mercury film electrodes (MFE). In HMDE new drops are created in each test which leads to creation of new electrode surface. This increases the reliability of the results obtained in case of these electrodes. MFE are more robust and highly selective than HMDE due to their high surface to volume ratio. The deposition potential of −0.3 or lesser (less than reduction potential of analyte) is applied during preconcentration and reverse scan is performed towards more positive potential. This leads to oxidation of metal in mercury. Peak oxidation potential give the information about the analyzed metal and peak intensity is related to the metal concentration [30]. The equation can be given as:

$$M^{n+} + ne^{-} + Hg \rightleftharpoons M\,(Hg)$$

Mercury electrodes are useful for a range of metal ions and MFE are more selective than HMDE. The smaller volume of MFE leads to more collection of metal into the mercury. These electrodes are covered with agarose membrane as an antifouling agent. They are useful in detection of metal ions such as Lead, copper, cadmium etc. in water samples [31]. Since mercury tends to have environmental toxicity issues, researches are being carried out on other materials based electrode systems. Some of the modified electrodes for Voltammetric sensors can be summarized in the Table 1.

Table 1 Electrode modifications for voltammetric sensing techniques

Analyte	Electrode modification		References
Pb^{2+}, As^{3+}	ASV	Gold Electrode (Good electrochemical inertness due to larger cathodic potential)	[32, 33]
Pb^{2+}, Cd^{2+} and Cu^{2+}		MFE microelectrode (Extraordinary detection limit)	[32]
Hg^{2+}		Au-Pt electrode and Au on Graphene electrode (High resistance to chemical reaction)	[34, 33]
Fe^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}		Amalgam electrodes (best cathodic potential window)	[35, 36]
Co^{2+}, Cr^{6+}	AdCSV	HMDE (smooth and uncontaminated surface which is self-renewing)	[37, 38]
Co^{2+}, Cr^{6+}, Ni^{2+}		Bismuth film electrode (environment friendly as compared to Hg and combine with metals just like mercury form amalgams)	[39–41]
U^{6+}		Bismuth coated carbon fiber electrode (High reproducibility of results)	[40, 41]
Imidacloprid, Acetamiprid		Bismuth film electrode	[42]

AdCSV method is very sensitive and is effective for analysis of many trace metals in water bodies. Ligands are added for inducing adsorptive quality to the electrode. They form complexes with the metal ions. This adsorption is the pre-concentration step and denotes selectivity as well as fast response time to the electrodes. Adding buffer solution to the electrolyte for maintain pH as complexes formation is pH dependent phenomenon. Adsorption potential slightly greater than reduction potential of metal-ligand complexes (0.1 V) is applied. Reverse Voltammetric scan is performed for reducing metal from the complexes. Peak intensity and peak potential are used to determine type and concentration of metal being investigated. AdCSV mainly employs both types of electrode (HMDE and MFE) where HMDE is mostly used one. They have very small adsorptive time and therefore can be used for fast detection of metal ions even at very low concentration [37–39]. Bismuth film electrodes are Nano-level sensing devices that are useful for interference free, on-site monitoring of pollutants such as U(VI) ions [40, 41].

2.4 Amperometric/Coulometric

They consist of two or three electrode systems that are dipped into an electrolytic solution. The diffused analyte species are measured on the surface of working electrode. Both Amperometric and Coulometric sensors work on the similar principle of applying a constant potential and measuring the current changes with time. The current obtained is related to the concentration of analyte. The basic difference between both of them is while in Amperometric sensors the fraction of electrolyzed species is much lesser than one, its equal to unity in case of Coulometric sensors. The most basic example of such sensor are one with Clark type electrodes (made of Pt electrodes). The electrode is modified by various forms for getting selectivity and stability [43]. Interferences are reduced by using Nafion coatings. Similarly for different types of analyte coatings are used which are explained in Table 2.

Some of the modified forms of above mentioned techniques includes cyclic voltammetry (measuring the resulting current on cycling the potential of the working electrode), chrono-amperometry (current is measured as a function of time at constant potential) and chrono-potentiometry (potential is measured as a function of time at constant current), electrochemical impedance spectroscopy (measures the changes of interfacial property of electrodes), and field effect transistors (electric field is used to control the effect of current):

- Cyclic voltammetry: Measurement of periodic variation in voltage variation with change in current (potentiodynamic electrochemical measurement technique). It involves ramping of electrode potential with time in cyclical manner. The variations in voltage are done in wide variety of patterns that gives rise to various methods of voltammetric analysis. This technique includes methods such as polarography, linear sweep voltammetry (LSV), differential staircase voltammetry (DSV), normal pulse, reverse pulses and differential pulses [3].

Table 2 Electrode modifications for amperometric sensing techniques

Analyte	Electrode modification	References
Hydrogen peroxide, Chloride ions, Bromide ions, Hydroquinone	Pt electrode sealed in Pyrex tube and polymer coating at base	[44]
Biocide such as Hypochlorites or hypochlorous acid	Bare Platinum electrodes	[45]
Formaldehyde	Mixture of noble metals such as Ru and Pt	[46]
Free chlorine	Disposable microsensor (Au deposited on cyclic olefin copolymer)	[47]
Choline	Polyethylene terephthalate on which an electrolyte film containing polyvinylchloride was layered	[48]
Bisphenol A	Electropolymerization of 2-aminothiophenol on a gold nanoparticles-modified glassy carbon electrode in the presence of BPA as a template	[49]
Acetaminophen	1. Poly(L-serine) film-modified electrode 2. DSA anode with biomimetic catalyst iron (III) tetrapyridinoporphyrazine	[50, 51]
H_2O_2	Prussian Blue	[52]
Phosphate	Mixture of ionic liquid and chitosans	[53]
Hydrazine and phenylhydrazine	Paste of ferrocene and CNTs	[54]

- Chrono-amperometry: Steady state measurement of current at a time on applying square-wave voltage signal (SWVS) is applied to the working electrode. The relation between measured current and analyte diffusion to the electrode is related using Cottrell equation.

$$I = \frac{nFA\sqrt{D}c}{\sqrt{\pi t}}$$

In this equation **D** is the diffusion coefficient (/s), **c** is the concentration of analyte in the bulk solution (mM), **A** stands for the surface area of the electrode in sq. metres, **F** is Faraday's constant, **t** is the time in seconds and **n** is the number of electrons exchanged during the reaction.

Similarly, Chrono-potentiometry is measurement of the voltage as a function of time on applying constant current or square-wave current [55]. Controlled-potential chrono-amperometry and controlled-current chrono-amperometry are two most common form of chrono-amperometry techniques.

- Electrochemical impedance spectroscopy (EIS): It measures current change on applying sinusoidal varying voltage. This is a frequency domain measurement that is calculated using sinusoidal perturbation on a voltage system. The frequency of the sinusoidal signal is used to calculate the impedance as the real as well as imaginary components in the electrochemical system. It analyses the intrinsic material or system property of impedance and hence of very informative for biosensor development and their applications in environmental pollutant detections [56, 57].

- Field effect transistor (FET): It is made up of bridging between two electrodes made of semiconductor devices and transistor. Electric field inside the channels are controlled along with their conductivity and charge is drained using third electrode. When a drain-source voltage is higher than gate-source voltage this set up functions as a switch conductive or non-conductive states. However when gate-source voltage gives constant current it acts as an amplifier. The FET technique hold advantageous for the systems with a weak signal and high impedance [58, 59].

3 Advantages of Electrochemical Sensors

Application of electrochemical sensors hold many benefits when it comes to detection of environmental pollutants. Various types of electrochemical sensors can be used in combination for higher selectivity and specificity as well as robust technique for the analysis of contaminants present in the solution or the system. Some of the advantages that these sensors hold may be listed as below [4]:

- Voltammmetric sensors holds additional advantage of higher selectivity and specificity and hence to probe speciation. Every chemical species such as atoms, molecules or ions owns a specific oxidation or reduction potential. Such amount of specificity is lacking in many kinds of detectors.
- Selectivity can be enhanced by proper selection of electrode material such as Ion selective electrodes. Interferences by other species can also be resolved by application of certain voltammetric sensors and some electrode materials.
- Electrochemical sensors (especially voltammetric) with controlled potential prove beneficiary because of high selectivity and low detection limits. Combinations of potentials can be used in case of analyte accumulation the surface of electrodes.
- Real time data monitoring and computerized control of the system will be effective in producing results at a faster pace.
- These sensors are battery operated, easily handling, portable sensing devices make them useable even at the site of contamination.
- Small size of the sensing devices increases their application at places where other devices can’t be used.

General criteria for designing of an electrochemical sensing device:

- Potentiometric sensors need extra electrode materials which must be free from interferences while Amperometric and voltammetric techniques, species to be determined must be electroactive in the potential range of sensors. Sometimes inert, supporting electrolytes are also needed to be added to consolidate the current perturbation.
- Concentration of analytical species must be determined carefully.
- The results obtained should be reliable and easily reproducible.
- The rate of electrode degradation with time and fouling of electrode surfaces should be kept in mind while deciding the electrode materials.
- Sensors must respond fast and should be calibrated easily.
- The extremely low detection limit for the sensors gives additional advantages to these electrochemical sensors.

4 New Developments in Electrochemical Sensing Techniques

4.1 Screen Printed Electrochemical Sensors

Screen printing techniques are old methods applied for textiles and art. However in recent researches it has been applied for the modification of electrode surfaces to make them stable, reproducible and easily disposable in mass production. Pastes most commonly used in screen printed electrodes are of silver or carbon ink. Silver ink is mainly used for conductivity purpose while carbon ink is used for working electrodes. Carbon ink is simple, chemically inert and easily modified. Some SPEs employ Gold paste but it is less cost effective as compared to carbon electrodes. Au forms self-assembled layers (SALs) on the surface of electrodes and therefore have much application in sensing devices [60]. Application of SPEs in electrochemical sensing ranges from pH sensing, organic compounds, heavy metals, radioactive wastes as well as biological samples. They can be used for replacement of Glass electrodes in pH sensing devices [61]. Three-electrode system was applied for sensing pH and was much more sensitive than two-electrode systems [62]. Nickel oxide bulk modified SPEs are applied for detection of hydroxide ion change [63]. Disposable CdS modified SPEs electrode are used to measure dissolved oxygen concentration by electro-chemiluminescence method [64]. MnO_2 based SPEs sensing devices are used to determine the nitrate ions in the sample [65]. In-situ determination of phenolic compounds and their derivatives was done using SPEs because their simple design, fast response, high sensitivity and low cost. However electro-oxidation of phenols leads to surface passivation and hence hinder the electron transfer mechanisms. Graphene or carbon based nanomaterials have been proved to be outstanding material for screen-printing of electrodes due to their high tensile strength, large electrical and active chemical properties. Application of surfactants having anti fouling properties proved to be major step in determination of phenolic compounds electrochemically. One such experiment involved CTAB (cetyltetramethylammonium bromide) in the analysis of bisphenol A in water samples obtained from sewages [66]. Dihydroxybenzene determination was done Multi walled Carbon Nanotubes (MWCNTs) and Gold nanoparticles (AuNPs) based SPEs; coating of MWCNTs increased the sensitivity while AuNPs provided conductivity to the surface [67]. Immobilization of enzyme (polyphenol oxidase) on MWCNTs modified electrode surface was done using electrodeposition techniques. Aiding of Bi^{3+}, PPO and MWCNTs was used for phenol detection and spunning Diaminobenzene (DAB) for the detection and determination of DAB [68, 69]. Disposable biosensors with magnetic nanoparticles of Nickel for determination of bisphenol A [70]. Surface enhanced Raman scattering (SERS) enhanced Silver deposited SPEs was used for detection of phenolic compounds. They are highly efficient for qualitative as well as quantitative determination of polar organic compounds with very low detection limits (0.1 nM) [71]. Aetylcholinesterase (AChE) immobilized SPEs with magnetic nanoparticles were used for determination of pesticides (as they inhibit the enzymatic activities). AuNPs were added to enhance the stability of Iron oxide nanoparticles. These are easily renewable electrodes and can be replenished after the removal of magnetic portion [72]. Methyl parathion is determined by using E. coli immobilized SPEs.

Electrochemical stripping analysis (ESA) esp. ASVs is most common method for the determination of toxic metal ions. Combining ASVs with SPEs increases sensitivity, robustness reduces response time and cost of electrochemical detection [73]. Some of the metal ions detection techniques are mentioned as below:

1. Lead: Sensitivity of the electrochemical detectors is mainly increased by using Carbon, Bismuth, Gold or other materials. Bismuth, because of their environment friendly nature and high analytical performances are most widely used technique for lead determination. The wide negative potential window and less necessity for the removal of dissolved oxygen increase easier handling and their more convenient use [74–77]. Thin film Hg electrode was also found effective for microlevel detection of Pb(II) ions [78].
2. Cadmium: Quasi noble behavior of Mercury makes it suitable for application over a wide range of pH. This holds an additional advantage over Bismuth which is easily hydrolyzed in neutral or alkaline media. Stripping voltammetry using mercury electrode can be used for a wide range of metal ion detection and requires low analysis time without degassing. So it is much beneficial for determination of trace metals but the only shortcoming associated with metal toxicity. This requires the development of new techniques to reduce the amount of mercury used for determination [79]. Ex-situ deposited Hg based SPEs, AuNPs amalgam and Microelectrode array of Hg are some of the most common modifiers for detection of Cadmium [34, 80, 81, 82].
3. Mercury: Bare or modified Au electrodes are mainly used in detection of Hg(II) ions because of the high affinity of gold which increases the preconcentration and thereby reducing time of detection. However the only drawback that limits

the use is the high affinity for amalgam formation which leads to structural changes over the surface of electrodes. The most common Screen printed Gold electrodes (SPGEs) are commercially available for detection of Hg(II) [83]. Thiol based SPEs, PANi modified SPEs and PANi-Methylene Blue modified SPEs are some of the modifiers used for electrochemical detections of Hg [78, 65, 85, 86, 87].

4. Arsenic: Arsenic detection is done by using PtNPs modified SPEs by electrochemically depositing K_2PtCl_6, citrate-capped AuNPs modified SPEs and AChE modified SPCEs with no interferences from Cu(II) [69, 89, 90].
5. Mixture of metals: Bi modified SPEs can be used for simultaneous determination of metal ions such as Pb(II), Zn(II) and Cd(II) [91]. Crown ether based SPEs on thin film Hg electrodes are used for determination of Pb(II) and Cd(II) [92]. Chitosan, poly-[-1-4]-2-amino-2-deoxy-d-glucopyranose (CTS) forms stable chelate complexes with many transition-metal ions through hydroxyl and amino groups. CTS and their derivatives with Glassy carbon electrode (GCE) are used for determination of metal ions [93]. Modified CTS-SPCEs are used for the detection of Pb(II), Cu(II), Cd(II) and Hg(II) with very less preconcentration time [94]. CTS-MWCNTs composite film showed noticeable improvements in robustness of the electrode [95]. In-situ Hg deposited on MWCNTs-CHIT/SPE was used for the simultaneous determination of Pb(II), Cd(II) and Cu(II) [96].

SPEs are proved to be effective method for the rapid detection of bacteria. Enzyme-linked immunosensing strip was fabricated for the specific detection of E. coli O157:H7 because of the use of double-specific antibodies [97]. Selective and detection of *E. coli* was done based on an impedimetric immunosensor using SALs modified gold SPEs in river and tap water samples without following preconcentration steps. Disposable SPEs were used for direct electron-transfer reaction at *Shewanella* sp. bacteria without redox mediator [98]. Easy drop-coating of bacteria was done to avoid tedious job and time-consuming step of growing a bacterial bio-film formation on the surface of electrode.

Radionuclide such as Uranium determination was done using 4-carboxyphenyl-grafted SPE has for sub-nanomolar U(VI) analysis using voltammetric methods [99].

U(VI) detection in aqueous solutions was also done using electrochemically induced, non-modified SPEs, with a detection limit of 4.5 nmol L^{-1} [100].

Stripping-based electrochemical sensors

Heavy metal contamination is a serious matter of concern and is leading escalating needs for monitoring these trace metals in environment especially water bodies. Stripping analysis has been proved to be powerful technique for ascertaining toxic metals in water samples [101, 102]. The ‘built-in’ preconcentration step adds to the significant sensitivity of this method. Preconcentration requires the accumulation of target metal ions on the surface of electrodes.

Electrolytic deposition for trace heavy metals and non-electrochemical preconcentration methods based on adsorptive accumulation of metal complexes have been developed for environmentally harmful trace metals such as Cr, Al, U, Fe, Ti, V, Mo. etc. which are very difficult to deposit on the surface of electrodes [103].

Stripping analysis provides important and highly accurate information on metal speciation. Varying oxidation states of metals can be measured by adjusting the stripping protocol, controlling solution or deposition profiles. Errors due to metal contamination or loss can also be monitored in-situ in this technique.

4.2 Molecularly Imprinted Polymer as Modifiers

MIPs are highly stable and specific that holds great potential to substitute enzymes, antibodies and other natural receptors in sensing technology. Three major criteria for designing of MIP based electrochemical sensors:

- High-sensitive transducer which are very capable in monitoring the binding and transformation of analyte into processed signal;
- Developing of polymers that interacts with the template-analyte under specific conditions with high affinity, selectivity and specificity;
- Integrating of MIP with transducer.

MIP Potentiometric sensors was first synthesized using electropolymerization of para-aminophenol and aniline for detection of phenols, amines and pyrrole [104]. Monomers react with themselves and target molecules acts as templates forming molecule specific polymers. Pyrrole, aromatic amines, substituted amines and phenolic compounds, based MIPs were prepared by copolymerization process. MIP-based amperometric device for the detection of aniline and phenol were developed. Their basic principle of functioning involves adsorption of target molecule on the template of MIP. Potentiometric sensors for the analysis and detection of lead and uranyl ions in aqueous medium were developed using 5-Vinylsalicylaldoxime ligand based MIPs [105].

4.3 Electrochemical Biosensors

Electrochemical biosensors are a proved to be breakthrough in electrochemical detection of pollutants. They are miniaturized electrochemical devices that are used for sensing pollution and are work at low detection limit of analyte and at very low sample volume [106, 107]. Their development depends mainly on basis of their sensitivity, specificity and parallelism. The electrodes used in these devices converts biological signals into output signals. The present necessity is to design highly specific sensing devices leading to development of biosensors. Electrochemical biosensors holds advantages such as extended miniaturization, enhance selectivity, high specificity and real-time monitoring of the samples [108]. Electrodes applied in these electrochemical biosensors converts biological signals into readable output signals. Electrodes used in biosensors allow the conversion of biological signals into a readable output signal. Modifications by specific biochemical (DNA, enzymes or cells). These electrochemical biosensors may be any type: potentiometric, voltammetric or Amperometric on the basis of output method applied. Electrochemical biosensors can be sub categorized as biocatalytic or affinity sensors on the basis of biological molecule used for modification. Electro-biocatalytic sensors are modified with biological entities (enzymes) that recognizes a specific target and induces a response of an electroactive molecule. AChE inhibition-based electrochemical biosensing has been proved to be easy, fast and extra sensitive method for pesticide such as paraoxoon, parathion, carbofuran and methemiodophos. Immunoassay based electrochemical sensors have been reported to be applied in the detection of Picloram, carbofuran, Atrazine and other pesticides. On the other hand, electro-affinity sensors have a binding recognition element (such as antibodies) and produces signals when they are coupled to target molecules [109]. Extensive literature is already been done for Pb(II), Cu(II), Hg(II), Cd(II) etc. Application of nanomaterials adds the benefit of smaller size and higher surface area to the electrodes.

4.4 Nanowire-Based Electrochemical Sensors

Application of nanowires can be other possible strategy for enhancing surface-to-volume ratio, and promoting the electrochemical sensitivity of sensors for the detection of analyte. Nanowires made of conductive or semiconductive materials (Au, Ag, CuO) depending on the nature analyte to be detected. The easier mode of preparation, higher surface-to-volume ratio, and increased stability due crystallinity, higher sensitivity and selectivity suggests them to be used effectively in sensing devices. CuO nanowires anchored on SWCNTs in an electrochemical sensor can be used for the detection of organophosphorus pesticides (parathion or Malathion) used in the field of agriculture. CuO-SWCNTs are much stable and show high specificity for Malathion and effective selectivity against pesticides, metal ions or cations and carbohydrates [58]. Silicon nanowires-supported AChE-based electrochemical sensors were used for the determination of organophosphate pesticides [110].

4.5 Paper-Based Electrochemical Biosensors

Paper is becoming an increasingly common support for developing microfluidic devices and biosensors because of their unique properties such as porosity, liquid wicking and affinity for surface to a number of analyte, etc. Such devices are much portable, on-site, and real-time monitoring, thereby establishing them for large number of applications in different areas such as medical, nutraceutical and environmental [111]. Some of the basic examples for their application in pollutants sensing can be cited as follows. Paper-based screen-printed electrochemical sensor to detect phosphate [112], lateral flow paper-based sensing device detection of for lead and cadmium ions [113], portable paper-based dual electrochemical/colorimetric system for detection and determination of gold and iron ions [114], [PMo11VO40] 5−on carbon electrodes for the electrochemical determination of chlorate [115] and many more literatures are available establishing their use in sensing devices. Introduction of cellulose blotting pad as a sink allowed continuous wicking of the solution through electrodes which promoted the efficiency and sensitivity of Pb(II) deposition in ASV [116]. A 3-D microfluidic paper-based electroanalytical device for detection of Pb^{2+} and Hg^{2+} based on the potential-control method was used for lake water and human serum samples, respectively [117]. [118] developed a fully integrated ready-to-use paper-based electrochemical biosensor for the assessment of nerve agent simulant (paraoxoon) in real environmental sites. Carbon black/Prussian Blue nanocomposite based paper sensor was used for determination of paraoxoon were also developed [118].

4.6 Ionic Liquid as Electrode Modifiers in Electrochemical Devices

Ionic liquids are liquids having positively and negatively charged ion joined through electrostatic interaction. While conventional liquids are made up of molecules, ionic liquids are ionic entities. They are liquid at room temperature and most of them stay liquid up to 200 °C. Ionic liquid based modified electrodes can be of great application case of electrochemical sensors. They serve as both binder and electron conductors on the surface of electrodes. High conductance, effective catalytic properties, intrinsic conductivity, longer shelf life as well as temperature resistance, low volatility, extreme sensitivity, wide electrochemical window and very high selectivity makes them more and more favourable when dealing with electrochemical sensing devices [119]. Task specific ionic liquid (TSIL) containing a bistriflimde anion and tetraalkylammonium cation in combination with Bi_2O_3 was found effective in electrochemical detection of heavy metal oxides such as CdO, CuO and PbO [105, 120]. The acid group enhances the solubilisation of metal ions in Ionic liquids and hence helps in analyte preconcentration. Nano-porous Au electrode coated with 3-mercaptopropylsulfonate (MPS) SALs was applied in the detection and determination of Cu(II) water by stripping voltammetry [56]. RTILs provide suitable alternative Hg free electrode techniques because of high temperature stability and wide electrochemical window.

Redox ions that are less active or inactive at conventional electrode-electrolyte surfaces can be detected at liquid-liquid interfaces by applying electrochemical analysis the interface of two immiscible electrolytes [104]. This technique holds an extra advantage of pre-saturation with water molecules, thereby less affected by humidity. MWCNT based ionic liquid (1-butylimidazole bromide immobilized on an epoxy group of poly(glycidyl methacrylate)-MWCNT composite) electrodes were used for voltammetric detection of phenolic compounds [121]. Ionic liquid can profoundly be applied as Ion Selective Electrodes (ISEs) as an alternative to plasticizers and ion exchangers. Hydrophobic RTIL [N8, 8, 8, 1] [C_4C_4N] containing dicyclohexano-18-crown-6 (DCH18C6) as ionophore was used for the potentiometric detection of K^+ in water [122]. Thin microporous membrane containing valinomycin and hydrophobic [N12, 12, 12, 1] [TFPB] ionic liquid was applied for amperometric detection of K^+ and Na^+ [123]. Low-melting ionic solids (LMISs) viz. [N6, 6, 6, 6] [BSB], [N8, 8, 8, 8] [BSB] and [N8, 8, 8, 1] [BSB] were applied for the potentiometric determination of salicylate, perchlorate, thiocyanate and iodide ions in water [124].

5 Limitations and Plausible Solutions

Fouling of the electrode surface appears as a serious matter of concern when it comes to detection of biological or organic pollutants. This creates a strong impact when it comes to on time monitoring of wastes in the stability as well as performance time. A large number of electrode surface cleaning techniques are available but it is preferred to have low cost electrochemical sensors. Poisoning of electrode surface is an important issue that must be solved while working with electrochemical sensors, which is time consuming and steps must be taken for continuous monitoring of the samples.

ISEs are simple-to-use and cost-effective devices which are highly effective for environmental analysis. However many practical challenges that are faced during their application in analysis (water samples from rivers or lakes) includes electrodes carryover, drift, their dissolution with the time, surface passivation and fouling [125]. The problem of surface fouling can be overcome by regular cleaning of electrode surface with analyte solution at a very low concentration. The preconditioning of electrode in analyte may lead to fast response, increased stability and reduce the problem of electrode drift and dissolution. Passivation and fouling can be combatted by using ISEs in Flow Injection Analysis and surface should be frequently calibrated.

Application of ionic liquids will prove an effective method for reducing toxicity due to mercury electrode. Some of the minor drawbacks related to electrochemical sensors includes their lower shelf life of six to one year depending upon samples they are being used with, limited temperature range which requires keeping the temperature of samples highly stable, low humidity and high temperatures dries out the surface of electrolyte.

6 Conclusions

The chapter tried to cover maximum aspects of materials that can be applied as electrochemical sensing devices. It was observed that potentiometric techniques especially ISEs have been proved to simple and inexpensive method of pollutant detection and determination. The robustness and miniaturization can be increased by application of solid contact support. Amperometric sensors were found to be highly sensitive and selective for metal ion pollutants as well as organic entities. For very low detection limits voltammetric sensors were seen to be very effective and preconcentration step adds to its sensitivity. Improvements are still needed for Conductometric sensors in terms of sensitivity by addition of more selective elements. Amperometric and Potentiometric techniques are much advantageous and reliable as compared to conductometric measurements. Introduction of new technologies such as screen printing and molecular imprinting methods adds to the selectivity and sensitivity of these electrochemical sensors. Screen printed electrodes are highly effective for in-situ determination of pollutants. Ionophores based electrodes and analyte preconcentration plays another important role in adding specificity and selectivity of the sensing devices. Overall analysis of these sensors provide a suitable ground for their extensive application in field pollutant detection. Majority of electrochemical sensors are fabricated using microfabrication or nanofabrication techniques for miniaturization of devices and thereby enhancing the portability of these sensors. Research need to carry out increasing the antifouling property of the electrode surface and adding more life to the electrodes being used. The field is growing slowly but with a steady pace. Both nanomaterials and biomolecules based electrochemical sensors are adding desirable benefits of sensitivity and selectivity to the devices and hence playing an important role in detection and determination of the pollutants. Upcoming time need more specific and selective systems for which molecularly imprinted polymers and nanosensors will play a major role.

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Materials in Bio-Sensing of Water Pollutants

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Abstract The continual increase of harmful pollutants in water has posed severe threats to the different types of flora and fauna, either directly or through the food web. They have become a source of origin of various infectious diseases which deteriorates animal and human health. This serious issue has led to the emergence of various technologies for the detection of water-based pollutants so that their presence could be revealed as well as treated. Various chemical methods have been developed for this purpose. Still, there is scope for simple, robust, accurate and economical techniques for rapid identification of such pollutants. For this purpose, different types of biosensors have been designed which either serve as an alternative or support to chemical sensors. The biosensors are analytical devices made by integrating a biological material or biomimetic based on its biochemical role with a transducer. These biological materials could be biomolecules such as antibodies, enzymes, nucleic acids or other natural products. This chapter aims at providing an insight of such biosensing devices and their materials which are used for monitoring the water quality.

Keywords Water quality · Detection methods · Biosensors · Pollutants · Biomaterials

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1 Introduction

The rise in pollutants in the water bodies poses health risks as well as other environmental problems which have become a global concern. This calls for simple, sensitive and efficient methods for detection of different types of pollutants present in water so that the remediation process becomes effective. Conventional methods of pollutants detection are less effective than biosensors in the detection of toxic components of wastewater due to their slow response, complex methodology and high cost. Thus, biosensors were conceptualized for real-time detection of analyte even at small concentrations. The application of biosensors in wastewater analysis and the materials used for their construction are discussed in this chapter. Cammann coined the term biosensor [1]. The IUPAC committee defined biosensor as "*A biosensor is a self-contained integrated device, which is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor), which is retained in direct spatial contact with a transduction element.*" [2]. Construction of biosensors requires a multi-disciplinary knowledge as the detection element is a biological material by which chemical conversion occurs, which is transduced with the help of an electronic component.

A biosensor is an integrated system consisting of (i) a biological detection element (ii) a transducer which translates the interaction between the analyte and biological element into an electrical signal. Figure 1 shows the simplified construction of a biosensor.

The advantages associated with the use of biosensors are their selective nature, reliability, high sensitivity, low cost, simplicity and real-time monitoring. History of biosensors can be traced back to 1962 when Leland C. Clark, Jr. invented a technique to determine the reduction in oxygen concentration using a platinum electrode. Due to his pioneering contribution, he was then known as 'Father of

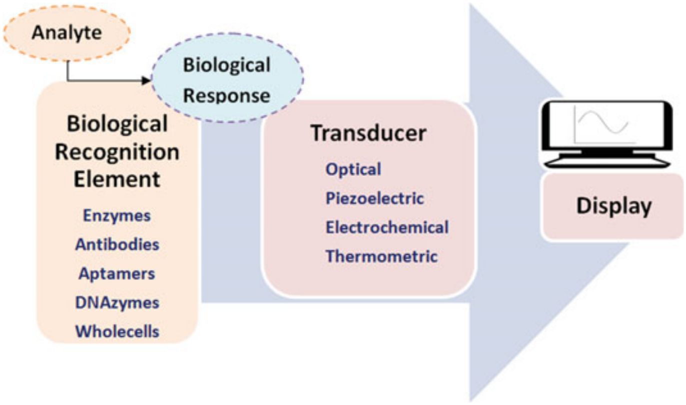

Fig. 1 Construction of a biosensor

Table 1 Major developments in the field of biosensors [2]

Year	Major milestones
1962	Lee Clark invented an oxygen sensing device based on enzymatic activity and termed it as 'enzyme electrode'
1969	George Guilbault gave the concept of potentiometric urea electrode which used immobilized urease
1973	Introduction of lactate sensor by Mindt and Racine
1974	The idea of thermal transducers by Klaus Mosbach and Bengt Daniellsson
1975	Yellow Springs Instruments (YSI) developed glucose analyzer
1977	Karl Cammann coined the term 'Biosensor'
1983–85	Different workers studied a combination of biological recognition elements such as antibodies, enzymes, nucleic acids and cells with various transducers

Biosensors'. Renneberg et al. reviewed the foundation laid by Clark and other workers in the area of biosensors [2]. Some of the major milestones in the process of development of biosensors have been summarized in the following Table 1.

2 Working of a Biosensor

The biosensor has an immobilized biological detection element which is in direct contact with the transducer. The analyte interacts with the detection element, which generates a biological response. The biological response is then converted into electrical signals by transducers which are then amplified and measured. The electrical signals generated by the transducer as a result of interaction are often low and are superimposed by the noise signal. These noise signals are generated by electrical interference or the instrument itself. Thus, the reference baseline (the signals from the same instrument without the detection element) is subtracted from the output. The signal so produced is then amplified and displayed. The output may be in the form of an analogue or digital signal. The later one is preferred, which is then sent to the microprocessor for data processing, manipulation, conversion to the desired unit and final display and storage [3].

An important aspect of biosensor working is the limitation posed by the mass transfer and kinetics of the analyte interaction with the recognition element. The working of the biosensors is affected by either of the two. When the mass transfer limitation occurs, the binding of the analyte to the receptor is at a high rate. On the other hand, when the kinetics-limited interaction occurs, the binding activity is at a low rate. Under optimized conditions, mass transfer is limited by the diffusion phenomena. Damkohler number (Da) is an index used to evaluate whether the limiting phenomena is mass transfer or kinetics based. It is defined as the ratio of the maximum reaction rate to the maximum mass transfer rate. If the Da is greater than one, it means that the interaction is mass transfer limited while if it is less than one, it signifies that it is kinetics-limited process [4].

3 Types of Biosensors

Thevenot et al. described the classification of biosensors as recommended by the International Union of Pure and Applied Chemistry (IUPAC) in [5]. Table 2 summarizes some of the biosensors used for wastewater pollutants detection.

Biosensors have been classified based on:

(i) Types of the biological detection element
(ii) Type of transducer.

3.1 *Different Types of Biological Sensing Elements*

Based on the materials used for detection, the biological sensing elements are further categorized as:

(i) Biocatalytic (e.g. Enzymes)
(ii) Bioaffinity (e.g. Antibodies and nucleic acids)
(iii) Whole cells (e.g. Different types of microorganisms.

Table 2 Biosensors used for wastewater detection

Transducer Type	Biological Detection element	Water contaminant	References
Electrochemical	Calf thymus DNA	Toxic components	[6]
Electrochemical	Urease enzyme from immobilized on non-woven cellulose swab	Chromium	[7]
Optical	The bioluminescent bacterium *Pseudomonas fluorecens* HK44	Naphthalene and salicylate	[8]
Conductometric	*Chlorella vulgaris* immobilized inside bovine serum albumin membranes	Cadmium	[9]
Microbial Fuel cell	Biofilm formed on anode	BOD	[10]
Electrical conductivity	Sulphur oxidizing bacteria	Potassium cyanide, lead, mercury, cadmium and zinc	[11]

3.1.1 Biocatalytic Biosensors

The enzymes used as recognition element by immobilization on the surface of the electrode. When more than one enzyme is immobilized in the same layer, there are many advantages which can be achieved. These may include conversion of an analyte into the final product through several steps of enzymatic conversions. Thus, the range of biosensor analyte is increased. Wollenberger et al. described this functionality of the multi-enzyme system [12]. Another advantage associated with multiple enzyme systems is an enhancement of biosensor selectivity by reducing the local interference of electrochemical substances. Another approach for enhancing the efficiency of the enzyme-based biosensor is the use of an organic solvent, which provides a hydrophilic microenvironment for the partition between the enzyme active site and the matrix. Andreescu et al. studied the detection of endocrine—disrupting chemicals (EDCs) by developing a tyrosinase based biosensor. Different polyphenol estrogens were studied such as resveratrol, quercetin and genistein and their structures were compared to the synthetic EDCs. Thus, a tyrosinase based biosensor was developed for the detection of many phyto and xenoestrogens having a polyphenolic structure in wastewater [13].

3.1.2 Bioaffinity Based Biosensors

The biosensor can also be fabricated by the use of bio-affinity agents. These are the macromolecules which are isolated from the biological sources and may or may not be engineered. When these components react with the analytes, equilibrium is reached after this, there is no further interaction with the analyte. The analyte-macromolecule complex so formed is measured by the integrated detector. A modification to this type of biosensor could be the measurement of the bio-complex reaction using another complementary biochemical reaction. The signals of these secondary reactions are then measured using a detector [5]. The bio-affinity reactions could be either an antigen-antibody reaction or receptor—ligand reaction.

Antigen-antibody reaction: The immunochemical reactions between the antigen and the antibody are utilized for the development of these types of biosensors. Antibodies (also known as immunoglobulins) are Y-shaped proteins produced by white blood cells and recognize a complementary macromolecule known as an antigen. This type of bio-complexing has been widely employed in the detection of pollutants in wastewater. Blake et al., in 1996, showed that 2A81G5 monoclonal antibodies could recognize 16 different types of metal—EDTA complexes. This study showed that equilibrium binding constants for cadmium and mercury were higher than other metal—EDTA complexes. It was suggested that histidine amino acid in the heavy chain of the antibody might assist in the binding of the cadmium-EDTA complex [14].

Similarly, antibodies ISB4 have been found to detect Cadmium [15]. Melton et al., in another study carried out to detect the presence of uranium in contaminated groundwater, developed two immunosensors. One was a portable field sensor, while the second was an inline sensor. Both of the sensors detected the complex formed by a 12F6 monoclonal antibody with U(VI)-dicarboxyphenanthroline complex [16].

The sensitivity of immunosensors could be enhanced by the use of enzyme labels, which are either coupled to the antibodies or the antigen. The enzyme coupled immunosensors operate under equilibrium condition. Kanso et al. developed an enzyme coupled immunosensor for the detection of estradiol and ethinylestradiol in wastewater. These endocrine disrupting chemicals are found in wastewater. The methodology adopted for the development of the biosensor was based on the competition between the free antigen and derivative of the antigen. The amine derivatives of estradiol and ethinylestradiol were immobilized on the surface of magnetic beads coated with a carboxylic acid. These immobilized magnetic beads were in turn fixed on the surface of the electrode. The fixation of the antigen derivative was followed by the addition of the free estrogen and anti-estrogen antibody. This step is followed by washing and addition of alkaline phosphatase labelled IgG antibody. The reaction involves the conversion of p-nitrophenyl phosphate by the enzyme into p-nitrophenol, which gives a yellow colour. This reaction gives the measurement of the endocrine disrupting chemicals present in the wastewater [17]. Another study was carried out by Merola et al., for the detection of β-lactam antibiotics using enzyme-conjugated immunosensor in water. The detection was carried out by using anti-penicillin G antibody and the response was measured by conjugated biotin extravidin peroxidase. Immobilization was carried out on Immobilon membrane, which was regenerated after the use. The antibody-antigen (β-lactam antibiotics) affinity was also determined and showed that this method of detection was sensitive and reproducible [18].

Receptor-ligand reaction: Many biosensors utilization channels, binding proteins and membrane receptors as molecular identification systems. An example of such a system is lactose permease as the sensing element. The transducer is covered by the planar lipid bilayer in which the protein is incorporated. The principle of detection is based on the co-transport property of the protein due to which when the concentration of lactose increases, the concentration of proton between the quartz surface and membrane also rises. This rise in proton concentration was detected by a fluorescence dye, which is pH-sensitive [19].

Another approach in this category is the use of aptamer-based biosensor for the detection of pollutants in water. Aptamers are single-stranded ribonucleic acids (RNA) or deoxyribonucleic acids (DNA). They can bind to different types of targets such as from ions, small molecules, cells and tissues. Their binding action is specific and based on electrostatic, van der Waals, molecular shape complementarities and hydrogen bonding. Aptamers are selected by a process known as Systematic Evolution of Ligands by EXponential enrichment (SELEX) including selection, separation and amplification. The selection is done by using single-stranded DNA or RNA library. Aptamers are preferred over proteins for detection elements as they show higher stability and tolerance for temperature and pH. The application of aptamers based biosensor for determination of water contaminants can range from lake water, tap water, seawater and wastewater. They are widely used for detection of molecular toxins [20], heavy metals [21], drugs [22], pesticides [23] and EDCs [24].

A toxin known as microcystins is a toxin secreted by cyanobacteria found in the aquatic ecosystem was found to contaminate food products [25]. Zhao et al. developed an aptamer-based biosensor for the detection of microcystins. Surface Enhanced Raman Scattering (SERS) was used to activate a bi-metallic nanosystems consisting of gold nanoflower (Au-NF) and silver nanoparticle (Ag-NP). This coupling of SERS active nanosystem led to the enhancement of the electromagnetic field for identification of microcystins with high sensitivity in lake water. This type of device may be developed to become a choice for portable biosensors for both qualitative and quantitative detection [26].

A temperature-based aptamer sensor was developed by Gao et al., for the detection of heavy metals such as lead and mercury. In this technique, the sample enters the capillary channel of a chip and reaches an exothermic reservoir containing sodium hydroxide as the exothermic agent. The entrance to the reservoir is guided by a microvalve made of an aptamer coupled hydrogel. When the analyte interacts with the aptamer the hydrogel shrinks, this leads to enhanced flow, causing a rise in the temperature due to heat dissolution. A thermometer detects this increase in temperature leading to quantitative analysis of heavy metals [27].

Aptamer-based biosensor is also used for the detection of drugs and other pharmaceutical ingredients found as water contaminants. A biosensor using an aptamer which was obtained using Capture-SELEX procedure was developed by Nikolaus et al., for detection of kanamycin A. The specificity and affinity of the analyte for the aptamer were analysed. Beads and microplate-based assay were carried out, and the fluorescence was measured. The affinity results were confirmed using a surface plasmon resonance (SPR) system. Thus an aptamer-based biosensor was proposed for the detection of aminoglycoside antibiotics in water [28].

Bala et al. developed an aptamer-based biosensor for detection of organophosphorus pesticide known as malathion. This sensing device used a cationic polyelectrolyte known as Polydiallyldimethylammonium chloride (PDDA) and an unmodified gold nanoparticle for the detection of malathion.

In another study, aptamers sensor for specific Bisphenol A determination using AC electrokinetics (ACEK) capacitive detection method was proposed by Lin et al. In this method an AC signal is given to an array of microelectrodes fabricated on silicon wafers. This signal causes microflows for binding of the analyte to the aptamers. This binding causes interfacial capacitance change, which is measured. This sensor was able to sense the presence of Bisphenol A within 30 s and had a limit of detection as 1.0 femtomolar [29].

3.1.3 Cells Based Biosensors

Cell-based biosensors have been fabricated to study the level of water pollutants, which are genotoxic, cytotoxic, membrane or protein-damaging or causing oxidative stress. These microorganisms are genetically modified to exhibit measurable signals in the form of charge, light or colour as an indicator of water contaminants. The advantages associated with cell-based toxicity evaluation include low cost, high sensitivity, rapid response. A biosensor was developed for detection of non-ionic surfactant nonylphenolethoxylate with a lower detection limit of 0.25 mg/L. The biosensor was analyzed for its ability to detect many organic compounds, which include surfactants, carbohydrates, polyaromatic compounds etc. *Comamonas testosterone* was the microorganism used for detection [30].

The performance of such biosensors is affected by the parameters such as rate of gene transcription, metabolism, membrane permeability, and protein synthesis. Whole cell based biosensors can be assayed based on increase and decrease of the light intensity emitted due to metabolic changes in the microbes in the presence of specific contaminants. The cells are frequently immobilized on the surface electrode. The immobilization of the cells on the surface of electrodes are governed by conditions as (1) maintenance of the biological activity of the cells (2) the distance between the transducers and the biological detection element (3) the constancy and robustness of the microbial layer (4) the specificity of the detection element (5) possibility of reuse [31]. The most commonly used methods for immobilization include cross-linking, adsorption, covalent binding, self-aggregation and entrapment. The covalent binding involves the binding of the biological element to the transducer with the help of a functional group such as carboxyl, amino, hydroxyl, sulfhydryl, imidazole and indole.

Premkumar et al. developed a whole cell biosensor by immobilization of luminescent *Escherichia coli* strain on aminosylilated glass surface. The immobilization was carried out by aminosylilation of glass surface which was immersed in glutaraldehyde followed by antibody (Rabbit, Anti-*E. coli*) solution. The *E. coli* suspension was then added and washed with LB medium. *E. coli* cells were attached to the optical fibres similarly. A gold-coated glass slide was also prepared with the same method. The recombinant *E. coli* strain was prepared by fusion of the lux genes to a heat shock promoter. The biosensor was analyzed for the detection of pesticides such as malathion, aldicarb and DDT. The presence of pesticide was confirmed with the increase in luminescence by the transducer. The repeatability, reproducibility and stability of the biosensor were studied [32]. A quick and simple method for detection of lead was proposed, which employed a recombinant strain of *E. coli* DH5α containing a regulatory protein and a lead resistance promoter which also controlled the expression of green fluorescence protein (GFP) reporter gene [33]. Different types of microbial cell-based biosensors have been developed, such as optical biosensor having bioluminescence [34], fluorescence [35] or colorimetric [36] detectors.

Yeast biosensors have also been designed for the detection of water pollutants [37]. A luminescence-based biosensor was developed for the detection of EDCs, which employed yeast cells immobilized in calcium alginate or polyvinyl alcohol-based hydrogels. *Saccharomyces cerevisiae* was genetically engineered by incorporating luciferase reporter gene. The expression of this reporter gene was mediated by estrogen receptor alpha. Thus, the detection of estrogen disrupting chemicals such as 17-β-estradiol was possible. The system was stable as the luminescence-based detection was maintained after storage of the biosensor at −80 °C for one month [38].

3.2 Different Types of Transducers

Based on transducers used in the fabrication of biosensors, the biosensors may be classified into the following four categories:

(1) Electrochemical
(2) Thermal
(3) Optical
(4) Piezoelectric.

3.2.1 Electrochemical Biosensor

An electrochemical biosensor typically consists of a transducer, which functions electrochemically. A typical electrochemical measurement incorporates the use of a working electrode and a counter electrode through which a current flows due to the difference in the respective electrode potential. A reference electrode is also included, which is maintained at a stable potential and helps in the transduction of the electrochemical reaction [39, 40]. The electrical circuit of the transducer consists mainly of an analyte medium, present in liquid form, which is a key distinguishing feature as compared to an electrical transducer. The analyte takes part in the electrochemical reaction and works as a detector. Depending upon the response from the analyte, the sensor relays the measurement to an electronic system in terms of voltage, current or impedance.

The electrochemical transducers depending on the type of measurement are discussed below:

Potentiometric type transducer: This type of transducer involves the measurement of the voltage between the electrodes at the indicator and reference or between two reference electrodes parted by a membrane. The measurement of the ion activity or the gas concentration in the logarithmic scale is proportional to the difference of potentials at the indicator and the reference electrode.

Amperometric type transducer: This type of transducer involves the measurement of the resulting current in an electrochemical setup from an electroactive specimen as a result of oxidation or reduction. The measurement is usually carried out by maintaining a constant potential difference at the working electrode with respect to the reference electrode or the auxiliary electrode. The generated current is proportional to the bulk analyte concentration.
Conductometric type transducer: This type of transducer monitors enzyme reactions by utilizing ion conductometric or impedimetric devices. An alternative measurement involving differential measurement is also suggested and performed between the sensor with and without enzyme, respectively.
Ion charge or field effect type transducer: This type of transducer uses the ion-sensitive field-effect transistor for determining the ion concentration.

Various materials have been explored as a candidate for fabrication of electrochemical biosensors. The potentialities of gold nanoparticle-based ensemble electrode as an electrochemical sensor was found useful for simultaneous detection of arsenic, mercury and copper found in wastewater [41]. A hybrid of gold-platinum nanocomposite has been discussed for the detection of mercury. The sensor was evaluated by monitoring samples collected from the river and tap water [42]. Multiwall carbon nanotubes dispersed in Nafion solution in combination with bismuth was used for detection of lead and cadmium by differential pulse anodic stripping voltammetry. Carbon nanoparticles [43] and carbon nanotubes [44] are also an effective sensing material for the detection of heavy metals. Recently, Graphene has been proven a good sensing material for wastewater analysis [45]. In an electrochemical sensor, the size of the working surface area of an electrode is directly related to the efficiency of analytes. Materials at nanoscale effectively utilize the increased surface of electrodes [45–47]. Screen printing fabrication technique at nanoscale promises to employ a maximum of the contact surface area of electrodes leading to higher efficiency in the measurement of analytes in samples [48–50].

3.2.2 Thermal Biosensor

Biosensors are enzyme-driven. A specific enzyme suits the need for a specific substrate. Any biochemical reaction in a biosensor is accompanied by the generation of heat. In totality, there is a change of enthalpy, which is used in principle for the development of thermal biosensors. With proper calibration, a wide range of biomolecules present in wastewater may be detected. The core of the thermal biosensor lies in the development of the sensitive and efficient design of the transducer element [51].

Based on the operating principle, thermal transducers may be classified as thermomechanical, thermosensitive, thermocouple—based, etc. In practice, the transducers commonly used in the fabrication of biosensors are thermistors and thermopiles and are discussed below-

Thermistors These types of transducers detect changes in resistance, which is proportional to a change in ambient temperature. Two types of thermistors exist, one that has a positive temperature coefficient and the other is a negative temperature coefficient. A key element of the thermistor is the enzyme, which serves as a bio-recognition element for the measurement. An important support material on which the enzyme is immobilized is also important for keeping the catalytic nature of the enzyme. Controlled pore glass works as a support material [52].

Thermopile These types of transducers work on the principle of Seebeck effect to detect changes in temperature. As per the Seebeck effect, two dissimilar metals in contact generate a potential difference at the junction. Thermocouples are fabricated based on the principle of the Seebeck effect. When several thermocouples are connected in series, the arrangement is called a thermopile. For example, an array of p-type silicon or aluminum thermocouple connected in series may serve as a thermopile. Thermopile serves as an amplifier of signals generated in a thermal process. The electrochemical activity of the enzyme immobilized on the thermopile results in an induced voltage over the thermopile. The induced voltage depends on the number of thermocouples used as they actively take part in the amplification of the induced voltage [53].

3.2.3 Optical Biosensors

An optical biosensor is a device containing a sensing element, which may be any biological material such as enzymes, antibodies, cells, tissues. The sensing element is conjoined with a transducer used for sensing purposes. A change in mass or concentration of the sensing element is observed when it comes in contact with the analyte. This change is sensed by the transducer unit in the form of change in light intensity. Optical biosensor finds application in the detection of organic materials, heavy metals in water-based solutions and is a good candidate for detecting the water pollutants. The transducer section of the biosensor generally comprise of a surface plasmon resonance based chip, interferometer, resonator, gratings or refractometers [54].

Depending upon the type of transducer element, some of the optical biosensors are discussed below-

Surface plasmon resonance based biosensor: Surface plasmon resonance phenomenon is observed on the surface of any conducting material such as the metal at the interface of two mediums having a difference in their refractive indices. The interface, when illuminated by a polarized light source, emits surface plasmons followed by a change in intensity of the reflected light at a specific angle known as the resonance angle. Interaction of an analyte with the bio-sensing element may then be directly correlated with the change in intensity of reflected light.

Bioluminescence-based biosensor Any biochemical reaction between the analyte and the bio sensing material is followed by the phenomenon of bioluminescence, which is transferred as a signal from the analyte to the optical fiber. The light output is thus helpful in the detection of harmful toxins present in wastewater.
Interferometry based biosensor: In interferometry, the difference between two light beams travelling along similar paths is compared. Planar waveguides are preferred for the development of interferometry-based biosensor. The sensing beam interacts with the bio-sensing element. The refractive index of the element comes into play and induces a change in the speed of sensing beam or a change in its phase. In order to measure this change, an interferogram is created with the help of a reference beam propagated adjacent to the sensing beam. A shift in the interference pattern is observed which is directly related to the chemical or physical changes associated with the sensing beam.
Refractive index based biosensor: In this type of biosensor, the change in refractive index is measured when the analyte comes in contact with the evanescent field emerging out as a result of total internal reflection of light interacting with the sensor surface. The change is refractive index is correlated with the chemical or physical changes associated with the analyte.

Optical biosensors are as a strong contender for bio sensing purposes. Varieties of elements were reported useful for the biosensor fabrication in terms of sensitivity and detection time. Gold nanoparticle-based optical biosensor has been used extensively for detection of lead [55] and mercury [56] in aqueous samples. The detection time averaged from six to ten minutes. A detection time around tens of seconds was reported in an optical biosensor with reduced graphene oxide as the primary sensing element for detecting mercury [57]. Carbon nanotubes were also found successful in detecting the concentration of cadmium in water-based samples with a detection time of 30 min [58]. Graphene also served as a good candidate for detecting *Escherichia coli* K12 bacteria found in water-based samples with a detection time of 30 min [59].

3.2.4 Piezoelectric Biosensors

A piezoelectric biosensor is a composition of materials, which generate a potential difference upon the application of mechanical stress. An analyte bound on the surface of a piezoelectric crystal when excited by an alternating voltage through electrodes attached to the surface, results in the change of oscillating frequency of the crystal. This change in frequency is correlated to the mass of the analyte bound on the surface of the crystal. Piezoelectric effect is found in organic, inorganic and some group of biomolecules as well. Quartz crystal is a commonly found inorganic material with piezoelectric effect. Other inorganic materials include zinc oxide, aluminum nitride, quartz SiO_2 [60]. Organic materials possessing piezoelectric effect include Rochelle salt, polyvinylidene fluoride, and polyamides [61, 62].

Antibodies and antigens are examples of biomolecules possessing piezoelectric effect. The biological sensing element experiences mechanical and electrical forces on application of acoustic wave. These acoustic waves are generated by applying alternating voltage to the electrodes attached to the surface of the piezoelectric substrate. A bio-sensing element interacting with the acoustic wave, results in a change in the viscosity, density, elasticity or the dielectric constant of the sensing element. This modifies the properties of the acoustic wave and results in the change of velocity or frequency of the propagating acoustic wave. Attenuation in the amplitude of the wave may also result. The piezoelectric element is responsible for relaying this change in the form of an electrical signal.

Based on the bio-sensing material, piezoelectric biosensor are further classified into following subtypes as discussed below:

Piezoelectric Immunosensors: The primary bio-sensing elements used in this type of piezoelectric sensor are antibodies. The detection of antibody is label-free, and these type of sensors are reusable. Successful detection of human cells like T-lymphocytes [63], bacteria such as *E.coli* [64] are noteworthy examples of piezoelectric immunosensors.

Piezoelectric DNA Sensors: DNA based piezoelectric sensors provide higher selectivity and reliability. However, the immobilization of DNA is a complex task. The identification of Genetic defects with a TSM biosensor [65] and enzymatic cleavage monitoring of nucleic acids in real time [66] are some examples of Piezoelectric DNA Sensors.

Piezoelectric Enzyme Sensors: The bio-catalytic activity of enzymes specifically in the bio-reactions is very well suited for a broad range of applications. Enzyme based piezoelectric sensor are found useful in detecting bio-catalytic activity. Enzymes are easily immobilized and are abundantly found. Piezoelectric glucose meter [67] is an important example in this category of the biosensor.

Piezoelectric cell-based Sensors. This type of sensor works in conjunction with living cells as the bio-sensing element. Cell-based piezoelectric sensors are useful in revealing functional information, for example, the effect of an analyte on a living cell. Other useful applications of this type of sensors lie in the area of environmental measurements, cell biology and toxicology [68].

4 Nanomaterials Based Biosensors

Different types of nanomaterials such as nanocube, nanoshell and nanorod have been used for analytical purposes [69]. The light scattering properties of various nanomaterials have been employed for the identification of various analytes. The scattering properties of nanomaterials are based on size, composition and shape of the nanoparticle. The efficiency of detection is comparable to the fluorescent label optical probes. The metal nanoparticles with a diameter greater than 30 nm have the strong light-scattering ability in the visible region. However, smaller nanoparticles do not exhibit scattering but can be used for detection of different types of chemical interactions such as avidin-biotin, antigen-antibody electrostatic attraction and DNA hybridization. These small size nanoparticles can assist in detection when they aggregate due to these interactions.

An application of nano-biosensors for identification of wastewater pollutants is urea detection. Nanosized porous alumina was used which was fabricated by the use of electrical anodization in acidic solution. Nano-alumina porous matrix was used as an immobilization system for bio-colloidal systems. The use of nanosized materials increases the surface area, which leads to enhanced sensitivity. Other workers have fabricated urea biosensor using lipid bilayer membranes [70], hydrogel membranes [71] and other inorganic matrices such as laponite and clays [69]. The interaction between the nanomaterials and proteins with opposite charges causes enhancement of light scattering signals. Thus the electrostatic attraction between the protein and metallic or non-metallic nanomaterials can increase the sensitivity to nanograms. Researchers have suggested the use of gold nanoparticles for the detection of heavy metals. The colorimetric based detection depends on the light scattering property of gold nanoparticles. Priyadarshini et al. have studied the effect of gold nanoparticles in metal ions detector. This strategy is applicable for the identification of heavy metals such as arsenic, mercury, chromium, copper, cadmium, lead, alkaline earth metals and rare elements [72].

Cadmium contamination is found in wastewater, which poses health risks. Some researchers have co-functionalised the gold nanoparticles with L-Cysteine and 6-mercaptonicotinic acid to develop a biosensor with high sensitivity for cadmium detection [73]. Another colorimetric detection method of heavy metals using peptide-modified gold nanoparticles was developed. The functional peptide ligand was used for the sensitive detection of three heavy metals such as nickel, cadmium and cobalt. This biosensor had the provision of simultaneous detection of the three metals existing together in the sample. The detection of cadmium was carried out by the use of EDTA and imidazole for masking of cobalt and nickel. For nickel detection, EDTA and glutathione were applied to mask cobalt and cadmium whereas imidazole and glutathione were used for masking the effect of nickel and cadmium. Thus, water quality can be assessed with the help of this strategy without complex preparation [74].

5 Application of Biosensors in the Detection of Water Pollutants

The constituents of wastewater pollutants can be broadly classified into three types (i) inorganic chemicals (ii) organic chemicals and (iii) microorganisms. Due to the advantages associated with biosensors, they have been employed in the detection of wastewater contaminants. The detection of pollutants is important for the design and scale of the treatment process. Thus, biosensors provide a robust alternative for identification and measurement of the pollutants with the least requirement of sample pre-treatment and frequent data sampling [75].

5.1 Biosensors for Organic Contaminants

Water pollution mainly caused by water release from domestic, industrial, and agricultural activities. Water pollution leads to the degradation of aquatic habitat and decline in the aquatic population [76]. Among all major water pollutant like organic materials, inorganic material and microbial contaminants, microbial contaminants majorly affect water quality and lead to many dreadful waterborne diseases [77, 78].

A wide range of organic contaminants are found in the wastewater are aromatic hydrocarbons, food and households related compound, organic solvents, herbicides, pesticides, fertilizers, preservatives, washing and cleaning agents. The information regarding the composition of wastewater is essential for designing of the wastewater treatment system. The variation in the presence of pollutants in different areas leads to the discovery of new technologies for the treatment of wastewater [79].

Many techniques are used to measure physical, chemical and biological characteristics of wastewater but the problem associated with these techniques is that they are costly and time-consuming [80, 81]. Due to these problems, researchers are focussing for developing new technologies that are more efficient in determining and treatment of different kinds of pollutants present in wastewater [82, 83].

Among these new technologies biosensors have given a great success in determining very less amount of contaminants present in wastewater in any forms like organic pollutants, inorganic pollutants, microbial pollutants and heavy metals, electrochemical, optical and piezoelectric and thermal biosensors are used for these purposes [84]. The application of biosensors is increasing due to several advantages associated with it like low cost, small size, quick and easy use, as well as a sensitivity and selectivity greater than the current instruments.

Domestic wastewater discharge, hospitals and clinics effluent discharge, agriculture effluents discharge industrial wastewater discharge are the major sources of organic pollutants in wastewater. These organic contaminants present in wastewater have a very harmful effect on humans and the environment.

Domestic discharge water and industrial effluents contain organic contaminants in the form of surfactants and their by-products include (e.g. alkylphenol polyethoxylates, and linear alkylbenzene sulfonates, hydrocarbons, aromatic substances and chlorine compounds. Among these organic contaminants polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and polychlorinated biphenyls (PCBs) are mainly present in industrial waste effluents [85].

Various organic herbicides and pesticides are used to control the growth of insects and weeds which are harmful plant growth are the main organic contaminants of agriculture wastewater. [86]. The production and use of new and old medicines and Pharmaceuticals drugs and personal care products including fragrances and antimicrobial agents such as triclosan has been enhanced so it increases the organic concentration in wastewater [87].

These industrial, domestic, agricultural activities increase the organic contamination of water bodies like oceans, seas, river, lakes, and groundwater. These are the causes of severe threatening of environment and its degradation. Detecting the concentration and chemical analysis of these organic contaminants present in wastewater is an essential step in controlling water pollution and ensuring clean water supplies. The detection procedure and chemical analysis of these organic pollutants present in wastewater is a costly process. In this context development of biosensor makes the detection of organics present in wastewater an easy and efficient process [88]. Kiran et al. found that gas chromatography-mass spectrometry (GC-MS) and Fourier Transform Infra Red spectroscopy (FTIR) techniques are useful in detecting the presence of organic compound such as alcohol, aromatic hydrocarbons such as phenols and amines [89].

Biological oxygen demand BOD and Chemical Oxygen demand COD and Total organic carbon TOC are important parameters of determining organic contents of wastewater. BOD is the amount of oxygen required by aerobic microorganisms to degrade organic matter present in wastewater, expressed in mg/l. BOD method requires incubation of sample for 5-days at 20 °C. The COD is a measurement of the oxygen required to oxidize all the organic matter present in a sample [90]. The measurement of TOC is an alternative method compared to BOD and COD. TOC is a quick online method and is most preferred then BOD and COD which oxidizes the entire organic content of the sample. These procedures are time consuming and difficult and required skill and expertise in handling these samples. Solutions of these difficulties are achieved by using BOD biosensors, which are fast and produces significant results [91].

Karube et al. discussed a microbial biosensors using immobilization of *Trichosporon cutaneum* on the oxygen electrode for BOD determination. These microbial film immobilize between cellulosic membranes and oxidizes organic contaminants present in wastewater [92].

Several other microorganisms like *Bacillus subtilis*, *Serratia marcescens* and yeast were used in microbial biosensor for detection of BOD [93–95].

Immobilization of single microorganism has certain limitations as it oxidizes limited range of organic pollutant present in wastewater so exact determination of BOD cannot be possible. In order to overcome this limitation an idea of mixed culture immobilization of *Bacillus subtilis* and *Trichosporon cutaneum* were introduced by Jia et al. in 2003 [96]. Immobilized *Bacillus licheniformis*on clark oxygen electrode based biosensor is capable of detecting even low concentration BOD in seawater. This biosensor is very much efficient in measuring BOD in high salinity condition with fast response [97, 98].

Another major organic contaminants of wastewater are pesticides. Nowicka et al. discussed in his paper that electrochemical DNA biosensors was developed for the detection of atrazine, 2,4-D, glufosinate ammonium, paraoxon-ethyl, carbofuran and difluorobenzuron pesticides. In DNA biosensors immobilized single stranded DNA on the surface binds with its complementary DNA. An example of such severe DNA damaging pesticide is atrazine [99].

Various amperometric microbial biosensors were developed for detection of organophosphate pesticides such as paraoxon methyl parathion, parathion, fenitrothion and ethyl pnitrophenol thiobenzenephosphonate (EPN) [100]. Su et al. and Lagarde et al. reported that some optical microbial biosensors are helpful in detection of pollutants such as phenols and heavy metals present in wastewater. Kumar et al. reported that for detection of parathion pesticide, colorimetric microbial biosensors are used. [101–103].

5.2 *Biosensors for Microbial Contaminants*

Microbial populations present in wastewater like bacteria, protozoa, viruses are the major contributor of water pollution. These microbial contaminants affects water quality and make water unfit for drinking as well as affect the quality of seafood. Presence of these pathogenic microorganisms in wastewater is the major causes of serious life threatening diseases. Presence of pathogenic and non-pathogenic microorganism in wastewater depends upon the type of effluents from different sources [104].

Some non-pathogenic microorganisms fecal bacteria (like *E. coli,* total coliforms, and RNA bacteriophagesare also present in wastewater but they are not harmful as other pathogenic microorganisms. Due to these harmful effects it becomes necessary to develop methods to treat microbial contaminated water before discharge. Conventional methods which are used for microbial detection have several disadvantages associated like low detection, less sensitivity towards detection, required more time in detection. In order to overcome above discussed disadvantages at present biosensors becomes an attractive approach for detection of microorganism present in wastewater [105–107]. Biosensors for microbe detection generally contain biological component like nucleic acid, antibodies, enzymes connected with transducer.

He et al. reported that poiezoelectric biosensors are very efficient, simple and cost effective in bacterial detection. Use of PZ biosensors in detection of wide spectrum microorganisms was reported by Plomer et al. and Le et al. . *Vibrio cholera* was detected by using PZ immunosensor [108–111].

Bao et al. reported the detection *Staphylococcus epidermidis* using quartz crystal microbalance (QCM) sensor. Quartz crystal microbalance is also used in detection of *Escherichia coli* [109] and *Salmonella* [112, 113]. Abbaspour et al. reported an electrochemical aptasensor used in *Staphylococcus aureus* detection in wastewater [114].

5.3 Biosensors for Inorganic Contaminants

Besides these organic and microbial contaminants present in wastewater, inorganic contaminants like heavy metals contributing major role in water pollution. Iron and steel and industries, metal industries, mining, are the sources of various heavy metals like chromium, nickel, zinc, cadmium, iron. Similarly other industries like aircraft plating and finishing industries releases harmful heavy metals like lead and mercury which are very harmful constituents of wastewater. Excessive accumulation of these heavy metals has very harmful and toxic effect on plant and animals [115, 116].

Ensafi et al. reported membrane-based 4-hydroxy salophen on tri-acetyl cellulose membrane optical sensor detect Cd (II) heavy metal present in wastewater. Limitations associated with this biosensor are that it has low time response and cannot detect Cd (II) if its concentration is less than 5 μg/L [117]. Pourbasheer et al. reported a optical biosensor using 6-Bromo-3-(2-methyl-2,3-dihydrobenzo[d] thiazol-2-yl)-2H-chromen-2 immobilized on triacetyl cellulose membrane used for detection of Cu (II) in wastewater [118]. Saber and Piskin reported metallothionein linked quartz crystal, a type of piezoelectric biosensor used in the detection of Zn (II) and Cd(II) [119]. Detection of Hg(II) using quartz crystal microbalance biosensor was reported by Chen et al. [120].

6 Conclusion

This chapter summarizes materials used in different types of biosensors for wastewater detection. Constant efforts have been done in the improvement of performance of biosensor by incorporating materials with better detection and signal conversion property. Nanotechnology application in the design of transducers and the biological detection element has catered the improved sensing mechanism. Material like nano sized graphene has also exhibited enhanced sensitivity and specificity. This 2D nanomaterial exists in a thermodynamically stable form and provides superior electronics property due to its unique electronic band structure [121]. The different types of biosensors based on the biological detection elements and transducers used for detection of pollutants present in water have been detailed. Also the applications of these biosensors in the detection of inorganic, organic and microbial contaminants have been discussed. Some of the major challenges involved in the development of biosensors are difficulty in real time monitoring and cost of equipment. The development of biosensors involves researchers from multi-disciplinary background such as biology, electronics and chemistry. Other problems faced during the development of biosensors are difficulty in immobilization of biological detection elements such as aptamers and antibodies and their regeneration ability. Thus, all these aspects pose the scope of future development of biosensors for detection of wastewater pollutants with high sensitivity and reduced minimum detection limit.

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Computational Design of Nucleic Acid-Based Bioreceptor for Contaminants of Emerging Concern

Patrizio Arrigo and Debora Baroni

Abstract Human activities have increased the variety chemical pollutants spread in air, water and soil. Every day new compounds potentially harmful or dangerous could contribute to increase the level of environmental pollution. These substances are known as Contaminant of Emerging Concern (CEC) because they have not previously detected or their toxicity is not yet clearly established. The capability to screen, almost prioritized CEC, requires new sensitive and rapid techniques capable to create an efficient monitoring network. In addition to traditional analytical a new class of monitoring systems is emerged: the biosensors. Their foremost characteristics is the use of a biological or biologically inspired receptor element, the bioreceptor, combined to a system capable to generate a physico-chemical signal. The sensor element, e.g. tissue, microorganisms, cell receptor, enzymes antibodies and nucleic acids, is biologically derived or inspire material. The detector transducer is the module which capture and transform the biological signal in a chemical-physics way: optical, piezoelectric, electro-chemical, electro-chemiluminescence etc., which can be easily measured and quantified. Nucleic acid-based technologies have been recently emerged as alternative to protein for bio-receptor design. The aim of this chapter is to offer, from a computational perspective, a framework of tools and challenge related to the selection of the most suitable bio-receptors to screen particular CEC chemicals: the pharmaceutical and personal care products (PCPPs).

Keywords Biosensors · PCPPs · Environmental monitoring · Nucleic acids · Bionanotechnology · Computational biology

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1 Introduction

The combination of climate changes and human activities is very dangerous both for natural biodiversity conservation and human health. There are two main types of pollutants: contaminants originated from natural sources and from anthropic activities. Nevertheless the natural contribution cannot be ignored the human is more prominent [1] since technological advancement originates every day new chemical which are dispersed in environment. The exposure to pollutants impacts the survival of the different animal species and ecological biodiversity. Human health is under an increasing environmental stress due to a multiple sources of contaminants derived from working activities, life style and socio-economical living context, acting during all the lifespan of human being [2]. Multidisciplinary approaches are in development in order to enhance the capability to monitor and analyze the impact of pollution in the short term (acute exposure) and, most importantly, on long time scale (chronic exposure). The development of environmental screening methods requires a multiplicity of expertise chemistry, engineering geology and biology.

The improvement in instrument miniaturization (lab-on-chip) [3], remote sensing and ICT support (Wireless communication, Machine Learning, IoT) offer the possibility not only to provide an efficient effort to develop new monitoring systems, but also to implement a large network to track the time course of pollution in different sites [4]. Unfortunately the list of toxic compounds could be, in principle, limitless and without information about toxicity. The heterogeneous group of contaminants belonging to the Contaminants of Emerging Concerns (CEC) [5] has attracted the interest or researchers and regulatory agencies. The prediction of CEC risk assessment their monitoring, remediation and damage mitigation are actively studied. The detection of low concentration of specific CEC can be efficiently supported by a new generation of biosensors represented by nucleic acid-based biosensors.

The aim of this chapter is to offer an outline about the use of nucleic acids to design and implement a bio-receptor module to sense, in the environment, a specific class of CEC: the pharmaceutical and personal care product (PCPPs). This chapter is organized into different sections: (1) a brief survey about CEC; (2) a short outline about basic characteristics of biosensors; (3) a description of nucleic acid characteristics, functional elements and their role in nanotechnologies; (4) an overview about different type of software than can be utilized to design a nucleic-acid bioreceptor; (5) a survey about the environmental application of nucleic acid-based biosensors

1.1 Contaminants of Emerging Concern

The definition of “Contaminant of emerging concern” (CEC) considers three types of CEC [6]: (1) totally new chemical or material that have not been previously screened in the environment; (2) existing substance whose information about environmental impact and toxicity is lacking; (3) substances, with known environmental impact and toxicity, but with previously unidentified adverse effects. The CEC, as the other pollutants, can be analysed taking into account the exposure route, the fate of pollutant and the bio-monitoring capability. A recent survey (EUROSTAT) has highlighted that almost the half of chemical production is constituted by CEC, including different products ranging from pesticides to nanoparticles from pharmaceuticals to micro-plastics. They can originated by all human activities: industrial production, agriculture, health and life-styles. It is important to underline that CEC could be derived from transformation and degradation of other chemicals not only toxic. The capability to efficiently screening and remove CEC released in water, is important to guarantee a good quality of water for all human need [7]. Availability of drinking water is becoming a global concern both for quantity and quality. It is particularly sensitive to CEC and micro-contaminants. The adverse impact is not only on human health however also on the whole ecosystem. There are five basic qualitative characteristics that one have to consider; (1) persistence; (2) mobility; (3) bioavailability; (4) bioaccumulation; (5) bio-amplification. The monitoring and risk assessment for these compounds is complex because it is necessary to take into account different features such as chemical-physics properties of the compound and the geo-climatological characteristics of the environmental compartment in which the pollutant is release. The resistance (persistence) to degrading agents, abiotic or biotic, is a pivotal feature to consider; another characteristics is the capability of a pollutant to be vehiculate, far from its origin, with a low level of compound absorbed by solid particles. The monitoring of CEC in the water follow standard sampling protocols for the different water resources or for bottled beverages. The sludge, produced by wastewater treatment plants, could contain high levels of more persistent pollutants including CEC. The employ of these sludge, as fertilizer, in agriculture can have an impact also on soil quality altering, for instance, the microbial and fungal communities or increase the bioaccumulation of toxicants in vegetables. The personal care and pharmaceutical products (PCPPs) and pesticide are very particular CEC contaminants because they are designed to have a biological activity. The exposure to PCPPs is generally consists of low doses of pollutant, for this reason large fraction of them is lacking of sufficient toxicological data to formulate an appropriate regulation. PCPPs are characterised by wide heterogeneity of structures, chemical-physics and biological activities. Furthermore not only the original compound can exert a toxic effect but also its metabolite. Some studies carried out on ibuprofen [8] have underlined that abiotic and biotic degradation of ibuprofen originate a toxic metabolite (4-chlorphenol). The PCPPs seem to rather persistent in water and soil and their impact on ecosystems is not yet clearly established. These compounds have been identified in regions far from the highly populate regions such as Arctic regions [9]. These finding underlines once more that PPCPs are a real global concern.

Prioritization of PCPPs pollutants and development of specific water monitoring systems is mandatory to control the PCPP level in order to determine their effects due to long term exposure.

2 3-0 Biosensors: A Brief Outline

A detailed description of biosensor architecture can be easily found in literature [10]. It is important to recall some element of these analytical system in order to better understand the role of nucleic-acids. A biosensor is defined as an analytical system combining a biological or bio-inspired component and a physico-chemical detector. The standard architecture of a biosensor includes several specialized modules: (a) a bio-receptor element; (b) a transducer system (c) an electronic module to amplify, process and visualize the acquired signal. Two are the compulsory features of a biosensor: the recognition element must have a biological origin or must be biologically inspired and the transducer material which transform the signal coming from the sensing element into another on (optical, piezoelectric, electro-chemical, electro-chemiluminescence etc.). The bio-receptor is the responsible of analyte sensing by molecular recognition. Molecular recognition identifies the elementary processes that lead the specific binding that occur between two or more molecules by non-covalent bonds such in the case of protein-protein interaction or enzyme substrate binding [11].

The signal, resulting in the interaction between the analyte and the probe, is transformed into a standard signal that can be captured by standard analytical methods. A bio-receptor has to be linked to a transducer surface. The simple way is to immobilize the probe on a surface or particle. Immobilization can be achieve by different methods; (i) adsorption; (ii) covalent bonds, (iii) crosslinking; (iv) entrapment. The signal, coming from the receptor-ligand interaction, can be measured in a direct or indirect manner; the first method records data during the time course of binding kinetic, the latter record only the variations that occur at the end of the process. Bio-recognition elements are roughly grouped into three different set: natural, semi-synthetic and synthetic. Proteins, as well enzymes as antibodies, are the widely used as *natural* elements in biosensor development; they s how a very high steric selectivity and the binding can be determined using different type of transducers. The *semi-synthetic* receptors require a partial laboratory synthesis to obtain the optimal specificity for a particular ligand. Nucleic Acids are included in this group. Totally *synthetic bio-receptors* are usually produced using or not a biological template. Molecularly imprinted polymers (MIPs) belong to this class of synthetic receptors. The template of a MIP can be a biological macromolecule or other organic compounds. At the end of polymerization process the template is removed and the resulting polymeric structure is able to recognize specific ligands.

The main advantage of this methodology is the possibility to develop biosensor array capable to perform a multiple screening [12]. In this group could be also include the xeno nucleic acids (XNA). There are several limitations in development of biosensors which basically depend on the intrinsic characteristics of a biological element, the production cost, robustness and reusability. The great challenge in biosensor production is to obtain a system having the maximal sensitivity for a specific ligand. It is also mandatory to underline the need to optimize the combination between bioreceptor and the material of transducing system.

Biomedicine is one of the fields in which biosensors are widely applied either for diagnostic and therapy [13]. Defence (bioterrorism) and food security [14] are other important operational fields of these systems. The use of biosensors in environmental monitoring has been stimulated by the need to design and implement instrumentation having high efficiency, portability and a rapid response over the time. The advancement of analytical integrated instrumentation offer the possibility to develop high-throughput monitoring using platforms with interchangeable bio-recognition elements robust, easy to use and relatively cheap.

2.1 Overview of Nucleic Acid Characteristics

Previous paragraph has briefly outlined some fundamental elements of biosensor architecture: this section ids focused on the characteristics of nucleic acids valuable for a bio-receptor design. A simple survey on Pubmed has found, at the date of this chapter, 9931 papers. A similar search however using the query "*RNA and Biosensors*" has found 2231 papers. A similar survey, adding the term "*pollutant (s)*" has identified only 33 papers for RNA and 254 for DNA. In order to offer a parameter for comparison the query "*enzyme and biosensors*" has found 19,090 entry and the query with the ad joint of the term *pollutant(s)* has retrieved 482 entries. This rough empirical survey underlines how the use of nucleic acids for biosensors, if compared with protein based biosensors, looks to be in the initial phase. It is necessary to distinguish DNA-, RNA- and XNA-based bio-receptor because each class of nucleic acid has different biophysical properties that have to be considered in the biosensor element design. XNAs are completely synthetic nucleic acids initially developed for xenobiology [15] researches. These macromolecules can be formed by unnatural nucleobases and sugar backbone. The chemical modifications are designed to increase the stability and their scaffolding characteristics [16]. The thermodynamical difference, between DNA and RNA, is the first information to take into account in a bioreceptor design phase. For long time DNA has been considered more stable than RNA, however several studies [17] have demonstrated a comparable stability between the two types of nucleic acids. A drawback that must be considered in the design of RNA biosensors is its higher sensitivity to enzymatic degradation by RNAses.

Contrarily to DNA, which is less affected by the ionic environment, the RNA conformation is strongly dependent on the type and distribution of counter-ions surrounding the molecule. Any variation in the ionic context could have a strong effect on RNA stability and consequently on its biological functionality. Differently from DNA, RNA molecules can have a natural catalytic activity, a valuable feature in the perspective to design a nucleic acid bioreceptor.

Another relevant characteristics of RNAs that should be considered is their higher sensitivity to chemical changes than DNA, actually hundred different RNA modifications are known [18]. This large number of variations gives strong indication that RNAs are highly configurable molecule. The design of biosensors based on functionalized nucleic acids have to take some key points into account.: (1) sequence heterogeneity; (2) hierarchical conformational organization; (3) component modularity; (4) selectivity stereochemical interactions; (5) cooperative effects (long range interactions) derived from folding [19]. The design of a RNA probe, taking its flexibility into account, have to minimize the number of metastable folded structures. The development of nucleic-acid based biosensor has been initially focused on the use of DNA. DNA can take different duplex conformations: A-DNA, B-DNA and Z-DNA; these conformation can be converted from one to by the effect of external factors [20, 21]. The identification of local structural elements is one of the reason for biosensor and nanotechnological application of Nucleic acids [22, 23]. Nucleic acids are, from a chemical-physics perspective, a class of natural foldamers. A foldamer is, from the chemical-physics point of view, a natural or synthetic polymer capable to originate, in solution, an ordered 3D structure [24] having well defined self-assembly, recognition and catalytic properties.

Among the different possible folding conformation originated by a nucleic acids [25] some of them have a relevance for biosensors applications: 3-way (3WJ) and 4-way (4WJ) junctions, G-quadruplex, hairpin, stem-loop, pseudoknot and triple helix (TFO). The junctions requires three o more DNA or RNA helices originating a branched conformations. The 3WJ requires three helices, linked together by a connection element, with one high flexibility helix. The 4-way junction (4WJ) (Hollyday-junction) is formed by four dsDNA joined together; these conformation are transient high order branched structure occurring during specific cellular processes. 3WJ and 4WJ structure have been also identified in RNAs [25] (Fig. 1).

Another important structural motif is the G-quadruplex, related with the presence of G-rich domains (Fig. 2) The G-quadruplex is the results of interaction between coplanar arrays of guanine called G-tetrads; they can occur on a single strand (intramolecular) or between two strands (intermolecular) DNA and RNA G-quadruplexes are capable to form, by charge transfer between donor and acceptor, an internal space [26, 27] in which ionic displacement depend on the specific ion affinity for the nucleic acid. The biological function of DNA and RNA G-quadruplexes is different; the DNA G-quadruplexes seem to be involved in maintenance of genomic integrity and transcriptional processes. RNA G-quadruplexes seem to be implied in several different biological activities. such as transcription termination, pre-mrna splicing and mRNA targeting [28] (Fig. 2).

High target specificity is the foremost feature of a nucleic acid-based biosensor; it is strongly correlate with the structure of sensing element that have to recognize the analyte.

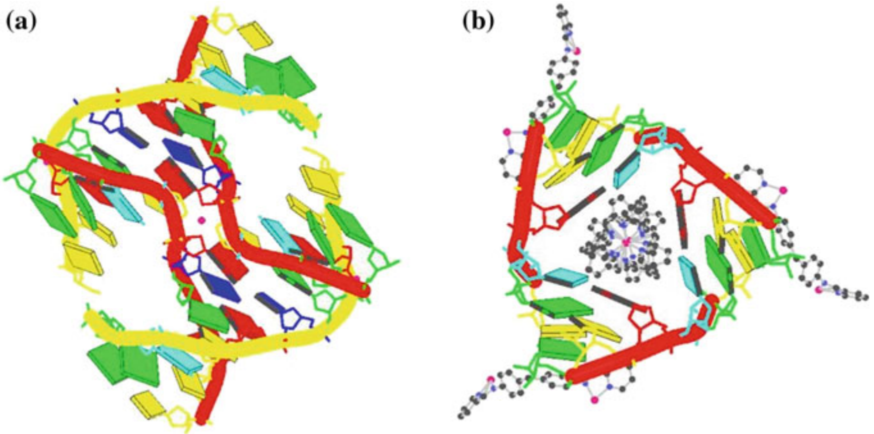

Fig. 1 **a** DNA 4WJ (Hollyday Junction **PDB 1P54)**; **b** RNA 3WJ (PDB 4JIY). The two images has been obtained using PDB structural visualization tools. The figure shows the biological assembly of two structure. This presentation gives a more intuitive view of the 3D structure

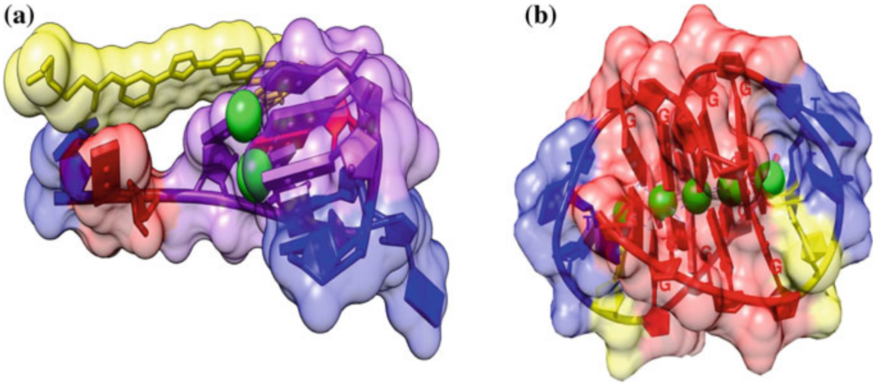

Fig. 2 Examples of G-quadruplex: **a** DNA G-quadruplex (**PDB code 6GE1**) The yellow residues are modified nucleobase and the green ball are potassium ions; **b** RNA telomeric G-quadruplex (**PBD code 3MIJ**) The yellow molecule is the ligand and the green ball mark the potassium ions The images have been obtained by UCSF CHIMERA visualization tool (https://www.cgl.ucsf.edu/chimera/)

The more common structures used for biosensors: (1) Aptamers; (2) DNAzyme; (3) Riboswitch and Ribozymes; (4) XNA-based biosensors. **Aptamers** are single strand oligomers, both DNA and RNA that can maintain the natural conformation such as G-quadruplex or hairpin and stem-loop. The aptamer selection and production requires the application of the well established combinatorial SELEX procedure [29] to obtain nucleic acid probe for a specific ligand.

DNAzymes (Deoxyribonucleotide enzymes) are catalytic DNAs with activity comparable to Ribozyme [30]. The break of dsDNA generates ssDNA capable to fold itself in different conformations that can have catalytic activity. DNAzyme have been considered for biosensor development but they are not yet well characterized. **Ribozyme**s are natural catalytic RNAs, known also as metalloenzymes [31]. RNAs are capable to catalyze different complex chemical reactions such as esterification, isomerization, etc. Ribozymes are roughly classified on the basis of their length. The short and medium length ribozymes, including hairpin, hammerhead and pistol, have been employed for bioreceptor development. The knowledge of natural ribozyme is an advantage for the design of artificial ribozymes sensing particular analytes. A ribozyme can be embedded in supramolecular structure; the aptazyme.

An aptazyme has different functional modules: (a) a sensing element committed to recognize the ligand; (b) an effector element, the true ribozyme, that perform the catalysis; (c) a connector element that bridge together sensor and effector. **Riboswitches** are natural regulatory elements, mostly recognized in bacteria, that control the gene expression sensing specific small molecules or ions. They are generally located in the 5′ region of a bacterial mRNA and can activate or deactivate the gene expression. A riboswitch is a complex structure formed by an aptamer to sense the ligand and an expression platform in which there is the gene to be regulated. An example of riboswitch and ribozyme is shown in Fig. 3. These regulatory structures can be considered ‘natural’ biosensors. The nucleotide motif, committed to sense a specific metabolite, is rather evolutively conserved. This point is rather important to modify the nucleic acid to recognize a different substance or to enhance its affinity for its specific analyte. The design of an artificial riboswitch is a not easy task because it is rather hard to couple a modified aptamer with the expression platform order to originate a fluorescence signal.

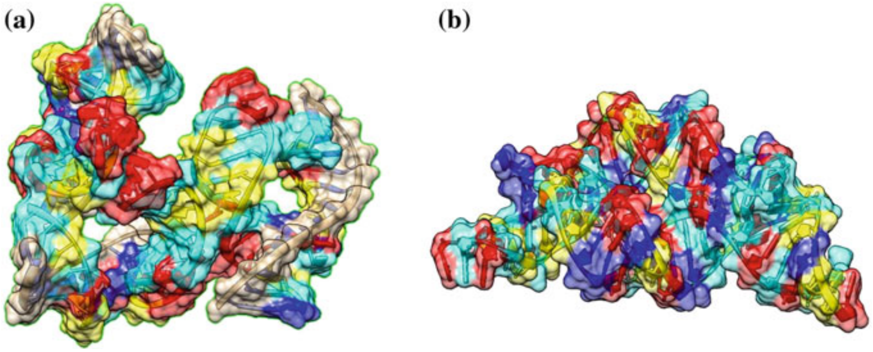

Fig. 3 Ribozyme and riboswitch: **a** Hammerhead Ribozyme (PDB 1HMH); **b** THF Riboswitch (PDB 4VLL). The different colour label the nucleotides. The images have been obtained using UCSF CHIMERA visualization tool

The RNAs, unlike DNA, can be employed to model a scaffold. A scaffold is natural or synthetic functional RNA structure able to optimize a reaction, recognize a molecule or intervent in molecular interactions [32]. The RNA scaffolds are designed using different computational methods and, for instance, applied for CRISP-Cas9 transcriptional control [33]. The RNA scaffolds could be included among nucleic acids nanostructures. Today there is the knowledge and technology to engineer complex nucleic acids nanoparticles. They can be utilized to control cellular processes, as carrier for drug delivery and to screen specific substances. Even if the majority of applications are biomedical it is reasonable to apply DNA and RNA biosensors in different sectors such as for instance, environmental monitoring. The design of DNA based nanostructure could be carried out using different approaches: (1) tile self-assembly [34] utilizes basic structural elements to originate an intermediate structure (the tile) capable to be arranged in a more complex architecture; (2) Folding method is founded on the capability of a large DNA to fold itself (DNA origami); (3) Kinetic based method requires the direct control of dynamic parameters governing the self-assembly process. The folding method, often indicated as DNA origami, seems to be the widely used; it is necessary to underline that the selection can be made taking the application into account. The term “DNA origami” defines the operational protocol to generate a complete DNA nanostructure starting from a ssDNA [35] or dsDNA and short oligonucleotides utilized as connecting elements; Fig. 4 displays the 3D structure solve with Cryo-EM of a DNA origami object and an xeno nucleic acids (XNA).

The initial choice of DNA relies on the technological limit to pick up enough good quality RNA. The advance of molecular techniques (SELEX) have consented to bypass this constrain. RNA has focused the interest of its possibility to be employed in nanotechnological applications.

In order to design an efficient bio-receptor, it is essential to investigate RNA surrounding ionic environment [36]. It is a well established knowledge that some

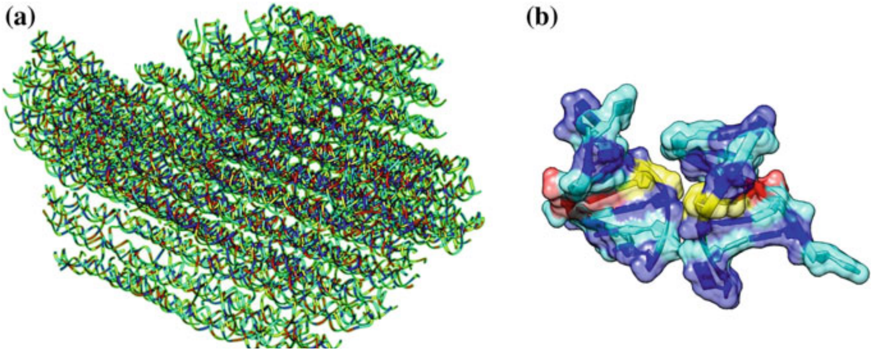

Fig. 4 Example of nucleic acids nanostructures: **a** cryo_EM image of a DNA origami supramolecular structure. **b** Example of xeno nucleic acids. The images have been obtained using USF CHIMERA visualization tool

cations such Mg^{2+} are crucial for RNA conformational stability and functionality [37].

Except the well known compositional and structural differences, RNA is also capable, conversely to DNA, to have long range interaction such as the kissing-loop. The knowledge of these biophysical properties have to be considered in the of RNA origami technique.

The term "RNA tectonics" [38] indicates the modularity of RNA structure that can disassembled and then reorganized into new units called "tecto RNA". These new module are capable to assembly themselves into more complex nanoparticles. The shape and dimension of new RNA objects can be designed in advance. The tecto RNA is often the result of computational simulations. This procedure consent to allocate in precise way the fragments, estimate and correct the distances among the elements. It is possible to control the supramolecular assembly of tecto RNAs in order to minimize the set of alternatively folded structures. The nucleic acid based nanotechnology is a fast evolving research area, triggered by the synthetic biology requirements [39], now utilized in several different advanced applicative sectors.

2.2 A Survey of Computational Tools for Nucleic Acid Based Biosensor Development

The design of bio-receptor and its interaction with the transducer material is an ICT complex task because it need the employ of bioinformatics, chemo-informatics and nanoinformatics tools into a automated and reusable computational pipeline: the workflow. Workflow management systems, initially developed for different industrial applications, has been recently also applied to nanotechnology [40]. Good workflows have to include advance Machine Learning tools to optimize the quality of the biosensing module (bioreceptor and transducer system). Three workflow management systems that could be considered for the design biosensing module: (1) **KEPLER** that can work on biophysical and genomic data [41]; (2) **GALAXY** that can operate on molecular biology, image and nanostructures [42]; (3) **KNIME** that is a more flexible and general purpose system [43]. The design of a biosensor, for environmental monitoring, can starts from the available information about a specific chemical Specific data mining can also to be used to obtain the maximal amount of chemical, biological and toxicological. Conformational characteristics are the core theme for each possible application of nucleic acid-based biosensors. There are different tools to design simple nucleic acid structure or supramolecular complexes. The repository more helpful to design a bio-receptor are: (1) the **Nucleic Acid database** (NDB) containing nucleic acid experimentally solved structures [44, 45] and the collection of 3D structural motifs of RNA; (2) **G4RNA** that contain information about these structural motifs in RNA [46]; (3) **G4IPDB** a more general repository encompassing the solved structure of G-quadruplex [47]; (4) **MODOMICS** database includes information about modified ribonucleosides and their biosynthetic pathways [48]. When possible and available, it is essential, for the design of a good bio-receptor, to acquire information about ligands to estimate both the sensitivity of the probe and the effects on receptor stability. The potential target can be easily extracted from chemical or toxicological databases.

There are other repositories, highly valuable for bioreceptor design, containing specific information about ligands (inorganic or organic) interacting with nucleic acids. Information can be also stored in generalist databases and even in small database such as the following: (1) **MINAS** that contains experimental data about metal ions interacting with nucleic acids [49]; (2) **NPIDB** that store data about protein-nucleic acid interactions [50]; (3) **BioMe** is repository of data about ionic binding site in protein and nucleic acids [51]; (4) **SMMRNA** consists of data concerning the small molecules modulating RNAs [52]. The selection and design of a biosensor depend on the ligand to be detected; it is different, for instance, to design a structure for molecular beacons [53] or for immobilization of the sensing element on a transducing surface or for a nanoparticle design. An initial 'in silico' structural analysis could consent to select the type of nucleic acid that better fit to sense a specific organic small molecule. The conformational characterization of a candidate probe can be performed using different bioinformatic tools. There is a large variety of available software to face the nucleic acid conformation. An outlook of the softwares used to predict 2D and 3D structures of nucleic acids is summarized in Table 1.

The quality control is committed to specific programs, as **Molprobity** [61], that one should apply before to proceed. The second phase of the 'in silico' design of a sensing element is focused on the simulation of the interactions between ligand and the nucleic acid model. Molecular mechanics (MM) or Quantum Mechanic (QM) can be used for any type of ligand (ionic, organic etc.), while docking methods are generally used for small organic ligands. MM/QM methods can work on different biomacromolecules (DNA, RNA, proteins. There are many different MM/QM programs, such as **AMBER** [62] **GROMACS** [63], that can efficiently applied to study the interaction between analyte and probe; particularly interesting, for the design **NAMD** [64] and **DELPHI** [65]. Molecular docking constitutes fast and less computationally heavy alternative to MM/QM. It is employed for different cheminformatic applications such as drug design. Not all available docking

Table 1 Bioinformatic software for nucleic acid folding prediction

Software name	DNA	RNA	Input	Type prediction	References
3DNA	Yes	No	Structure	3D	[54]
SimRNA	No	Yes	Structure	3D	[55]
NUPACK	Yes	Yes	Sequence	2D	[56]
MFOLD	Yes	Yes	Sequence	2D	[57]
Assemble2	No	Yes	Sequence	3D	[58]
Vienna package	No	Yes	Sequence	2D	[59]
COMPOSER	No	Yes	Sequence	3D	[60]

Table 2 Software for nanomaterial design that could be used for nucleic acids

Name of software	Availability	Capability be applied to nucleic acids	References
LAMMP	Yes	Yes	[70]
MBN explorer	No	Yes	[71]
CaDNAno	Yes	DNA origami	[72]
CanDO	Yes	DNA origami	[73]
NanoTiler	Yes	RNA	[74]
MANIP	No	RNA	[75]

programs are capable to process nucleic acid: **AUTODOCK** [66], **DOCK6** [67], **HADDOCK** [68] and **rDOCK** [69] are to perform a docking between ligand and nucleic acids. The refined results of interaction analysis nucleic acids-ligand are employed as starting point for supramolecular structure design (DNA and RNA origami). This phase is constrained by availability of specific design suites. Many of available tools are specifically developed for specific chemical materials. It is not rather clear if they can be easily utilized with nucleic acids. The software listed in Table 2 is valuable to design nucleic acid base nanostructures. We have mostly considered the open-source programs, however there are some commercial that perform very well. Open-source program and some commercial suite (i.e. Schroedingar's Material Suite) are also very useful.

The main challenge, from a informatic point of view, is the efficient integration of different type of programs into decision support system to optimize the choice of bio-receptor and its integration with transducing platform.

2.3 Nucleic Acid Based Biosensors for Environmental Monitoring

Biosensor with nucleic acid receptors can operate in wide range of different chemical-physics conditions. Biomedical field (diagnostic and theranostics) require to satisfy more stringent biocompatibility constrains (i.e. immunogenicity), other applications could require to satisfy other requires. Protein based receptors, enzymes and antibodies, are currently the favorite type of receptors for environmental biosensors [76]. The exploitation nucleic acid amplification technologies has encouraged the usage of DNA and RNA in biosensor development. The early application of nucleic acid-based biosensor was focused on pathogens genetic modified organisms detection. Heavy metal ions are another valuable field of application of nucleic acids bio-receptor. The role played by ions on nucleic acid conformation and stability indicate the possibility to develop specific monitor system for these chemicals. The list below exemplifies application for nucleic acid-based biosensor in environmental monitoring. It is interesting to underline that for Pb2 + a G-rich DNA coupled with Electrical Impedance Spectroscopy (EIS) is

Table 3 An excerpt of environmental application of nucleic acid biosensors

Analyte	Sensor element	Type of signal	References
PCB77	DNA aptamer	Electrochemical	[77]
Pb^{2+}	DNA hairpin	Electrochemical	[78]
Melamine	DNA triplex	Electrochemical	[79]
Hg^{2+}	DNA aptamer	Fluorescence	[80]
Quinolone	DNA aptamer	Fluorescence	[81]
Ochratoxin A	DNA a	Voltammetry	[82]
Ricin A	RNA aptamer	Fluorescence	[83]
Pb^{2+}	G-quadruplex DNA	Fluorescence	[84]
Antibiotics	RNA aptamer	Electrochemical	[85]
Bisphenol A	DNA aptamer	Fluorescence	[86]
Phthalate	DNA aptamer	QD	[87]
Cocaine	DNA aptamer	Calorimetric	[88]

more sensitive (0.5 nM) than a DNA-zyme coupled with electrochemical system (0.3 μM) [77]. These examples underline that DNA is the favoured type of nucleic acids for bio-receptor design; RNA is used for antibiotics and toxin (Table 3).

3 Concluding Remarks

Published literature offer a large variety of results about environmental application of biosensors, this fact is a clue that this research field is in fast development. The availability of an efficient network to monitor microcontaminants as PCPPs is important to support the cumulative risk prediction due to PCPPs long-term exposure. Nucleic acids have some characteristics valuable to design sensitive and miniaturized environmental monitoring systems. The knowledge about chemical and biological functionality of nucleic acids is deeply changed in the last decade disclosing new perspective to employ these macromolecules as 'materials' in different technological field. The maximization of ligand specificity is a key element biosensor design, mostly for those are nucleic acid-based. The environmental complexity is the first element the have to be considered when is evaluated the possibility to use nucleic acids as receptor element. In the case of major applicative areas, such as biomedical food safety and biodefence, the external environmental conditions can be rather well characterized. In diagnostic implementation, for instance, the knowledge about characteristics of a body fluid are well determined and it possible to take them into account during the probe design phase. The need of ready to use method has privileged the methods based on nucleic acids hybridization (PCR, molecular beacons aptamers) rather than those operate by conformational changes. Further factors must to be more accurately evaluated in the design phase of nucleic acid-based sensing element capable to monitor and screen

CEC pollutants on field. It is necessary, for instance, to delineate the climatological and geological characteristics of the area to monitor. The knowledge of environmental temperature range is also important to develop and use thermal stable nucleic acid sensors (XNA). Temperature variations could have less influence on bio-receptor for water monitoring, however other chemical-physics features as ionic strength, conductivity and pH have to be considered. The application of a nucleic-based biosensor could have different performance if applied directly a water resource or on sampled water. The first case can necessitate the use of continuous "on field" screening systems (early warning) to fast detect a specific analyte; the latter application implies the use of a biosensor for the screening of a pollutant content on sampled water in a laboratory. The performance of on field real time systems could be influenced by the composition of the blend of organic and inorganic pollutants. It is reasonable that nucleic-acid bioreceptor, designed for a specific analyte could be also targeted by other compounds chemically similar to the analyte of interest. The seasonal variation of concentration of (micro)contaminant to sense could be another aspect that can deeply influence the performance. The development of a system for laboratory control is clearly less complicated because it is possible to have different analytical information to characterize the sample; in this case the main advantage of this class of biosensors is the high sensitivity. Taking the previous concerns into account, the monitoring of PCPPs, mostly the personal care, is rather complex because they are almost always present at low concentration in the environment, mostly in the water. Highly sensitive monitoring systems are necessary to control the environmental distribution of non-pharmaceutical chemicals. Nucleic based-biosensors are a promising alternative to other biological receptors to sense these microcontaminants.

The development of multianalyte methods is a great challenge. The employment of ad hoc nucleic acid nanoparticle (DNA, RNA origami) is one possibility, the alternative is the use of microfluidic or lab-on-a-chip architecture to build multi-sensing platforms for this purpose.

The sensitivity of bio-receptor element and its functional compatibility with a transducer surface is the first pivotal step for nucleic acid biosensor design. Here we would like to offer a general framework about the computational aspects that could efficiently support the design of a bio-receptor maximizing the specificity and sensitivity for microcontaminants such as PCPPs that are assuming a real relevance in water pollution.

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Immunochromatographic Strip Based Sensor for the Detection of Water Pollutants

Megha Pant, Deepika Pancholi, Veena Pande and Anirban Dandapat

Abstract The ever-increasing demand for the clean and fresh water with the rapid population growth has been emerged as one of the major issues now. The widespread problem of water pollution is not just jeopardizing our health but is equally damaging to the aquatic environment. There are several techniques available for detection of various kinds of water pollutants but most of them either utilize sophisticated instruments and are expensive or time consuming. Therefore, a portable, sensitive, stable, low cost and rapid strategy is highly essential. In this area, the use of lateral flow immunochromatographic strip based portable sensor appears to be an effective approach for the detection of water pollutants. Immunochromatographic strip combines the use of specific antigen-antibody (Ag-Ab) immunoreactions. This chapter will describe how coloured (e.g. colloidal gold, silver nanoparticles) and luminescent (e.g. quantum dots, up-converting phosphorus NPs) nanoparticles are modified with the Ag/Ab and integrated into paper-based sensors for the detection of target pollutants. Advancements in the technology will further improve the limit of detection which validates its superiority over existing conventional strategies for the detection of water pollutants.

Keywords Immunochromatography · Portable sensor · Water pollutants

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1 Introduction

Water pollution refers to the deterioration of water quality due to the presence of toxic components present in water. It has become a major widespread problem that has affected everyone globally. The problem of water pollution has been faced by both the developed and developing nations where the mortality rate caused due to water pollution appears to be quite high [1]. There are numerous factors which are affecting the water quality, for example climate change, pesticides and fungicides used in vegetation, industrial waste dumping/leaching in waterbodies, mining activities [2]. Nonetheless several techniques like gas chromatography, high performance liquid chromatography, spectrofluorometry, cyclicvoltametry, enzyme linked immunosorbent assays are available for detecting the water pollutants but a portable, cheaper, and rapid technique is needed for the detection of the pollutants. The immunochromatographic strip (ICS) based assay also known as lateral flow assays (LFA) is a paper-based platform appears to be cheap, rapid and portable tool for both qualitative and quantitative detection of the pollutants. Earlier ICS based sensors are mainly used for the detection of specific antigens [3] and antibodies [4], thereafter a diverse kind of biological samples are being tested using lateral flow strip, such as urine [5] saliva [6] sweat [7, 8], serum [9] plasma [10] whole blood [11, 10], and other fluids. Very recently, ICS based sensors are also used in the environmental monitoring including the detection of different water pollutants, such as, heavy metals, different organic pollutants, pathogens etc.

1.1 Principle of Immunochromatographic Strip Based Assay (ICA)

ICA is based on the simple principle that the analyte, which is to be detected, moves through capillary action along the strip having different zones where various molecules are attached to interact with the analyte molecules in higher or lower specificity. Finally, the result will appear as visual observation at the control or test lines. Intensity of the lines appears on the test line is directly proportional to the concentration of the analyte [12–14]. Different zones or components of the ICS are described below.

1.2 Components of Immunochromatographic Strip (ICS)

ICS mainly consist of four components as shown in Fig. 1.

Sample Pad. The sample pad is generally composed of cellulose, glass fiber, rayon etc. The sample/analyte is first drop casted on this zone of the ICS and then

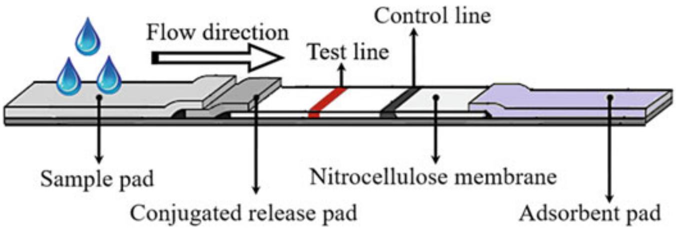


Fig. 1 Components of a immunochromatographic strip (ISC)

transferred to the conjugated pad in smooth and continuous manner. Sometimes, pre-treatments like the separation of the components of the sample, adjustment of pH are also necessary before the transport of the sample [15]. To increase the sensitivity of these pads they should be well treated with appropriate buffers, blocking agents and other reagents.

Conjugate Pad. The conjugate pad is composed of cellulose, Polyesters etc. Biorecognition molecules i.e. antibodies are modified at the conjugated pad zone. When sample is transported from sample pad to conjugated pad, these antibodies are released upon contact with the sample. To maintain homogeneity of the pad pre-treatment is required, where the conjugated pad needs to be properly dispensed and hydrophilic materials used in these pads give better flow rates.

Nitrocellulose membrane. Nitrocellulose membrane is a porous membrane with pore size ranges from 0.05 to 12 µm. It is also known as reaction membrane which carries the test and control lines. These lines are modified with specific biological components (usually antibodies or antigen) to detect the target analyte. The sample is wicked through the membrane and responses appear at the control and test lines. Substances bind to the membrane through hydrogen bonding, hydrophobic and electrostatic interactions. The sensitivity of lateral flow assay is highly based on the suitable modifications at the nitrocellulose membrane. There are other important factors which further affect the sensitivity of nitrocellulose membrane. For example, proper dispensing and drying of the membrane is crucial. In addition, non-specific adsorption and humidity are other vital factors, which need to be controlled.

Adsorbent pad. It is present at the end of the strip and basically prevents the backflow of the sample. The result assay is largely affected by the properties of the adsorbent pad as false positive result can be obtained if there is a backflow of the fluid. High-density cellulose is preferred for the wicking material [16]. Proper assembling of all these components is done over a backing card. It provides support so that the strip could be easily handled.

1.3 How Does ICS Work?

- The sample to be detected is first applied on the adsorbent sample pad which is used to wick the excess reagent and prevent backflow.
- Then the sample will flow through the conjugate release pad where the analyte will interact with the conjugated antibodies that are specific to the analyte.
- The whole sample will then migrate to the porous nitrocellulose membrane. The membrane is immobilized with mostly antibodies or antigens. The sample will then move through the capillary action towards the end of the strip. Nonspecific interactions will be blocked by chemicals. Recognition of the analyte will show different responses as the control and test lines [17, 18].

For the test to become valid a visible line will appear at control line. If any color line appears at the test line, the result is considered to be positive and the absence of any line at the test line indicates the negative result, as shown in Fig. 2. For simultaneous detection of the multiple analytes, different antibodies can be immobilized in multiple test lines [19, 20].

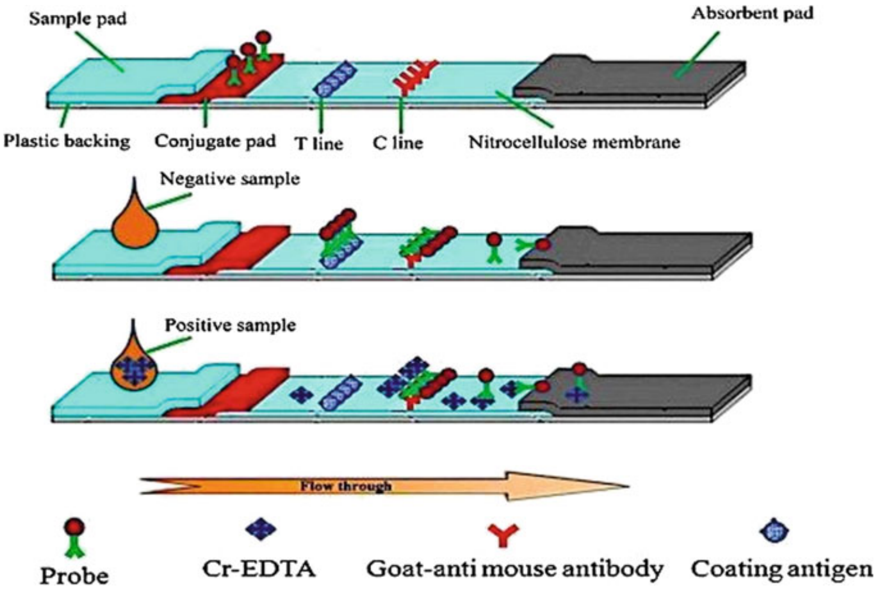


Fig. 2 Schematic representation of the assay's mechanism. The sample is deposited on the sample pad and migrates towards the conjugate pad where the conjugated antibodies bind with the target analyte. Then it is migrated towards the test line and captured to produce a positive result. Reproduced from Ref. [21]

1.4 *Factors for Developing ICS*

Performance of ICS depends on the following factors:

- Reaction time—rapid reaction time is better than slower reaction time.
- Flow rate—reaction rate and flow rate are inversely proportional to each other.
- Pore size—when pore size of membrane increases there appears to be a decrease in the amount of bounded protein.

These factors should be optimized for the development of ICS with desired performance. In addition, color intensity at the control and test line, better sensitivity towards the analyte and low consumption of immunoreagent are also very important for the development of ICS [22].

2 Format of ICA

Various formats used in ICA are briefly described below.

2.1 *Sandwich ICA*

Earlier, it was mainly used for testing HIV, luteinizing hormone and human chorionic gonadotropin (hCG) hormone. However recently, water pollutants are also being detected by this assay. A general structure of sandwich ICS is shown in Fig. 3. Three types of antibodies are being used in this assay: (i) Antibody 1, also known as reaction antibody, will migrate to test and control lines. (ii) Antibody 2, also known as detection antibody or primary antibody, is highly specific for antigen immobilized on the test line. (iii) Antibody 3 is the specific anti-immunoglobulin

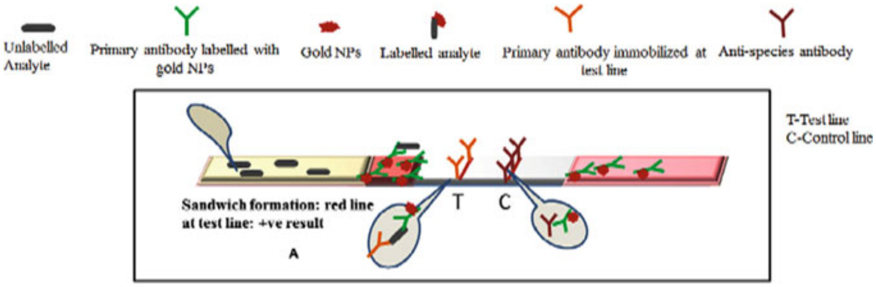


Fig. 3 Format of antibody based sandwich ICS. Reproduced from Ref. [23], copyright 2015, Elsevier

antibody which is known as secondary antibody immobilized at control line. Further steps involved in Sandwich ICA are as follows:

- At the beginning, analyte is applied to the sample pad where it migrates through conjugate pad.
- Then the analyte present at the conjugate pad is captured by labelled antibody and an analyte-antibody complex is formed.
- Next, the complex migrates towards nitrocellulose membrane where it binds with primary antibody present on the test line and thus a sandwich is formed.
- Remaining labelled antibody conjugate will be bounded by secondary antibody present on the control line.

Occurrence of test line confirms presence of the analyte and the color intensity of the line determines the concentration of the analyte. A portable strip reader can quantitatively measure this intensity.

2.2 *Competitive ICA*

It is also known as inhibition immunoassays. These kinds of assays are mostly suitable for detection of low molecular weight compounds but can also be applied to large molecular weight compounds. Steps involved in competitive ICA are:

- First the analyte to be detected is applied on the sample pad which will be then migrated to the conjugate pad.
- Then the prefixed antibody present at the conjugated pad will be hydrated and start flowing with the moving sample.
- After that the sample reaches at the nitrocellulose membrane and migrate through the membrane towards the zone of control and test lines. The test line contains pre-immobilized antigen which will bind specifically to labelled conjugate and control line contain pre-immobilized secondary antibody which also have the affinity for labelled conjugate. If the target analyte is present in sample solution, there will be a competition between the antigen to be detected and the one which is already immobilized at test line of strip to bind with labelled conjugate [24]. However, in absence of any analyte, labelled conjugate will form a complex with the secondary antibody present at the control line and will show visual line at the control line only as shown in Fig. 4.

2.3 *Multiplex ICA*

This type of immunoassay is mainly used to detect multiple analytes present in the sample. Multiple test lines appear in this type of format as shown in Figs. 5 and 6.

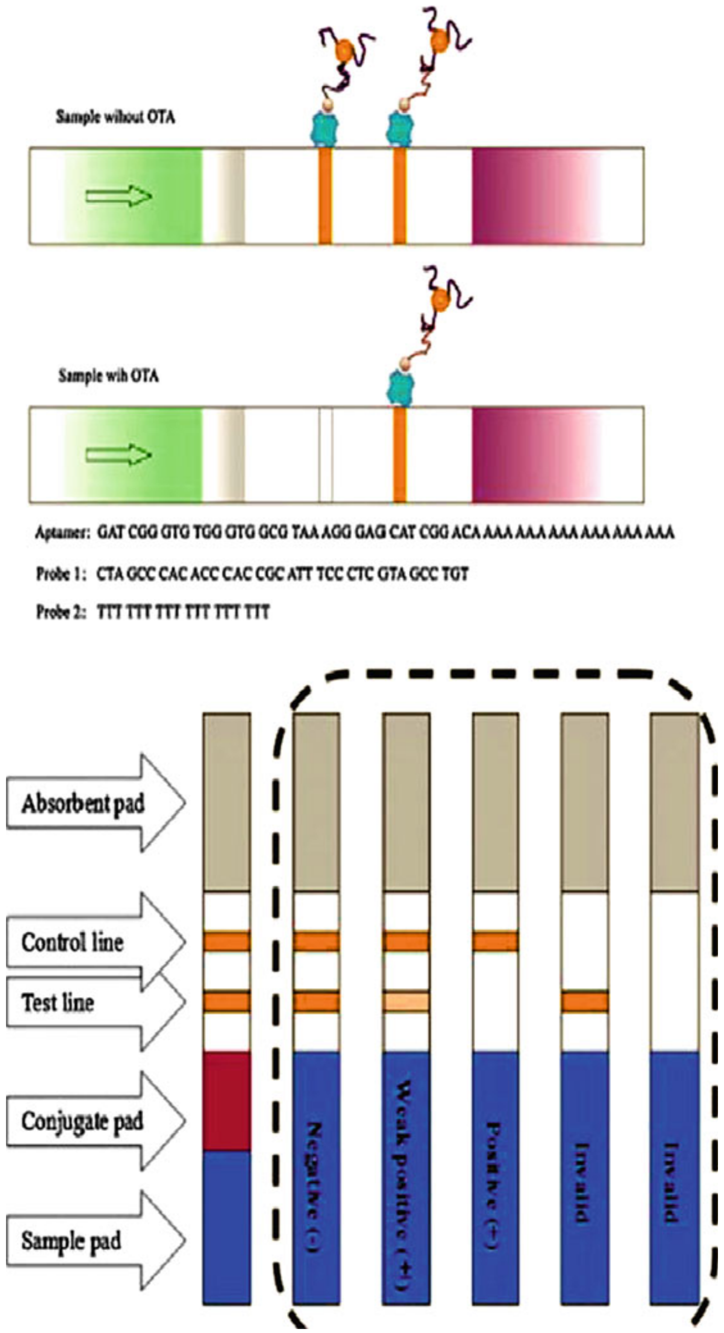


Fig. 4 Competitive ICA based sensor for ochratoxin A (OTA) detection (reproduced with permission from [25], copyright 2015, Elsevier)

Fig. 5 Multicolor test strip. Reproduced with permission from [26], Copyright 2018 Elsevier

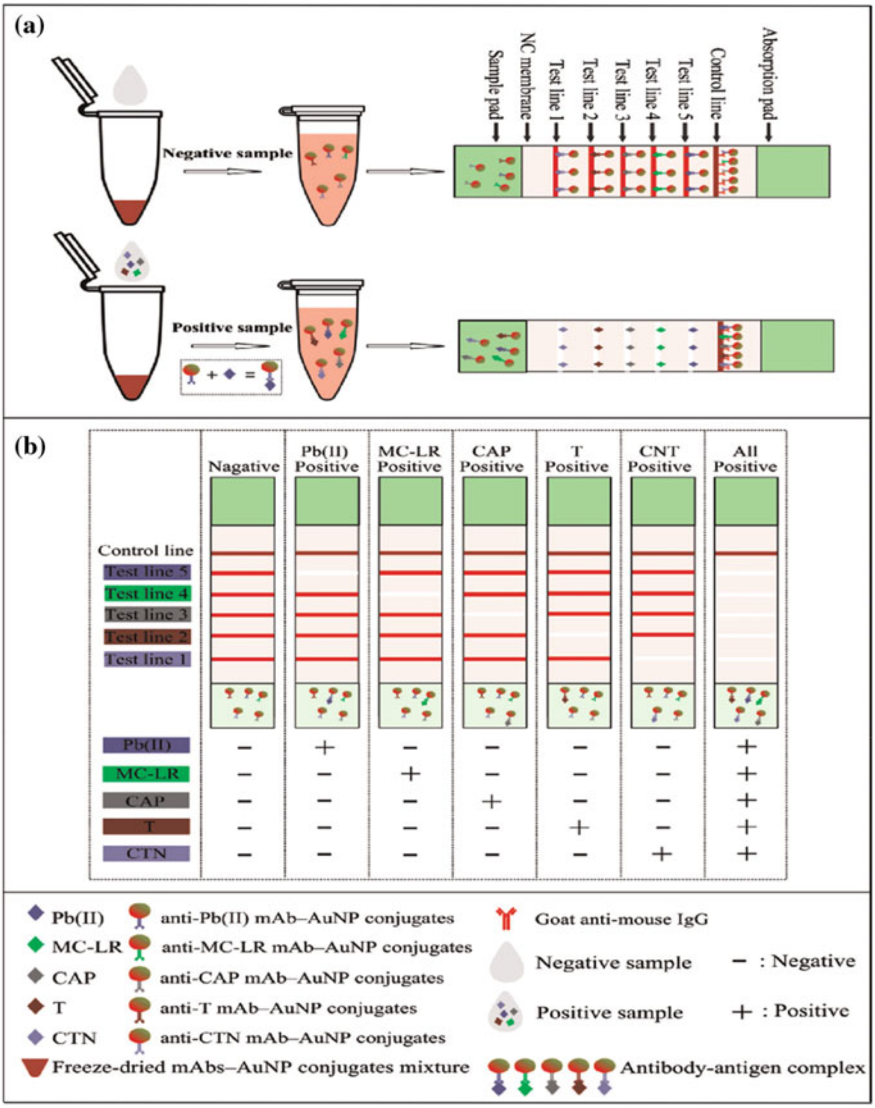
Multiplex ICA has several advantages over other immunoassays, since in this assay multiple analytes can be detected by maintaining same set of conditions in the strip, so a lesser amount of test reagents and sample volume is required for the detection, and multiple analyte can be detected in very short time [27]. Multiplex immunoassays are mainly used in the clinical diagnosis [28] of different diseases. For example, four different kinds of human papilloma viruses (HPV) can be detected by using a series of test lines immobilized with probes. Although it is not popularized yet in the detection of water pollutants, further advancements in this area of research will certainly help to use the multiplex ICA in the detection of different pollutants. The use of microarrays will further improve its sensitivity of the detection method [29].

3 Biorecognition Molecules

These displays the heart of immunochromatographic assays. Mainly antibodies and aptamers are being used as biorecognition molecules.

Antibodies: Two types of antibodies are used; primary antibody which binds to a certain antigen and secondary antibody which binds to antigen containing antibody. Antibodies present on the test and control lines will bind to the analyte which contain these primary and secondary antibodies. These primary and secondary antibodies are first raised in mice and then used for the detection of analytes. Generation of these antibodies is a temperature sensitive process [30]. Nanomolar to picomolar limit of detection range could be achieved by using these antibodies and by adjusting various physical parameters [31, 32].

Aptamers: These are known to be short, single stranded DNA or RNA those tend to bind with specific target molecules. These are generated through a process



	Nagative	Pb(II) Positive	MC-LR Positive	CAP Positive	T Positive	CNT Positive	All Positive
Pb(II)	−	+	−	−	−	−	+
MC-LR	−	−	+	−	−	−	+
CAP	−	−	−	+	−	−	+
T	−	−	−	−	+	−	+
CTN	−	−	−	−	−	+	+

Fig. 6 Schematic representation of multiplex ICA. **a** The NC membrane, absorbent pad, and sample pad were assembled sequentially onto a plastic backing sheet. The NC membrane was modified with the goat anti-mouse IgG antibody and five kinds of antigens to form one control line and five test lines, respectively. **b** In absence of any analyte, mAb–AuNP conjugates would bind to the five test lines and the control line, forming red bands at all the lines. However, in presence of the analytes, the mAb–AuNP conjugates would bind to the corresponding free analytes and analyte–mAbs–AuNP complexes would be formed. Those complexes would not bind to the hapten–protein conjugates or aggregate on the five test lines and thus no red bands would be formed when they passed through the test lines. However, they reacted with the goat-mouse IgG antibody at the control line, and gathered there forming deep red bands (reproduced with permission from [33], copyright 2015, Elsevier

known as SELEX (systematic evolution of ligands by exponential enrichment) [34, 35]. Aptamers possess high association constants which helped them to bind to target molecule with high affinity and specificity. Aptamers can be easily synthesized, simply amplified and also the process is easily reproducible. Initially, aptamers are used in the field of oncology, biosensing, cell imaging, drug delivery etc. [36–39], however, recently those are also used in the detection of different metal ions (e.g. Cd^{2+}, Hg^{2+} etc.).

4 Labels

Labels are the molecules conjugated with the biorecognition molecules to generate a signal. They play important roles in maintaining the sensitivity of the strip. Different types of labels are used in immunochromatographic assay as given below.

- Colloidal gold nanoparticles
- Silver nanoparticles
- Quantum dots
- Carbon nanotubes
- Upconverting phosphor nanoparticles
- Liposomes
- Enzymes etc.

However, gold NPs, semiconductor QDs and carbon-based nanoparticles are mostly used in the ICS-based sensors.

4.1 Colloidal Gold Nanoparticles

These are the most widely used nanoparticles in ICS for signal visualization. Colloidal gold NPs are chemically stable, easy to synthesize and take short time to analyze [40–43]. Au NPs can be easily functionalized with different proteins and oligonucleotides by ionic and covalent interactions. In case of ionic interactions, the stability of NPs depends on surface charge of the functionalized NPs where electrostatic repulsion force exists among the similarly charged NPs. However, electrostatic attraction force results in aggregation of the AuNPs turning the color from red to blue [44, 45]. Shape, size and stability of gold nanoparticles affect the performance of ICS. During the synthesis of Au NPs, size and shape of the particles can be controlled by the amounts of the reagents i.e. reducing agent, stabilizing agents, gold-precursors etc. [46]. Gold nanoparticles of size 20–30 nm with strong absorbance at around 520 nm [46, 47] are generally used as labels here, however,

Table 1 Gold NPs based ICA

Analyte	Biorecognition element	ICA type	Linear range	Detection limit	Reference
Hg^{2+}	Antibody	Sandwich	0.1–1000 ppb	0.1 ppb	[48]
Hg^{2+}	Antibody	Competitive	8–14.8 nM	5.2 nM	[49]
Cd^{2+}	Antibody	Competitive	6–11.5 nM	4.4 nM	
Pb^{2+}	Antibody	Competitive	6–11.5 nM	4.4 nM	
Influenza A virus	Antibody	Sandwich	102–107 copies	102 copies	[50]
E. coli O157: H7	Aptamer	Sandwich	0–108 cfu/mL	10 cfu/mL	[51]
Ochratoxin A	Aptamer	Sandwich	0.18 ng/mL	0–25 ng/mL	[52]
Brevetoxins	Antibody	Sandwich	10–4000 ng/mL	20 ng/mL	[53]
Streptococcus suis	Antibody	Sandwich	103–106 cfu/mL	104 cfu/mL	[54]
Clenbuterol	Antibody	Competitive	0–10 ng/mL	0.08 ng/mL	[55]
Triazophos	Antibody	Competitive	–	4 ng/mL	[56]
Vibrio cholerae O1	Antibody	Sandwich	– –	108 cfu/mL 107 cfu/mL	[57]

larger particles with diameter i.e. 60–70 nm [58] are usually unstable therefore have limited applications.

In current literature, gold NPs have been extensively used for detection of water pollutants, especially, toxic metal ions and pathogenic micro-organisms in contaminated water as given in Table 1. ICS based nanosensors utilizing DNA probes and gold NPs are developed for the detection of mercuric ions [59–64]. In the working principle of this nanosensor, DNA was designed in such a way that initially thymine-thymine base mismatch were there, and due to the specific interactions of mercury with the thymine bases, mercury stabilize these mismatches and thus mercury-thymine complex is formed [65].

4.2 Quantum Dots (QDs)

These are semiconductor nanocrystals having size in the ranges of 2–10 nm. They are used as fluorescent labels for performing better sensitivity of lateral flow assays. QDs possess properties such as broad UV excitation band, high quantum yield,

Table 2 Quantum dots based ICA

Analyte	Biorecognition element	ICA type	Linear range	Detection limit	Analysis time (min)	Reference
Hepatitis B virus	Antibody	Sandwich	–	75 pg/mL	15	[66]
AFP	Antibody	Sandwich	1.56–150 ng/mL	1 ng/mL	10	[67]
Avian influenza virus (AIV)	Antibody	Sandwich	0.2–6.25 μM	68 nM	30	[68]
Streptomycin	Antibody	Sandwich	0.3–500 ng/mL	0.2 ng/mL	–	[69]
Chloramphenicol	Antibody	Sandwich	0.14–10 ng/mL	0.1 ng/mL	–	
Ofloxacin	Antibody	Sandwich	1.5–200 ng/mL	0.3 ng/mL	–	
Zearalenone	Antibody	Competitive	0.125–10 ng/mL	0.0625 ng/mL	10	[70]

large absorption coefficients, photostability, which make them a great asset in distinguish fields like water pollutant detection cell labelling, cell imaging, DNA hybridization, drug delivery etc.

Proteins can be conjugated with water soluble quantum dots and make them more specific as labels. Proteins can be conjugated through their carboxyl and amine groups. EDC (1-ethyl-3-3-dimethylaminopropyl) and NHS (-N-hydroxy succinimide) activates the carboxyl group in the QDs which further reacts with the amine groups present in antibodies and makes them specific towards the analyte [69, 71]. Based on this principle, QDs based ICS are used the detection of different analytes (Table 2).

4.3 Carbon and Carbon-Based Nanoparticles

Carbon- and carbon-based nanoparticles like carbon nanotubes [72] carbon nano strings [73, 74] carbon quantum are mostly preferred in lateral flow assays as they possess properties to conjugate with the antibodies present in the immunochromatographic membrane. Mostly used carbon-based nanoparticles are the carbon nanotubes (CNTs) as they have different physical, chemical and electrical properties including very large surface area and good optical properties which help CNTs to generate a good signal and thus be used as excellent labels in the field of sensing and immunochromatography (Table 3).

4.4 Upconverting Phosphor

Up-converting phosphor (UCP) is basically lanthanide-containing, ceramic sub micro sized particles, and its composition and structure provide brilliant optical features which emit visible light during excitation with infrared light. UCP based ICAs have various applications those are currently limited by assay sensitivity, however, it can increase the probability of a diagnosis by verifying the presence of several analytes in the same sample. UCP particle is used as label to increase the sensitivity of ICA and is also used to detect various water pollutants and diseases like hepatitis B [75], Brucella [76], Schistosoma circulating anodic antigen [77], interferon-γ (IFN-ɣ) [78], clenbuterol [11] and target-DNA molecule [79].

5 Advantages and Disadvantages of ICA

Advantages	Disadvantages
Naked eye detection	Pre-treatment required
Rapid qualitative detection	Normally semi-quantitative
Cost effective	Cross reactivity
Longer shelf life	Unspecific adsorption
User friendly	Difficult to control capillary action
Easy to operate	Analysis time relies on surface tension, viscosity etc.

6 Application Strategies

Although a major part of the ICA based sensors used in clinical analysis, it is now spread over the other applications, which include food analysis, detection of pharmaceuticals, pesticides, pathogens, toxic metal ions etc. Representative examples are given in Table 4. Different nanomaterials (e.g. AuNPs, quantum dots, carbon-based nanoparticles, up-converting phosphors, magnetic NPs etc.) could be used for the development of ICS, however, AuNPs are the most commonly used nanoparticles reported in ICS devices due to its unique optical properties, very high stability, and ease of modification and functionalization.

Table 3 Carbon material based ICA

Analyte	Biorecognition element	ICA type	Linear range	Detection limit	Analysis time (min)	Reference
DNA sequence	Aptamer	Sandwich	0.1–20 nM	0.04 nM	20	[72]
Phytoregulator for chlorfenuron	Antibody	Competitive	89 ± 9–916 ± 22 ng/L	45 ± 9 ng/L	30	[80]
Methiocarb	Antibody	Competitive	0–1000 ng/mL	0.5 ng/mL	10	[22]
Thiabendazole	Antibody	Competitive	0.11–4.13 ng/mL	0.08 ± 0.03 ng/mL	10	[81]
α-amylase	Antibody	Sandwich	1–10 ng/mL	–	10	[82]
Influenza A	Antibody	Sandwich	–	–	15	[74]
Erythropoietin	Antibody	Sandwich	1.7–51 ng/mL	1.2 fM	15	[73]

Table 4 Applications of the ICAs in various fields

Application area	Analyte	Label	Sample type	Detection limit	Time of detection (min)	Reference
Pesticides	Carbofuran	Gold NPs	Water	32 µg/L	8–10	[83]
	Triazophos	Gold NPs	Water	4 µg/L	8–10	[83]
	Atrazine	Gold NPs	Water	1.0 ppb	5	[24]
	Paraoxon Methyl	Magnetic Fe_3O_4 aggregate	–	1.7 ng/mL	–	[24]
	Carbaryl	Gold NPs	Agricultural products	100 µg/L	–	[84]
Metal ions	Hg^{2+}	Gold NPs	Water	1.1 nM	–	[85]
	Cr^{3+}	Gold NPs	Water and serum	5 ng/mL	5	
	Hg^{2+}	Gold NPs	Water	6 nM	5	
	Cd^{2+}	Gold NPs	Drinking and Tap water	0.4 ppb	–	[86]
	Cu^{2+}	Gold NPs	Water	10 nM	–	[87]
Toxins	Clenbuterol	Fluorescent Nano silica	Urine	0.037 ng/L	–	[88]
	Clenbuterol	Gold NPs	Urine	0.1 ng/mL	10	[84]
Pathogens	*Escherichia coli* mRNA	Liposome	Drinking water	5 fM	15–20	[89]
Pharmaceuticals and drugs	Enrofloxacin	Gold NPs	Chicken muscles	0.138 µg/kg	5–10	[90]
	Sulphonamide	Gold NPs	Egg and chicken muscles	10 ng/mL	15	[91]
	Morphine	Gold NPs	Urine	2.5 ng/mL	–	[92]
	Chloramphenicol	Gold NPs	Milk	10 ng/mL	10	[93]

7 Advancements

There are some foremost advancements in lateral flow assay in recent years. These are as follows:

- Better and improved systems for quantification of analyte have been developed.
- Techniques and strategies to enhance the signal in which silver is used have been adopted [48]. Other nanoparticles like colloidal gold nanoparticles are also used to enhance the signal and this could be achieved by using light emitting diodes, laser where the contrast signal can be enhanced up to 1000-fold [94].
- By using several kinds of magnetic, microspheres and immune based nanoparticles sensitivity and range of detection of immunoassay has been reduced to 0.1 ng/ml.
- Simultaneous detection techniques have also been emerged in past few years. These include simultaneous detection of two proteins by using two conjugated pads where antibodies and antigens are detected simultaneously using colloidal gold NPs. Computational methods have been developed for sensing in which 'OR' and 'AND' logic gates are employed.

8 Conclusion

ICS based sensors have demonstrated to be rapid, cheap and portable tools to detect various water pollutants including toxic metal ions, pesticides, other organic and inorganic pollutants, pathogenic microorganisms. Although earlier it was mainly used for the detection of different bio-molecules, however its simplicity, quick response time and ease of operation trigger its applicability in other areas including the environment monitoring. The use of ICS based sensing does not require any sophisticated instrument and can be visualized even with naked eye, thus does not require any trained personnel. To increase the sensitivity of the ICS based sensing, it is coupled with different nanomaterials, such as, gold NP, carbon QDs, fluorescent materials etc. Besides, the sensitivity of the ICS can also be increased by tuning the microfluidics within the ICS. With the developing technology, new materials and strategies will be provided for further development of ICS-based sensing. Although there are only few studies for the simultaneous detection of multiple analytes, we believe new technologies will emerge in near future to develop multiparameter ICS for environmental monitoring. Further improvement in this area of research along with the integration of ICS with smart phones for quantitative detection will certainly direct the presence of ICS based sensors at every home in future for onsite detection of pollutants and environment monitoring.

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Materials in Emerging Water Pollutants Detection

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Abstract Contamination of water bodies is a global concern. Water quality monitoring has been carried out using different techniques and materials, in different parts of the world using a different kind of strategies. Investigating a wide range of potential organic pollutants that may be present in the aquatic environment is a huge challenge faced by environmental scientists. A wide-scope "universal" screening methods have been required for the detection and identification of a broad range of water pollutants, offering a piece of more realistic and complete information on undesirable compounds present in water samples. Most analytical techniques developed recently involve the application of chromatographic techniques coupled to mass spectrometry. Full spectrum acquisition methods such as high-resolution mass spectrometry offer the possibility for screening a huge number of pollutants. Biosensors have been well studied and emerged as sensitive and high specific tools for the detection of pollutants. Bio-monitoring has also emerged as effective techniques in environmental analysis.

Keywords Environmental monitoring · Techniques · Spectrometry · Biosensors · Nanoparticles · Bio-monitoring

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1 Introduction

Development of human civilization and resulting industrialization has given rise to environmental pollution. Environmental pollution is a major issue since it has its influence on human health and is linked with the sustainable development of both society and economy. It has become a matter of increasing concern due to the exceeding limits of both regulated and unregulated organic contaminants present in the aquatic ecosystem. These pollutants are mainly chemicals which are used in industries and agriculture. A large portion of such pollutants are recalcitrant and persist in the ecosystem for a longer duration. These toxic compounds possess the ability to enter the food chain and pose threatening effect to the receiving ecosystem and also to human health (Radovic et al. 2015) [36, 73, 85]. Environmental monitoring comprises the measurement of selected physical, chemical and biological environmental variables over a time period. The intent is to accomplish assessments on the quality of environment of a selected area.

Regardless of progress and advances in analytic techniques, the determination of organic pollutants present in water is still challenging in the current scenario [72]. The major hurdle behind this failure is complexity, high concentration and number of pollutants that might be present in the water sample. This fact, along with distinct chemical characteristics of analytes, makes the application of a single analytical technique, inappropriate for all potential pollutant present. In the current scenario, various common techniques have been applied in environmental monitoring which includes atomic absorption method, thin layer chromatography, UV-Vis spectroscopy, high-pressure liquid chromatography, inductively coupled plasma mass spectrometry, liquid chromatography-mass spectrometry, ion chromatography, immunoassay and other advanced instrumentations. Because of their promising characteristics including simplicity, cost-effectiveness, high sensitivity these techniques are widely accepted. TLC (Thin layer chromatography) is a comparatively cost-effective technique for environmental monitoring, with less reliability on higher instrumentation, but possesses low sensitivity. Generally adapted instrumental approaches such as HPLC (High performance liquid chromatography), GC–MS (Gas chromatography-Mass spectroscopy), and LC-MS (Liquid chromatography-Mass spectroscopy) are widely accepted as official methods for the determination of environmental pollutant [42]. But, they offer certain disadvantages of being time-consuming due to complicated sample preparation and expensive. In current scenario, most of the analytical approaches have coupled chromatographic techniques to mass spectroscopy, as single quarupole or ion trap and more recently triple quadrupole. In these approaches, number of analytes hardly exceeds 200–300 compounds and pollutants other than target pollutant that possibly is present in the environmental samples are generally ignored. Hence, there is urgent requirement for the development of broad range "universal" detection techniques possessing the ability to detect and identify a large number of pollutants. In this way, a more realistic and complete knowledge on pollutants present in environmental samples is obtained. High-resolution mass spectroscopy is a full spectrum acquisition techniques, which offer the possibility for screening of a large number of pollutants in post-target driven approaches without the requirement of pre-selection of analytes for the development of technique.

Environmental sensor research generates considerable interest and activity nowadays. Research studies involving biosensor design and development for environmental monitoring in terms of toxic elements, organic pollutants and pathogens contribute to the betterment of the health of the ecosystem. As compared to traditional methods, biosensors are more sensitive, cost-effective, rapid, easy to operate and portable equipment. They are helpful and reliable for the in situ measurements of water pollutants, where they provide rapid and miniaturized services [38, 94]. Nanoparticles have applications in various fields, such as pharmaceuticals, energy, environment, electronic, catalytic and material applications [7]. Nanoparticles are traditionally defined as particles having a size range between 1 and 100 nm, displaying unique properties different from bulk-sized materials. They also have potential application in environmental monitoring. Nanoparticles as nanosensors offer advantages of rapid and high output detection of pollutants present in aqueous environments. Surface modified nanoparticles such as gold nanoparticles, magnetic nanoparticles, carbon nanotubes and quantum dots possess specific target binding characteristics [34]. Their nanoscale scale and exceptional properties make them useful for modern age environmental monitoring. Different nanoparticles possess specific magnetic, surface, optical and fluorescence properties and interaction between these properties makes these nanoparticles potential candidate for environmental monitoring. Nanoparticles based approaches have application for the improvement of water and soil quality.

Environmental biotechnology-based tools aid in the protection of the natural ecosystem, on the basis of which marine-related social and economic activities relies on. These approaches including biosensors play a vital role in addressing marine environmental issues. Whole cell biosensor is monitoring tool based on living bacteria possessing ability in signal sensing a delivering an output response that can be detected and quantified using a suitable detector device. Biosensors find application in fast and cost-effective screening of pollutants present in aqueous systems [84, 90] (Diplock et al. 2010). Although not aimed for substitution of analytical techniques, biosensors are attractive tools for the in situ determination of pollutants in a cheap and flexible way without needing heavy equipment. Biosensors respond to the amount of pollutant that is bioavailable, while chemical and traditional techniques determine the total concentration of pollutant present in the sample, which may overestimate the real risk in terms of toxicity [47].

In this chapter, we summarized recent progress in emerging techniques and materials for water pollutants detection. This chapter includes chromatographic techniques and other advanced methods for environmental monitoring. Role and advances of biosensors in the sensing of water pollutant is briefly discussed. With a controllable structure and interface interaction properties, nanoparticles and nanocomposites exhibit novel physical and chemical features that will be essential for widespread sensor applications. Biotechnological approaches involving microbial biosensors play a vital role in the monitoring of pollutant present in an aqueous system.

2 Chromatography Based Techniques for Pollutants Detection

Chromatographic methods are reference analytical techniques for environmental monitoring. Universal detectors such as UV or mass spectroscopy are applied which possess the ability to detect multiple compounds simultaneously, providing high sensitive and accurate measurements in the range of ng L^{-1}. Numerous multiresidue techniques for the analysis of a wide range of contaminants in environmental samples have been reported in the last decade being most of these examples based on the use of high resolution chromatographical techniques such as gas chromatography [11], liquid chromatography [2], high-performance liquid chromatography (HPLC) [16] or ultra-performance liquid chromatography (UPLC) [65]. Gas phase chromatography with fluorescence detection allows the selective determination of hydrocarbon-based microplastics pollutants sampled from marine and freshwater coastal sediments [10]. A novel Liquid chromatography-Mass spectroscopy based technique was developed by Peng et al. [63] and authenticated for the determination and detection of twenty drugs of abuse and pharmaceuticals from potable water. The developed method was based on the application of solid-phase extraction followed by liquid chromatography-mass spectrometry. Five drugs of abuse and two pharmaceuticals were detected at the range of 0.14–2.81 ng/L, including cocaine, ketamine, mephedrone, methamphetamine, methylone, citalopram and fluoxetine. In a study reported in Canada, in potable water ketamine has also been reported at a higher concentration of 15.0 ng/L [74]. A series of novel cationic gemini surfactants with pyrrolidinium groups, 1,1-(butane-1,s-alkyl) bis (1-alkylpyrrolidinium), were employed as carriers in sweeping–micellar electrokinetic chromatography for simultaneous detection of nine organic water pollutants, including polycyclic aromatic hydrocarbons, sulfonamides and steroids [82].

Kim et al. [50] developed a quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction method for pesticide analysis which has substituted less efficient traditional extraction methods due to its numerous advantages. In addition to pesticide analysis, this method has been widely used for the detection and analysis of pharmaceuticals, polycyclic aromatic hydrocarbons, and several persistent organic pollutants, including polychlorinated biphenyls, dioxins, perfluoroalkyl substances, and brominated flame retardants in food, biological, and environmental samples. These approaches include dispersive solid phase extraction and have generally been pooled with either gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS) analysis.

3 Advanced Methods for Detection of Contaminants in Environmental Samples

Most of the emerging contaminants possess high water solubility due to their chemical configuration and thus pose a potential risk for the aquatic ecosystem and humans being through the water cycle [58]. A continuous increase in the concentration of xenobiotic and recalcitrant compounds has been observed in various water bodies such as groundwater and surface water [1, 71]. The assessment of such emerging pollutants in the aqueous system has turned into a key scientific task, which demands highly sensitive analytical approaches for determination at nanograms per litre scales [81]. Different analytical techniques have been developed among which, major techniques are comprised of gas/liquid chromatography coupled with mass spectroscopy. The mass spectroscopy approaches have exhibited better outcomes in the precise determination of contaminants present in the complex composition of effluent or surface water currently, because of its sensitivity and specificity [1]. Advanced mass spectroscopic techniques including ion trap and triple quadrupole are applied for the determination of contaminants in the ng L^{-1} scale, whereas for the structural interpretation of transformed intermediates, more advanced techniques such as triple quadrupole, linear ion traps quadrupole, triple quadrupole and quadrupole-linear ion trap are applied [58].

Other advanced techniques reported for the determination of emerging pollutants present in water include microbiological assay, capillary electrophoresis and immunoanalytical techniques. Capillary electrophoresis possesses disadvantage for being less sensitive as compared to liquid chromatography, whereas immunoanalytical based approach relies more on antibody involved and has limitations for the determination of various analytes simultaneously and in the case of microbiological assays a large amount of samples are required [12]. Nowadays a significant improvement has been achieved in the field of advanced analytical techniques. But there is still a need for more sensitive techniques for the determination of unknown and more complex compounds. There is a high need for the development of novel identification techniques for the low cost and accurate determination of unknown emerging contaminants. For the precise and accurate detection of pollutants in environmental samples, prior treatment of the samples requires significant consideration for an analytical method. Liquid-liquid extraction has been used largely in previous studies. However, the use of solid phase extraction has been increased in recent times owing to its several benefits over liquid-liquid phase extraction, such as reproducibility, applicability, and simplicity. Prior concentration of aqueous environmental samples is also considered exercise before the final determination of lower detection limits and low quantification limits and is supporting in declining of both the values.

A wide range of toxic pollutants when present in the environment even at low concentrations pose a threat to human health [4, 14]. This increases the demand for the development of a sensitive analytical technique for the determination and identification of trace and ultra-trace micropollutants in water. Recently, an increase had been observed in the number of emerging pollutants such as pharmaceuticals and persistent organic pollutants present in water and other ecosystems. Thus, it is highly urgent to develop corresponding specific and sensitive analytical techniques [28].

Traditional analytical approaches, including high-performance liquid chromatography and liquid/gas chromatography-mass spectrometry, have gradually been evolving to improve their detection capabilities [9]. Simultaneously, novel techniques with ultra-high sensitivity, simple operations and portability have also emerged for the determination of pollutants in environmental samples [3, 95, 97]. Among these technologies, surface-enhanced Raman scattering appears to be one of the most suitable methods for detecting environmental pollutants.

Raman scattering spectroscopy was discovered in 1928 [69]. Due to containing abundant structural information of analytes, Raman scattering spectroscopy has been considered as a ubiquitous tool in analytical science. Surface-enhanced Raman scattering, exhibiting a significant enhancement of Raman scattering from a rough metal surface, has greatly promoted the development of Raman technology towards the practical applications [8, 22]. Recently, this approach has become a powerful analytical technique for the detection of environmental pollutants because of its outstanding advantages, such as "fingerprint" information, ultrahigh sensitivity, and rapidity [62, 80].

4 Advances in Biosensors for Environmental Monitoring

Biosensors are analytical devices that can identify and detect a signal within a cell or tissue. These are composed of bio-recognition elements and different kinds of physicochemical transducers [27, 57]. Biosensors deliver the required portable analytical tools and early warning systems owing to their specificity, sensitivity, reusability, speed along with their ability for permanent and unattended operation in the field. Enzyme-based biosensor is most commonly used for the determination of heavy metals in the aqueous system. For serving this purpose, a wide variety of enzymes such as glucose oxidase, urease, tyrosinase, peroxidase, etc. have been reported [30, 70] (Maleki et al. 2017). Also, electrochemical sensors have been proved to be a promising approach in heavy metal monitoring, due to their stable and strong interaction with ultra-low levels of metal ions present in the system [40, 96]. A highly sensitive microfluidic Pb^{2+} biosensor was designed by immobilization of a lead-specific catalytic DNA on the polymethylmethacrylate microchannel [25]. With the covalent attachment of metallothionein onto a quartz crystal, a piezoelectric biosensor was designed to monitor Zn^{2+} and Cd^{2+} in the aqueous system [75]. Chen et al. developed a piezoelectric nano-biosensor for accurate determination of Hg^{2+}, using quartz crystal microbalance with dissipation monitoring technology [19].

Recently, ion sensors based on Aluminium gallium nitride/Gallium nitride high electron mobility transistors have been developed to monitor various ions. These devices are sensitive towards charge characteristics at the surface and have the distinct advantage that a reference electrode is not required for operation, unlike many other types of ion sensors. Asadnia et al. showed that such devices coated with plasticised poly(vinyl chloride) based membranes containing an ionophore can be used to detect Hg^{2+} [5] and Ca^{2+} [6] ions in water.

5 Nanoparticles in Environmental Monitoring

Owing to their unique physicochemical characteristics and vast applications, currently, metal nanoparticles have attracted a great deal of attention. Metal nanoparticles exhibit properties such as ultra-small size, strong fluorescence and low toxicity. These are considered as a kind of novel fluorescence probe for the development of optical sensors. Nanoparticles possess a broad range of application in the field of environmental, pharmaceutical, cosmetics, energy, optoelectronic and catalytic. Recently, in the field of environmental monitoring nanoparticles have been widely applied for the analysis of toxins, metal ions, and organic pollutants. Water and wastewater treatment approach using nanoparticles have gained increasing attention owing to their specific properties such as large surface area, antimicrobial activity [31], photocatalytic activity [35], and chemical stability [96]. In addition to this, they also possess potential application in environmental monitoring. Nanoparticles provide with advantages as nanosensors in rapid and high-output detection technique. Extremely small size and exceptional nanoscale properties make nanoparticles useful for the new-generation environmental monitoring. The recent progress in their applications in environmental monitoring, involves pH sensing, the detection of heavy metals and inorganic anions.

The main reason behind the pH sensing ability of metal nanoparticle is its response characteristics towards pH. It was recently reported by Wang et al. [87, 88] and Chen et al. [18] that copper and gold/copper nanoparticles could be effectively used as reversible fluorescence indicators for pH sensing The response behaviours for the pH change were opposite to that of reported by Qu et al. [67]. Results showed that the fluorescence signal was gradually declined with the increase in pH value.

Ecological pollution by heavy metal is a great matter of concern worldwide. Heavy metals when present in high concentration can pose adverse effects on the receiving ecosystem as well as on human health. This highlights the importance of heavy metal ion monitoring of the environment. For serving this purpose a large number of selective heavy metal ion sensors have been developed from nanoparticles. Darbha et al. [26] reported a gold nanoparticles-based sensor for the easy, rapid and reliable screening of Hg^{2+} ions in aqueous solutions, with a sensitivity of 5 ng/ml (ppb). Yang et al. [92] demonstrated visual detection of Cu^{2+} by L-cysteine-functionalized gold nanoparticles in aqueous solution. In the presence of Cu^{2+}, the gold nanoparticles solution changed from red to blue. This colorimetric nanosensor allows rapid, quantitative detection of Cu^{2+} with a sensitivity of 105 M. Peng et al. [64] developed a fluorescent-based microfluidic chip using magnetic multi-walled carbon nanotubes for tracing small amounts of Cr(III) and Cr(VI) in various water samples, with a detection limit of 0.094 nM. An in situ preparation technique was reported by Chen et al. (2004) for gold nanoparticles in poly(*N*-isopropylacrylamide) gels. The thus obtained gold nanoparticles/poly(*N*-isopropylacrylamide gels offered similar optical properties as of the bare gold nanoparticles. Only 9% increase in its fluorescence intensity was observed in the presence of 500 mM NaCl, supporting its characteristics of good salinity resistance. For the detection of Hg^{2+} in samples, the sensing approach was successfully applied. The developed gold nanoparticles/poly(*N*-isopropylacrylamide) gels was observed to possess good thermosensitive properties and showed possibility to be also applied and designed as a temperature sensor relied on the change in the fluorescence intensity. Xie et al. [89] reported a selective and sensitive approach for Hg^{2+} sensing using Bovine serum albumin (BSA) templated gold nanoparticles. There was about 17% gold on the surface of BSA-Au, the red fluorescence of Bovine serum albumin (BSA) templated gold nanoparticles was quenched by the unique metal affinity between Hg^{2+} and Au^{+} in a few seconds. A method for in situ synthesis of fluorescent gold nanoparticles on bovine serum albumin/poly(ethyleneoxide) (PEO) electrospun membrane was reported by Cai et al. [13], and it was applied in the detection of Hg^{2+}. On the surface of BSA/PEO fibrous membrane nanoparticles were immobilized and emitted bright red fluorescence under visible light irradiation. A rapid quenching of the red fluorescence signal was carried out by Hg^{2+} due to the relatively large specific surface of nanofibers and strong affinity between Hg^{2+} and Au^{+}. Guo et al. [39] reported that denatured bovine serum albumin-Ag nanocatalyst could be assembled as a chemical sensing material for the detection of Hg^{2+}. Recently, Wang et al. [87, 88] demonstrated a novel fluorescence enhancement technique for the determination of Hg^{2+} using carbon nanotubes and DNA-Ag nanocatalysts. For the determination of copper ions, an electrochemical sensor possessing a limit of detection below 1 pM was developed. Modification of electrodes were first carried out using gold nanoparticles, followed by modification of gold colloid surface with cysteine for the detection of copper. For the detection of Hg^{2+} and Ag^{+}, Freeman et al. [33] developed and reported a multiplex assay using an electron-transfer-quenching route. Modifications of quantum dots of different sizes were carried out with thymine or cytosine bases. The formation of T–T and C–C base pairs was induced by Hg^{2+}/Ag^{+} ions. Development of several optical sensors has been carried out based on photoluminescent-quenching principles. A gold nanoparticle–rhodamine 6G-based fluorescent sensor ave been reported by Chen et al. [20, 21] for the detection of Hg^{2+} in aqueous solution with a lower detection limit of 0.012 ppb. Similar assays involved monitoring photoluminescent intensity before and after Hg^{2+} addition, with photoluminescence increasing with increasing Hg^{2+}. However, this assay was sensitive only to 2.0 ppb [43]. He et al. [41] also demonstrated a homogeneous assay to detect Cu^{2+}, based on modulating photoluminescent-quenching efficiency between a perylene bisimide chromophore and gold nanoparticles in the presence of Cu^{2+}.

Cyanide, a highly toxic ion, inhibits the cytochrome C oxidase activity in mitochondria and obstructs respiration in cells. Recently, gold nanoparticles have been applied for the determination of cyanide. In the presence of oxygen, generally, cyanide can transform gold atom into water soluble $Au(CN)^{2-}$ ion and results in the gold nanoparticles fluorescence quenching. Keeping this principle in mind, Liu et al. (2010) developed BSA-Au nanoparticles for the determination of cyanide. In a study conducted by Faghiri and Ghorbani [32], a new composite nanosensor of sodium alginate-silver nanoparticles was synthesized in order to solve the issue of low sustainability of sensors by solvent casting technique and was applied in naked eye and colorimetric detection of ultra-low concentration of Hg^{2+} ions in aqueous environmental samples.

The developed nanosensor was characterized for the determination of structural features by using instrumental techniques. The synthesis of silver nanoparticles was confirmed with the help of obtained results showing an average size of 13.34 nm. Under specific environments, the colorimetric sensing of Hg^{2+} was carried out (6pH and reaction time of 7 min) with a linear correlation obtained between the absorbance at 402 nm and different Hg^{2+} ion concentrations within the 0.025 μM–60 μM range. For the detection of Hg^{2+} ions in the aqueous environmental samples, the developed sensor was successfully employed for the detection of Hg^{2+} ions with recoveries ranging between 81.58 and 114.73%. The developed nanosensor exhibited good selectivity toward Hg^{2+} ions in the presence of several competing ions. Maleki et al. [54, 55] studied the synthesis of second-generation polyamidoamine dendrimer functionalized with magnetic nanoparticles (Fe_3O_4/G2-PAD) and its application in the determination of Pb^{2+} and Cd^{2+} ions in aqueous environment. The performance of the modified magnetic electrode by recording the impact of changing experimental variables was determined and optimized. Under optimized environment, the developed sensor showed a linear response to lead and cadmium ions over a concentration range from 0.5 to 80 ng mL^{-1}. The developed sensor was successfully employed for the determination of Pb^{2+} and Cd^{2+} in the presence of some potentially interfering ions.

Some accomplishments are also there in using carbon nanoparticles to characterize the biological variable of the environmental sample. The work by Mandal and Parvin [56] has verified the application of carbon nanoparticles for rapid determination and enumeration of bacterial cell from a water sample collected from the contaminated environment. For the sensing/detection of bacterial cells gold nanorods can be applied as optical sensor. The presence of *Escherichia coli* in the drinking water as well as in aqueous environmental is an ongoing serious, worldwide health concern. Singh et al. (2009) demonstrated a sensitive assay for *E. coli* using a gold nanorod-based antibody-conjugated two-photon scattering system, with lower detection limit up to 50 colonies forming unit (cfu)/mL.

6 Biotechnological Approaches for Pollutant Detection

In recent years, environmental pollution detection and monitoring are being done by approaches involving bio-systems. For this, purpose, several groups of plants, animals and microorganisms are utilized. The environmental protection agencies consider bio-monitoring of pollution as a useful device to monitor environmental pollution from the point of diagnostic, preventive and remedial measures.

The biotechnological methods adopted for pollution measurement can be briefly described in the following: (a) General bioassays; (b) Cell biological assays; (c) Molecular biological assays; (d) Biosensors.

(a) **General bioassay**

In the early years, conventional physical and chemical methods were used for the detection of environmental pollution. Bioassays are preferred these days since the biological responses that reflect the damages to the living organisms are very crucial for the actual assessment of pollution. Certain algae, bacteria, lichens, mosses and vascular macrophytes are commonly used in bioassays.

Among the plant systems, algal bioassays are the most commonly used. Algae are considered to be reliable indicators of pollution due to their high sensitivity and easy availability, besides simple culturing techniques. The criteria adopted for algal bioassays are the growth rate, biomass accumulation and photosynthetic efficiency. The algae used in the test assays include Chlorella, Microcystis, Spirulina, Navicula, Scenedesmus, Anabaena, Ulva, Codium, Fucus and Laminaria. In water, organic pollution can be detected by using the blue-green algae, Microcystis, while metal pollution can be measured by Navicula.

Lund Yi et al. (1984) reported a sensitive, simple and rapid bioassay involving two-species of marine algae for the determination of the toxicity of chemical contaminants. The bioassay employs the marine diatoms *Phaeodactylum tricornutum* and *Cyclotella cryptica*. After screening 40 clones of 32 species, an optimum pair i.e. *P. tricornutum* and *C. cryptica* were selected. These algal species are easily cultivated in the laboratory environment, and the algal cells can be differentiated and enumerated with the help of electronic particle counter. For the sake of toxicity determination alteration of species ratio and total biomass were applied. Polychlorinated biphenyls at 10 parts per thousand million (10^9; ptm) considerably transformed species ratio in the favour of *P. tricornutum*, and 10 ptm of DDT (l, l,1-trichloro-2,2-bis(p-chlorophenyl)ethane) and 20 ptm of dieldrin produced a significant species alteration in contrast to that created by polychlorinated biphenyls.

Bacterial bioassays are commonly used for the detection of faecal pollution in potable water, the most widely employed test being the coliform test. Ames test that detects mutagenic pollutants is carried out by the bacterium Salmonella. Bacterial bioluminescence is a recent technique used for the measurement of gaseous pollutants and other compounds e.g. sulfur dioxide, formaldehyde, ethyl acetate. Photobacterium phosphoreum is the organism of choice for bacterial bioluminescence.

Environmental metal pollution can be detected by using the certain forest and aquatic mosses e.g. Stereophyllum, Sphagnum, Brynus. Capozzi et al. [15] reported the application of moss *Sphagnum palustre* to immobilize polystyrene nanoparticles for the first time in an aqueous environment; these research observations opened novel applicative perceptions to biological monitoring approach. It encouraged the application of mosses for the determination of microplastics in fresh-water ecosystems. Experiments of Hg bioaccumulation was carried out by Cesa-Bianchi et al. [17] using aquatic moss *Rhynchostegium riparioides* with the aim of (1) measuring the metal uptake at increasing water concentrations, and increasing exposure time, (2) studying the influence of pH and water concentration of Na, Ca and Mg on the metal uptake, (3) achieving a database for mathematical and statistical elaborations, and, (4) producing an equation modelling the uptake.

(b) Cell biological assays

Methods based on cell biology are chiefly targeted to trace the detrimental effects of contaminants on various cellular components for example, mitochondria, chloroplast, cellular membranes and chromosomes. In addition to this, nucleic acids and proteins are also used. Also, these techniques aids in determination of mechanism of toxicity of pollutant compounds. Extensive studies have been carried out on the presence and formation of DNA adducts [59, 61]. The detection of these DNA adducts in aquatic fauna is used as exposure indicators since last twenty years [52]. Stein et al. [78, 79] reported some of the pioneer work on the kinetics of formation of adduct and removal in fish liver, where the persistence of DNA adducts followed by exposure to benzo[a]pyrene and 7H-dibenzo[c,g] carbazole was observed.

(c) Molecular biological assays

The use of molecular probes and immunoassays in the monitoring of environmental pollution is gaining importance in recent years. Molecular biological bioassays are particularly useful for the detection of bacteria, viruses and other pathogenic organisms that cause diseases. DNA probes and polymerase chain reaction (PCR) can be effectively used for water quality monitoring, particularly potable water. However, these techniques are expensive and not practical in all places. Immunological based techniques are prove to be beneficial for the monitoring of environmental pollutants (such as pesticides and herbicides) and identification of pathogens that show immunological characteristics. Immuno based assays are in use for the measurement of several pesticides for e.g. aldrin, triazines DDT, glyphosate.

(d) Microbial biosensors

Various biological tools for the rapid screening of vast number of chemicals present in environment that could pose hazard have been developed by scientists. Living cells have evolved to sense numerous environmental stimuli, thereby presenting a completely unique platform to engineer bio-sensing devices. Because of simplicity in genetic modification and preservation, microorganisms have established

Table 1 Advantages and disadvantages of microbial biosensors [44]

Sr. No.	Microbial biosensor	Advantages	Disadvantages
1	Bacteria-based	– Easy and cost-effective – Results obtained in short time duration (hours or day) – High-throughput formats scalable – Portable device adapted	– Lower significance for eukaryotic organisms – Involves genetic engineering and thus there is possibility of ethical issues – Requires aseptic environment
2	Yeast-based	– Eukaryotic microorganism – Easy and cost-effective – Transfection process with entirely functioning vertebrate genes possible – Results obtained in short time duration (hours or day) – High-throughput formats scalable – Portable device adapted	– Unicellular organism – Involves genetic engineering and thus there is possibility of ethical issues – Requires aseptic environment
3	Algae-based	– Easy and cost-effective – Results obtained in short time duration (hours or day) – High-throughput formats scalable	– Require specificity in light conditions – Nutrients present in complex samples may cover the toxic pollutants effect

themselves as ideal host candidates. Moreover, microbially derived biosensors are comfortable to use, compact, cheap and easy to relocate.

Biosensor constitutes of bacteria, yeast and algae, possessing a unique advantages and disadvantages (Table 1). The exceptional structural and functional characteristics of biosensors facilitate monitoring of wide range of environmental pollutants. Wide array and unique characteristics of a biosensor such as selectivity, sensitivity and range of target compound (Fig. 1) could be figured out by regulatory genes manipulation. Currently application of such genetically modified microbial origin biosensors show unprecedented capabilities for monitoring environmental contamination.

Genetically modified yeast is currently used in biosensors as in vitro model due of its time and cost-effectiveness, sensitivity, reproducibility and scalability to high-throughput formats. Vopálenská et al. [86] reported a new copper biosensor

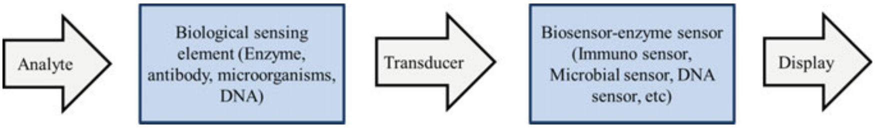

Fig. 1 Components of biosensor

based on specifically modified *Saccharomyces cerevisiae* strain immobilized in alginate beads. This biosensor was capable of detecting copper ions at concentrations of 1–100 μM. The biosensor beads change color to white, when copper is present in concentrations below the detection limit, while increase in copper concentration is determined by pink or red color. The biosensor was successfully tested to determine copper concentrations in copper contaminated water samples. When compared to other fluorescent protein based biosensors or analytical methods, the developed biosensor did not required specific equipment and facilitated rapid detection of copper in parallel samples.

In their research, Ponamoreva et al. [66], used methylotrophic *Pichia angusta* and oleaginous *Cryptococcus curvatus* yeast cells immobilized in a bimodal silica-organic sol–gel matrix with tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) as hydrophobic additive and polyethylene glycol (PEG) as the porogen for pollutant monitoring. Under controlled experimental conditions and catalysts, yeast cells formed nucleation centers for a silica-organic capsule fabricated over cells. Effect of MTES composition on the nature of encapsulated yeast cells together with the architecture of the three-dimensional sol-gel biomatrix formation during the encapsulation was well demonstrated. Each yeast cell was examined and detected as to be encapsulated by silica when 85 vol.% MTES was used. These silica capsules were found to protect microorganisms from harmful exposure of heavy metal and UV radiation. *P. angusta* cells were used in biosensors for the detection of methanol.

Microbial cultures were mixed and co-cultures were created to develop the receptor element of a biosensor for assessment of biological oxygen demand (BOD). These co-cultures had broad substrate specificities and enabled water and fermentation product assays within a broad BOD range (2.4–80 mg/dm^3). Use of the co-cultures constituting yeasts *Pichia angusta*, *Arxula adeninivorans* and *Debaryomyces hansenii* immobilized in *N*-vinylpyrrolidone-modified poly (vinyl alcohol) resulted in a BOD biosensor possessing the characteristics not inferior to those in the known biosensors. The results indicated potential use of these co-cultures as the receptor element base for broad application in prototype instruments [93]. Kim et al. [48, 49] designed a whole cell array biosensor for the effective detection and monitoring of neurotoxic organophosphate compounds. In 2012, Jouanneau et al. [45, 46] skillfully demonstrated use of two varieties of biosensors (Lumisens III and Lumisens IV) for on-line detection of heavy metals in environmental samples, based on different storage modes of luminescent bacteria. Bacterial suspension was staged in a micro-well driven by continuous flow with 4% agarose solution in Lumisens III system having a higher biological activity. Freeze dried bacteria in 96-well microplates were used in Lumisens IV system having relatively low biological activity. Both systems were enclosed in the dark chamber, and the light signals emitted by bacteria were captured and recorded by CCD camera. In 10 days, the two biosensors were used to continuously detect mercury (Hg) in distilled water and environmental samples. Kolahchi et al. [51] developed a fast and sensitive conductometric biosensor for direct detection of phenol and phenolic compounds using immobilized *Pseudomonas sp.* on the surface of gold interdigitated microelectrodes by glutaraldehyde cross-linking in the presence of bovine serum albumin. Cui et al. [23, 24] determined the cytotoxicity of heavy metal-polluted seawater samples by constructing a toxicity biosensor *Acinetobacter baylyi* Tox2 with a luminescent bacterium *A. baylyi* harboring a medium-copy-number plasmid. Yagur-Kroll et al. [91] proposed four methods to enhance the performance of luminescent bacterial biosensors via promoter manipulation by: (1) modifying the length of DNA fragments containing promoter regions; (2) introducing a random gene mutant through directed evolution; (3) introducing more specific site mutants into promoter sequences and (4) replicating promoter sequences to increase binding sites of RNA polymerase. Through these four methods, the sensitivity, response time and emission intensity of biosensors would be significantly improved.

A wide range of algal bio-mediators based optical biosensor has been reported to monitor significant pollutant compound in marine samples. A prior study was conducted to determine the most appropriate biomediator for the determination of pesticides in marine samples. The ability of *Chlorella vulgaris-Tetrahymena pyriformis* symbiotic association as a sensitive biological mediator for the development of biosensor was determined [83]. In a study carried out by Gosset et al. [37], a self-driven portable fluorimeter was reported to determine the A-chlorophyll microalgal fluorescence, introduced by capillarity into disposable and low-cost microfluidic chips based on xurography. Three microalgal cultures: *Chlorella vulgaris*, *Pseudokirchneriella subcapitata*, and *Chlamydomonas reinhardtii* were used for the development of the biosensor. A prior optimization of feasibility and sensitivity parameters of biosensor, such as concentration of algal cells and intensity of light, were carried out to calibrate the biosensor sensitivity with Diuron (a toxic pesticide for microalgae). After that, the biosensor was engaged in monitoring of ten aqueous urban polluted samples to prove its consistency, reproducibility and performance for the determination of toxic discharges in the soil ecosystem. Scognamiglio et al. [76] developed a paper and algae based biosensor for the optical determination of nano encapsulated-atrazine, a well-known herbicide with a highly effective post-emergence herbicidal activity. In this study, immobilization of the photosynthetic green microalgae *Chlamydomonas reinhardtii* was carried out on a paper based substrate soaked with an agar thin-film and positioned in a glass optical measurement cell, resulting in a totally eco-friendly technique. An encapsulated atrazine was determined by varying parameter such as fluorescence, which inversely proportional declined to the concentration of herbicide, in a range of 0.5–200 nM. In order to determine storage stability, studies were conducted and good results were obtained for up to 3 weeks. These results showed the applicability of the reported paper-based optical biosensor in smart agriculture for in situ, eco-friendly, cheap and sensitive atrazine analysis.

7 Future Challenges

The development of novel approaches for environmental monitoring should focus on the sensitivity and selectivity features, along with equal focusing on the disposal aspect after the environmental analysis is over. It will be completely futile to have the ultra-sensitive performance of an analytical probe, but the probe itself is made of toxic materials that can be harmful to human beings and the environment. For the aspect of future development, the application of synergistic approach could be a remarkable solution to define and design standalone strategies to remediate emerging macro and micropollutants of great concern. Several critical issues of the traditional approaches applied for the nanoparticle synthesis can be solved by coupling the whole synthesis procedure with modification strategies involving surfaces. In order to achieve a deeper insight in this context, the influential and important aspects of numerous surface modification strategies should be included in future studies. For the elimination of emerging and priority contaminants, another interesting possible research alternative is the look-out for unique and new materials and bio-nanocatalysts following green approach to achieve highly effective and ecological friendly remediation procedures.

8 Conclusion

The presence of a vast group of emerging contaminants in the natural environment is of continuous threat for the safety and health of human being along with the ecosystem. Extensive research work is required specifically dedicated for the development of treatment technologies in recent years for the elimination of recalcitrant pollutants in water. In current situations, owing to recent improvements in analytical instrumentation techniques, it is possible to achieve the desired “universal screening” of environmental pollutant. In terms of analytical probe for environmental monitoring, the options available are diverse and it will be the choice of the analyst to make the decision on which system to be employed. Economic, sustainability and robustness are the major parameters which should be considered. As compared to traditional chemically-based sensors, biosensors could detect a wide range of water pollutants or xenobiotic compounds in a unique way with high sensitivity and selectivity. It can be said that with the progress in the field, metal nanoparticles will support many novel analytical techniques in the near future, for the sake of environmental monitoring, and carry out research in new fields for solving issues related to environmental pollution. From the field application point of view, the most attractive approach/technique while performing environmental monitoring is the application of wide-scope screening methodologies, able to screen and identify as many water contaminants as possible, in order to obtain wide and realistic information on the actual water quality.

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Emerging Techniques and Materials for Water Pollutants Detection

Richa Soni, Mahesh Soni and Dericks Praise Shukla

Abstract Rapid industrialization and population boom have led to deterioration of water quality, rising health issues and environmental damage, which made it imperative to monitor and regulate the water pollutants. Earlier, water samples were monitored using grab sampling method and then analysis was performed in the laboratory. This process is arduous and time consuming; also, there are poor chances of detecting a periodic pollution. For a proactive response sensor technology is popular these days for pollutant monitoring. A variety of sensing techniques and materials are available. But recently nanomaterials have absorbed attention for fabricating sensors owing to their high surface to volume ratio, ease of functionalization which enable them to have high specificity and sensitivity. This chapter intends to review the emerging materials used for making water pollutant sensors and gives an insight into the emerging techniques like microfluidic sensors, biosensors, wireless sensor network and smart sensors.

Keywords Biosensors · Microfluidic · Nanomaterials · Wireless network · Water pollutants

1 Introduction

The problem of clean water availability is worsening day by day owing to the rapid industrialization and population boom. Clean water is crucial in sustaining life, and has a major role in health of living beings. Water contamination can occur due to several factors like biological, chemical or anthropogenic posing health hazards.

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The contamination broadly includes organic, inorganic and microbial pollution. With increasing industrialization, new contaminants are introduced each day. Water-quality monitoring is challenging due to the unpredictability and complexity of various pollutants and their concentrations that need to be detected [1]. Thus, monitoring of water quality used for consumption is important. Water quality issue can happen broadly in two ways, either the source of water supply is contaminated or there is some intermittent issue which took place due to some accidental contamination. Proper monitoring of such issues can't be done by conventional sampling, methods of grab sampling and laboratory testing, instead a regular monitoring with quick analysis is required [2].

Earlier, manual detection of water contaminants was done in the laboratories, which required skilled manpower and specific instrumentation. A number of traditional approaches were available to detect contaminants like; multiple fermentation tube technique [3], filtration method [4], DNA amplification [5], fluorescence in-situ hybridization (FISH) techniques [6], capillary electrophoresis, field-flow fractionation [7], chromatography [8] and mass spectrometry [9]. Since a long time, these methods were used and are still used but they proved to be inefficient for on-site monitoring of contaminants. Traditional approaches of water pollution detection are cumbersome and time consuming.

Effective water quality monitoring is the need of the hour which includes the data collection at several locations, at regular intervals to procure data for establishing trends and assessing the current water quality [10–12]. Water quality monitoring is required to provide timely warning or identification of any potential hazard to be caused. The current demand for monitoring tools includes: disposable systems, biocompatible, monitoring multiple analytes, high sensitivity, low cost and on-site monitoring [13].

With the rising demand for techniques of water pollution detection, a lot of progressive research is being done in this area to meet the needs. A wide variety of water quality sensors are available in the literature to detect various contaminants. Water quality sensors have their origin from late 1990s and from then till date a lot of technological and material-based advancement has been done. This chapter gives an overview on recent advancements in techniques like microfluidics, biosensors and wireless sensor networks for water contaminant (biological and non-biological) detection. Figure 1 presents the data obtained from Web of Science which informs about the number of publications over years for water pollutants (the keywords used for search are the same as presented). It can be observed from Fig. 1 that maximum research in past five years is done on biosensors for water pollutants followed by wireless sensor networks. To add to this, after analysing the information, it was observed that most of the sensors irrespective of the type of sensor, uses nanomaterials in their fabrication to enhance the sensitivity and reliability. This chapter also discusses the significant limitations of the techniques and provides suggestions for future development in the water quality monitoring. Also, on the material front, nanomaterial enabled sensors have received increasing attention from the researchers owing to their novel properties and promising performance of rapid detection and reduced analysis time. Therefore, this chapter also summarizes the

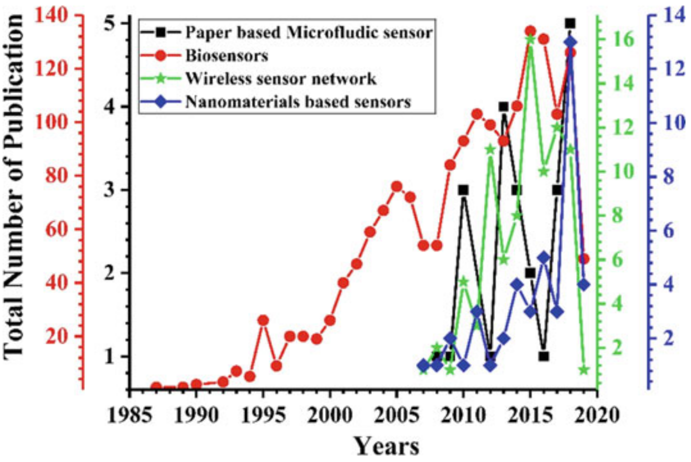

Fig. 1 Data obtained from web of science to give a projection of research publications over years for water pollutants. The different keywords used for the search of water pollutants are the same as presented

recent developments in the nanotechnology-based sensors for water quality monitoring.

2 Microfluidic Sensors

Development of portable sensing devices for field use is trending now-a-days, thus small devices are gaining popularity having low cost, high sensitivity, specific and easy to use. Microfluidic sensors were earlier used for mostly detecting non-biological contaminant in water like pesticides, mercury, arsenic, phosphate. But with the progress, microfluidic devices have found their way in detecting biological contaminants too [14, 15]. Microliters of samples in micron length of reaction chambers can be used by Microfluidic devices [16]. Microfluidic devices are capable of providing biological assays and on-chip chemical assays with lesser quantity of reagent and consumption of sample, controlled manner of handling the sample and reaction, well-controlled microenvironments, high-throughput experimentation [17]. A variety of materials like silicon, glass, PDMS have been utilized for fabricating microfluidic sensors. Timeline for substrates used for making microfluidic based devices has been shown in Fig. 2. But recently paper based microfluidic sensors have received attention from researchers [18–20] for water monitoring. The paper based microfluidic devices were first reported in 2007, and later on a lot of advancements were done in them like use of new printing techniques, integrating the devices with cameras/smartphones, use of nanomaterials in the devices. In 2018, a new substrate thread, was reported for microfluidic devices

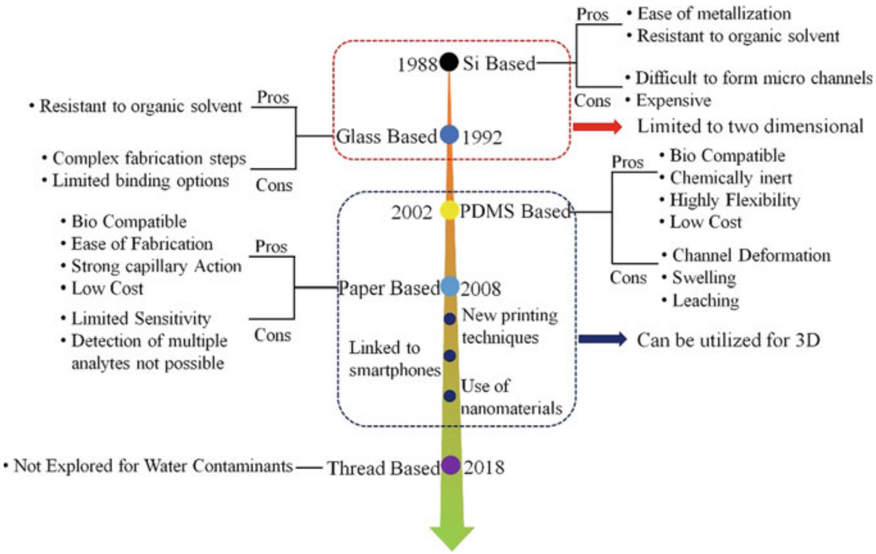

Fig. 2 Timeline for development of substrates used for microfluidic devices

but it was used for therapeutic purposes so not discussed here. Using paper as a substrate for microfluidic sensors has many advantages: ease of availability, cost effective, disposable, biodegradable, light-weight, ease in printing and patterning to make channels for samples, self-capillary action [21]. But, paper made devices has its own limitations, it lacks the resolution and sensitivity when compared to the silicon and glass devices.

2.1 *Fabrication and Detection Methods of Paper Based Microfluidic Devices*

The fabrication of paper based microfluidic devices is based on creation of hydrophilic zones on paper which are patterned using physical barriers, various cutting procedures or hydrophobic agents [22]. Depending on the user application, the paper type is selected. The type of paper used has an impact on the performance and fluidic transport. Paper substrates that have been used for making microfluidic devices are Whatman chromatography paper 3 MM Chr [23], Whatman filter paper grade 4 [24], Millipore MCE membrane filter [25], Canson paper [26], JProLab JP 40 filter paper [27], and Advantec 51B chromatography paper [28]. Fabrication usually involves the paper type selection and then applying it to various fabrication techniques such as cutting, photolithography, inkjet printing, wax printing, screen printing, wax patterning, wax pencil drawing and contact stamping [21]. Details of fabrication techniques can be read in the work of [19, 21]. Fabrication methods involves both two-dimensional (2D) or three-dimensional (3D) flow-systems. Various techniques are used for making 3D systems like sticking various patterned layers together or folding a single patterned layer. 3D devices are getting popular as they have increased functionality without increasing the size of device [29].

2.2 Recent Studies Based on Paper Based Microfluidic Sensors

The common detection techniques used by the paper based microfluidic devices are namely colorimetric, luminescence, electrochemical, and photoelectrochemical detection [21]. For on-site analysis, it is important that the detection method used is portable and user friendly. Khanna et al. [30] reported the estimation of Bisphenol-A concentration in ethanol. They used nanostructured manganese dioxide as a receptor. Meelapsom et al. [31] developed a microfluidic Paper-based Analytical Device by using alkyl ketene dimer-inkjet printing. They used unmodified silver nanoparticles which disintegrated on exposure to mercury (II). Several options are available for onsite analysis like use of smartphones [32–34], portable scanners [35] or purpose built-in detector [36, 37]. Recently, smartphones have gained attention from researchers as they are more advantageous than use of a simple camera. While using smartphones applications can be developed for internal monitoring as done by Sicard et al. [33], which helps easy collection, storage and real time sharing of data. Care must be taken for uniform light exposure when the cameras of mobile phones are used. Ortiz-Gomez et al. [32] kept phone with flash off condition in a box having LED to control light exposure. Smartphones can be used both with [38] or without flash [33] with the use of forming a control zone when taking the picture. Santhiago et al. [34] demonstrated the use of mobile phone for detection with incorporation of a Quick Response (QR) code reader which reads the information from the microfluidic device.

2.3 Future Trends and Recommendations

Paper based microfluidic devices are developed to be portable, but a few have been used for the field tests. Wax printing/paper cutting is the commonly used fabrication methods used for the development of paper based microfluidic devices. Fabrication methods selected should be simple and low cost and must be suitable for scaling up of devices. It has been reported that smart phones and tablets with dedicated applications are fit for image capture, real time processing, storing and sharing of data. Use of such tools helps to make the device user friendly and portable. Smartphones connected to the microfluidic devices are also beneficial to areas having low resources, where wireless transmission is an issue due to network limitations. In such cases smartphones may be able to store the data locally and then transmit it when the network connection is available. Alternative power sources like solar power is also useful for such areas. Main issues that needs attention in paper based devices are proper validation, ability for long term storage of devices without hampering its features and enhanced sensitivity.

3 Biosensors

A biosensor is an independent device, which provides specific quantitative or semi-quantitative analytical information using a biochemical receptor [13]. As shown in Fig. 3, a biological component act as a receptor for a specific analyte, this interaction results in a signal is transformed using a transducer into a quantitative signal which can be detected. The main advantages of biosensors are, miniatured device, ability to perform in complex solutions, easy sample preparation and on-site usage. But several of such devices are not able to compete with the conventional sensors with respect to accuracy and reproducibility. A variety of biorecognition methods like, molecularly imprinted polymer, immunochemical, whole-cell and DNA elements, enzymatic, non-enzymatic receptor, are available, owing to which biosensors can be classified into types: electrochemical, optical, piezoelectric and thermal biosensors, based on their transducing mechanism [39]. Biochemical specificity of bioreceptor defines the function of biosensor. Biosensors can also be classified as enzymatic biosensors, immunosensors, genosensors or DNA biosensors, or tissue-based biosensors depending on the type of bioreceptor [40].

3.1 Recent Studies on Biosensors

Few latest developed biosensors for detecting water contaminants are listed here. Zeng et al. [41] developed a portable and quantitative biosensor for detection of cadmium using glucometer as the point-of-use device. Wee et al. [42] reported

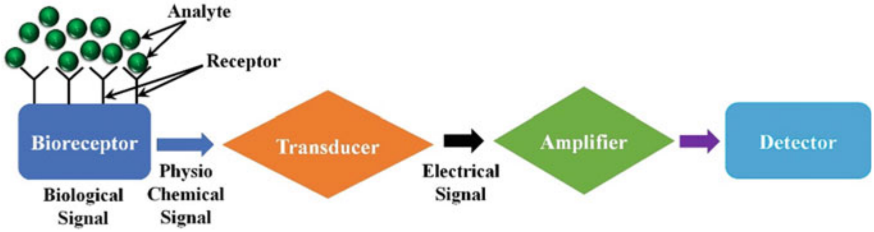

Fig. 3 Basic working of a biosensor

detection of phenols using Tyrosinase-immobilized carbon nanotube. Yu et al. [43] developed a Dandelion-like copper oxide microspheres decorated with gold nanoparticle modified biosensor on the specific thymine-Hg^{2+}-thymine base pair for the highly sensitive detection of mercury ions. Atar et al. [44] designed molecular imprinted nanosensors for detecting organic matters such as triclosan, by simulating their biological receptors. Nomngongo et al. [45] made a sensor having a bioreceptor of horseradish peroxidase to detect persistent organic pollutants in wastewater samples. Yamashita et al. [46] studied an electrochemical biosensor for the in-situ monitoring of Biological oxygen demand in the wastewater. Biswas et al. [47] developed an enzyme based biosensor to detect chromium in water. Verma et al. [48] integrated microfluidics and optical transduction system to develop a biosensor to monitor lead concentration. Several optical techniques like surface plasmon resonance [49, 50] and resonant mirror [51] have been used to detect pathogens. Yildirim et al. [52] developed a portable optical fibre biosensor using a fluorescently–labeled specific aptamer to detect E-coli O157: an H7 strain in wastewater samples.

3.2 Microbial Fuel Cell (MFC) as Biosensors

Recently, microbial fuel cell (MFC) has been found to show promising results as a tool for water quality monitoring [53]. MFC biosensor is an electrochemical microbial biosensor; it consists of an electrochemical cell with electrodes usually separated by a membrane [54]. The MFC utilizes microorganisms as a bio-catalyst for oxidation of organic matter and generate current at the anode, which produces electrical power, when coupled to the reduction of oxygen occurring at the cathode [55]. Microorganisms are present on the anodic surface and their metabolic activities are converted into electricity [56].

Zhou et al. [57] have reviewed several MFC based biosensors for water quality testing. MFC based biosensors have found there use not only for checking dissolved oxygen, biological oxygen demand and chemical oxygen demand but also considered for identifying and analyzing different organic pollutants in water samples [57, 58]. Real time chromium monitoring has been demonstrated by [59] based on the variations in voltage signal via the activity of immobilized electrogenic bacteria. Chouler et al. [60] developed a paper based microbial fuel cell for detecting bioactive compounds in water.

To be approved as a standard analytical method, more research is required in this area. Discovery of new microbial consortia with superior electrogenic potential which enables fast metabolization of wide range of organic materials is required [58]. Moreover, the integration between microbial electrochemistry and nanotechnology could result in super conductive electrodes which possess improved efficiency; this area has a lot of potential and is yet to be extensively explored. The researchers should focus on low cost fabrication and simple designs of MFC-based sensor devices by using inexpensive and reliable electrode and membrane materials.

3.3 Future Trends and Recommendations

A lot of attention is given to biosensors for detecting water pollutants; still finding an appropriate biorecognition element for a particular pollutant remains a challenge; which in turn limits the scope of biosensors. When whole-cell based biosensors are used, production of secondary metabolites results into anomalous readings of target organic pollutant in water; and hence in such cases a precise correction method is required. For development of efficient and commercial applicable biosensors, it is imperative to design a sensor which can simultaneously detect several pollutants and can detect low concentrations of specific pollutant. One of the main aspects to be considered for biosensors is stability of the bioreceptor through shipment, storage and application condition. To overcome the limitations, research is to be progressed in the area of producing recombinant target specific bioreceptor and integrating biosensors with nanomaterials to improve the detection limit and sensitivity of biosensors.

4 Wireless Sensor Networks

Evolution of water quality monitoring systems have taken place from manual lab-based to manual in-situ monitoring to modern Wireless Sensor Network (WSN) based approaches. The traditional approach was collecting the samples manually and transporting to laboratories for analysis of contaminants. But, this approach required trained personnels, special instruments and equipments, is time consuming, costly and does not provide real time monitoring to judge a change in water quality. To overcome the problems mentioned above in-situ sensors were developed for real time monitoring of water quality in field. This approach developed hand held devices which can monitor water quality and store the data, but was unable to send the data automatically to users for processing further.

WSN is gaining attention of researchers and end users for monitoring the water quality. The gaining popularity is owing to as mentioned reasons; on-site fixing of sensor to collect real time data, adjustment of sampling frequency to user's wish without investment of any additional money and time, anytime visualization and processing of data by end users, configuration and control of sensor unit using a remote [61]. A basic architecture of WSN constitutes of isolated sensor nodes for sensing, processing of signal, embedded computing, and connectivity [62], which enables the communication between persons/computers and the surrounding environment via wireless link [63]. WSN working steps include acquisition of data, transmission of data, storage of data and redistribution of data. The transmission of data of such water quality monitoring systems is usually built on cellular network (GSM/GPRS) [64, 65] or satellite data link [66]. New network protocols such as WAVENIS, Z-WAVE, LoWPAN, INSTEON, NB-IoT, ZigBee, LoRaWAN, etc. have been developed [61]. Data can be stored in local server or cloud and thereafter can be redistributed to the end users using email, text messages, web page, mobile app etc. A basic architecture of wireless sensor network is presented in Fig. 4. Wireless sensor is a device having a sensing element, signal amplifier, filtering system attached to a software for data processing. These sensors are also attached with wireless transmission element. Wireless sensors are positioned in the water to be tested; sensors convert the physical parameter to be detected to measurable electrical quantity. The electrical signal is transferred to the controller via wireless device. Thereafter, the controller reads the data and send it to the communication module. The advantages of WSN are low consumption of power, redundant data procurement, remote monitoring, wide coverage area, fast network establishment, low duty cycle and high monitoring precision [62].

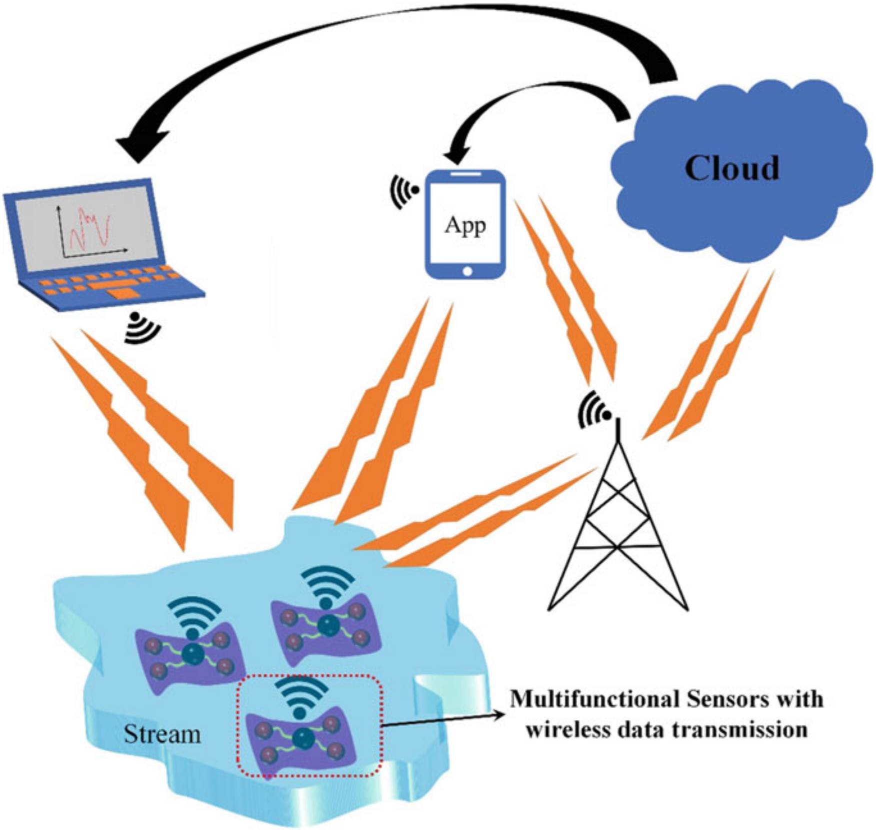

Fig. 4 A basic architecture of wireless sensor network (WSN)

4.1 Recent Studies Done on Wireless Sensor Network

Now-a-days research is progressing on combining robotics and WSN for water quality monitoring [67]. Ma et al. [68] provided a scalable total solution, investigating a distributed localization method in wireless sensor networks equipped with mobile ultraviolet-visible spectrometer probes. Eichhorn et al. [69] and Vasilijević et al. [70] designed an autonomous underwater vehicle (AUV) for analysis of water quality parameters. Jadaliha and Choi [71] developed robotic sensors for monitoring temperature of swimming pool and gave a concept of Autonomous Surface Vehicles (ASVs). Ferri et al. [72] also designed and developed ASV for monitoring the coastal water quality. Liu et al. and Wu et al. [73, 74] designed a novel design and multimodal locomotion control, prepared with many onboard sensors, which permit it to be a self-propelled and self-contained system for a biomimetic robotic dolphin capable of water quality monitoring. Robotic systems for water monitoring, provide better spatial coverage for data collection using built-in GPS or sonar positioning system as compared to fixed sensors. Ravalli et al. [75] studied a bio-inspired artificial fish unit capable of changing its swimming patterns according to the directives sent in form of chemical messengers from PANI-modified sensors. The researchers [75] introduced the proof-of-concept for developing multi-sensors fish robot as future core technology in aquaculture farm management. Zhang et al. [76] proposed a novel scheme for autonomously sampling multiple water columns using gliding robotic fish. The energy harvesting, wireless data transmission, harsh aquatic environment is still a problem area when robots are to be deployed for longer durations [77].

4.2 Smart Sensors

Smart sensors are intelligent devices which takes input from the environmental factors and has built-in resources to detect and process the data. Smart sensors differ from integrated sensors as they have built in programmable microprocessors. Technically, a smart sensor has a sensing element, signal amplification and filtering system in combination with a software for data processing and compensation [78]. Cloete et al. [10] reported an inexpensive, wireless, multi-sensor network for measurement of physico-chemical water parameters with real-time monitoring. Data from all the sensors is processed, analysed and then transmitted wirelessly to a notification node which further informs the end user about the water quality. Yifan and Peng [79] developed a wireless sensor network for water quality parameters (temperature, turbidity, pH, dissolved oxygen and conductivity). Data is transferred from monitoring nodes and data video base station to remote monitoring centre via ZigBee and CDMA (code division multiple access) technology. Jiang et al. [80] analysed water quality parameters (pH, conductivity, dissolved oxygen and temperature), an alarm was heard in the presence of a water contamination and data is sent to a base station via GPRS (general packet radio service). Parra et al. [81] developed a turbidity sensor which can differentiate between turbidity types which is based on the Beer-Lambert law and the absorption of light.

4.3 Future Trends and Recommendations

Wireless sensor networks have enormous potential in water pollution detection and monitoring, as they help us to monitor and interact remotely and collect huge amount of data. Lifetime of a sensor is dependent on the battery life, which has to be replaced or recharged when depleted. Managing power requirements of a sensor is a challenge. Harvesting of energy has been suggested to manage wireless-based sensor power supply, though most energy harvesting systems depends on solar cells [82]. Several self-powered mobile sensors were used in water distribution pipelines [83]. Deployment of sensor nodes at various locations need special techniques which needs to be ad dressed. The primary goal of wireless sensor design is to create miniature, efficient and low-cost devices. Security of sensor nodes and their information also needs attention of researchers as the remote and unattended operation of sensor nodes increases the chances of malicious invasions. The security requirements in WSNs comprises authentication of nodes and confidentiality of data. For the development of multiparameter, high performance sensor, it will be important if different sensors like biosensor, nanosensor, smart sensors can be incorporated in a programmable microprocessor.

5 Nanomaterials: Emerging Materials for Sensors

Nanomaterials are extensively researched for detection of water contaminants owing to their unique structures and excellent catalytic and electrical properties [84]. Advancements in design of the sensors such as small size, portability, and fast signal response times have been enabled using nanomaterials [85]. Nanomaterials have high surface to volume ratio and it is easy to functionalize nanomaterials for enhanced sensitivity. In few cases increased sensitivity of nanomaterial used sensor is owing to the fact that nanomaterials have size similar to that of analyte and therefore are capable of interrogating previously unreachable matrices [86]. In general, nanomaterials can be differentiated into three classes quantum dots, metal based nanomaterials, carbon based nanomaterials.

5.1 Quantum Dots

Quantum dots are nanometer-sized semiconductor crystals possessing exclusive chemical and physical properties which is due to their highly compact structure. Quantum dots possess narrow fluorescence emission bands with broad absorption bands; making them excellent choice as optical transducers [85].

5.2 Metal and Metal Oxide Nanoparticles

Metal and metal oxide nanoparticles can be produced in various sizes and can be easily functionalized to serve as a good sensor [87]. Colloidal solutions of gold and silver nanoparticles, show unique colors based on the size of the colloidal nanomaterial; are stable biocompatible and extensively used in sensing applications [88]. Nano based metal oxides include oxides of iron, titanium, zirconium, cerium, zinc and tin. Magnetic nanometal oxides of iron are popular owing to low toxicity, economic, facile functionalization and easier separation process [89].

5.3 Carbon Based Nanomaterials

Recently, One and two dimensional materials, for instance Carbon nanotubes (CNTs) and graphene its derivatives (graphene oxide, reduced graphene oxide) are frequently employed for the fabrication of nano-based sensors owing to their high surface area, mechanical strength, excellent electrical conductivity, and high thermal conductivity [90]. Graphene and derivatives are studied widely for fabrication of sensors due to its high sensitivity to electronic perturbations on introduction of any foreign molecule [84, 91].

5.4 Recent Studies Performed on Nanomaterials Based Sensors

Xie et al. [92] developed a voltammetric sensor for dichlorophenol based on beta-cyclodextrin functionalized boron-doped graphene composite aerogels. Rapid mass transfer is ensured by high specific area, large pore volume and conductivity; also uneven charge distribution is introduced by boron doping on graphene enabling several active sites for catalytic oxidation of dichlorophenol. Liu et al. [93] detected mercury (II) ions using high-fluorescent carbon dots originated from China grass carp scales. The obtained carbon dots has large amount of cysteine-containing sulfhydryl groups which enables to be used as specific fluorescence probe for detecting mercury (II) ions and has low toxicity too. Li et al. [94] monitored cerium (III) using a color-evolution based paper sensor by incorporating fluorescent nanoprobe (carbon dots) onto the cellulose paper substrate. Ramírez et al. [95] quantified lead (II) by developing an electrochemical affinity biosensor that combines glassy carbon electrodes and an aqueous dispersion of single-walled carbon nanotubes covalently modified with cysteine residues. The sensor demonstrated high selectivity for lead in complex solutions. Dong et al. [96] reported a simple and green sensing system for the detection of free residual chlorine in water based on fluoroscence quenching of Graphene quantum dots. In the work done by [97] an "on-off" fluorescence phosphorus/nitrogen dual-doped carbon quantum dots probe was developed for the determination of Chromium (VI). Liu et al. [98] reported a simple and effective way to fabricate a ratiometric fluorescence sensor based on dual-emission carbon dots-gold nanoclusters functionalized with dithiothreitol for detecting mercury ions in water samples. Tang et al. [99] developed an electrochemical sensor by combining DNAzyme with quantum dots to detect lead with a limit of detection of 7.8 pM. Yang et al. [100] combined reduced graphene oxide and gold nanoparticles for detection of organophosphate paraoxon-ethyl with a detection limit of 0.5 nM. Cui et al. [101] developed electrochemical acetylcholinesterase biosensor for detection of organophosphorus based pesticides by using adsorption properties of titanium oxide sol-gel, chitosan and reduced graphene oxide based multi-layered immobilization matrix. Nie et al. [102] proposed label-free aptamer surface-enhanced Raman scattering sensor for detection of trace malathion residue; silver nanoparticles were modified with positively charged spermine which served as capture reagents for the aptamer. Yang et al. [103] labelled a specific antibody against E. coli O157: H7 using carboxyl functionalized graphene quantum dots and generated a strong fluorescent signal with the detection limit of 100 cfu/mL as minimum. Parimaladevi et al. [104] designed a sensor using a graphene boosted silver nanoparticles platform through surface enhanced Raman scattering technique which was able to detect the toxic components in real textile effluent. Parvathi et al. [105] reported another sensor for textile effluents based on graphene oxide mediated surface enhanced Raman scattering on gold/reduced-graphene oxide nanocomposites. Chen et al. [106] developed reduced graphene oxide-modified electrodes toward electroanalytical determination of sulfamethoxazole in aqueous environments. Wong et al. [107] simultaneously determined three drugs: terbutaline, nimesulide, and methocarbamol by designing a composite electrode based on graphite oxide-polyurethane modified with beta-cyclodextrin.

5.5 *Future Trends and Recommendations*

Research shows that nanomaterials-based sensors have shown promising results with enhanced sensitivity and response time. Unique properties of nanomaterials like size-tunable and shape-dependent physicochemical properties, allow them to find way for numerous sensor applications. Combining nanomaterials with functional probes can help achieve a reduced detection limit for water pollutants. Nanomaterial based sensors show enhanced sensitivity, quick response, small size, facile sample preparation and detection, and are cost effective. Recent advances in nanomaterial engineering have opened up new opportunities for development of sensors having multifunctions or sensor arrays which can detect multiple analytes. For testing bacteria, differentiation between live and dead bacteria is also a challenge as dead bacteria also give a signal if the cell structure is intact. Although a lot of efforts have been put to commercialize the nanomaterial based sensors but still there is no breakthrough due to challenges at the technical and fabrication fronts. There is still a need of progressive research to improve performance, lower the cost, more facile fabrication methods for better implementation.

6 Conclusions

Sustainability of water quality is becoming more and more challenging because of which it is imperative to find a pollutant detection technique which has an early warning detection, is quick, sensitive reliable, cost effective and can continuously detect contaminants. Though continuous and real time monitoring of water contaminants is hard, remarkable achievements have been made in this area. The use of wireless networks in monitoring system is being introduced but they have their own shortcomings and are in developing stage for water contaminants. Nanomaterial based sensing has gained popularity due to various merits like high sensitivity and miniaturization of device but health/environmental implications of nanomaterials has to be taken care of. Also, hybrid technologies are more appreciated as they are more advantageous than their single counterpart. Recent trend is to integrate the sensing device to smart phones/other portable electronic devices and convert the signals to useful information using embedded system app. A plethora of literature is available for techniques on water contaminant detection but commercialization of the techniques is still a challenge due to instrumental complexity, storage capability and stability of sensing devices. For a successful design of sensor fundamental understanding of sensing mechanism and sensor components is required as degradation, variation in sensor performance and reliable calibration process is a common issue which needs to be addressed.

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Nanofiber Based Sensors for Water Pollution Monitoring

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Abstract Monitoring of water contaminants is essentially required in order to ensure a continuous supply of potable water, as well as, for ensuring protection of aquatic and marine environment. Numerous sensing techniques have been developed, though the key aspect of all of them is the material used for detection. Nanomaterials, and in particular the nanofibers have an edge over other available alternatives owing to the fact that they offer higher sensitivity, ease of design, faster response and recovery as well as high specificity. In the present chapter, we summarize the recent progress in Nanofiber based Sensors for water pollutant identification and monitoring. It reviews the different available nanofiber chemistry and a comparison vis-à-vis their sensing characteristics is presented. The chapter also reviews the fabrication methodology of the various different types of available sensors based on nanofibers for water monitoring. The role of nanofibers for water contaminant monitoring is discussed and its efficiency presented.

Keywords Nanofiber · Sensor · Heavy metal ions · Biological contaminants · Water pollutants monitoring

1 Introduction

Ecosystem balance is a prerequisite for the survival of humankind on earth. There are a variety of ways in which we have been disturbing this balance for our vested interests in a bid to bring about the industrial and economic growth. Water is the lifeline of our society and also a major driving force for maintaining the balance in

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the ecosystem. Beyond doubt, the reason of existence of life on earth is the presence of water and in fact some theories even suggest that the life originated in water [1, 2]. Water happens to be the key necessity for us, as well as, for the marine and aquatic life and hence any non-natural additives to it leads to the disturbance in the ecosystem balance. Therefore, it is vital to protect the water from being polluted and contaminated for the survival of the human race. In order to achieve this, the first and foremost step is to identify or *sense* the existence of the contaminants or pollutants in water, followed by taking remedial action for its rectification and purification. Hefty amounts of money are being spent on water remediation around the globe and still a lot needs to be done.

Water can become contaminated through multiple sources of impurities. These can be of industrial origin, agricultural or due to human interventions. Some of the common impurities are heavy metals ions (lead, arsenic, chromium, mercury and cadmium), hydrocarbons, organic compounds (volatile organic compounds, phenols and dioxins), dissolved toxic gases like sulfur dioxide, nitrogen oxides, particulates, organophosphorus (OP) compounds (pesticides and insecticides), and biological impurities like pathogens [3–5]. All of these ultimately can damage the ecosystem and are unfavorable for the human health and environmental security. Long term exposure to heavy metal and particulate matter is a significant leading factor in causing health problems in the form of various diseases, while on other hand it can cause many disorders in ecological environments (including plant and animal life) and tend to affect the food chains [5, 6]. The heavy-metal accumulates slowly in human bodies and causes various chronic diseases. Therefore, it is imperative to develop economical, sensitive, selective, and simple detection methods to monitor and ultimately remediate these toxic substances from water. Organic pollutants and biological impurities in water also needs to be regulated. The effect of presence of coliforms and pathogens in water leads to many disease like diaorrhea, urinary tract infections and respiratory disorders [7–9]. Organic pollutants on the other hand are more dangerous to aquatic life but can enter human body through these sources. They can lead to cancer risk, reproductive and immunological disorders, neuro-impairment, genotoxicity and increased birth defects. World Health Organization(WHO) has laid down specific guidelines for the control of all water specific pollutants and contaminants [10].

There are a variety of techniques available for identification of water pollutants, such as surface plasmon resonance (SPR) [11, 12], gas chromatography-mass spectrometry (GC-MS) [13, 14], high-performance liquid chromatography (HPLC) [15, 16], inductively coupled plasma mass spectrometry (ICP-MS) [17]. However, many of these are either expensive or time-consuming and require complicated sample preparation. For optimal utilization, the sensing methodology needs to be extremely specific, and suitable for day to day or even field monitoring of water pollutants. We can increase the incidences of contaminant monitoring and process control only if the available detection technology is sensitive, selective and less expensive. In recent years, many different kinds of sensors have been developed for chemical and biological water pollutant detection. The target is to achieve ease of fabrication, low-cost, high sensitivity and selectivity for sensors. The role of materials is extremely important when it comes to sensor fabrication and detection of water pollutants. The choice is extremely varied due to the advancement in the material synthesis techniques though it is often dependent on the type of contaminant whose presence needs to be ascertained. Amongst the available alternatives, nanomaterials, owing to their high surface to volume ratio, are one of the most viable candidate for sensor fabrication [18, 19]. Due to large number of exposed surface atoms, the sensitivity of nanomaterials is far superior than other materials. Despite these advantages, most nanomaterials have a drawback of not being easily addressable as far as device fabrication is concerned. Nanofiber, as a sensor material, have the advantage that they can be easily manipulated and fabricated in the form of sensors [20–22]. In addition, the use of these sensors is also inexpensive (cost-effective) because they are prepared with conventional microelectronics manufacturing equipment and mostly non expensive instrumentation is required for its fabrication.

Herein, we review the role of the nanofiber as a sensor material for water pollutant monitoring and contaminant detection. Nanofibers of various shapes, size, and compositions often exhibit unique and exquisite physico-chemical, optical, catalytic and electronic properties, which are immensely useful for sensor research. A brief introduction on the synthesis of nanofibers is presented followed by the recent developments in the application of nanofiber as a sensor material. Though the list of contaminants as well as materials for their detection is large, the present chapter reviews the application of nanofibers for the detection of following categories of pollutants: (1) Heavy metals, (2) Organic compounds, and (3) biological contaminants. These Nanofiber-based sensing techniques have great impact in the field of environmental monitoring water pollution detection.

2 Nanofiber: An Appropriate Sensing Material

The role of materials in fabrication of sensors is extremely important. Nanomaterials, as mentioned above, are a material of choice for most sensing applications [4]. Nanofibers are 1-D nanostructures, which implies that their two dimensions are in the Nano range (<100 nm) while the third dimension is in the micro/macro range [23, 24]. This provides a unique benefit as compared to their other counterparts in the family of nanomaterials. We all know that it is much easier to control and manipulate micro/macro materials as compared to nanomaterials thus leading to ease in the device fabrication and material integration. Since nanofibers have one dimension in the micro/macro range, it is easier to control them and fabricate sensors using them. They are also an excellent tool for water remediation from different type of industrial and biological pollutants [25].

In the field of environmental monitoring, nanofiber-based sensors offer great potentials in trace contaminants detection due to their large surface area, high surface reactivity and catalytic efficiency, strong adsorption characteristics, readily functionalized, and can be easily fabricated in the form of a nanosensor or nanodevice for ultrasensitive pollutant detection [26]. The type of sensors which can be fabricated with nanofibers as the active/passive material are electrochemical, optical, spectroscopic, thermal, piezoelectric and other detection principles [18, 20–22, 26].

2.1 *Synthesis Techniques*

There are a variety of ways of synthesizing nanofibers which can be broadly categorized into electro and non-electro spinning techniques [27, 28]. Though the conventional jet spinning techniques combine well with the current fabrication techniques, yet in order to achieve the nanorange fibers with controlled morphology, electrospinning based techniques are more preferred [23]. In this technique, a polymer solution is electrically driven into a fiber structure and collected in a non-woven matrix or aligned fiber sheet as shown in Fig. 1 [24, 29]. The technique is extremely versatile and a wide variety of nanofibers can be synthesized using this technique with excellent control over the shape size and morphology of the nanofibers. In order to enhance the sensing capabilities of the fiber, it is often doped with different additives depending on the technique involved to do the analysis. The electrospinning synthesis technique is extremely versatile as it offers great ease of introducing dopant which can be easily fed in the polymer solution to be used for electrospinning. Other synthesis techniques include melt-blowing, bi-component spinning, force-spinning and flash-spinning for the fabrication of polymeric nanofibers [29, 30].

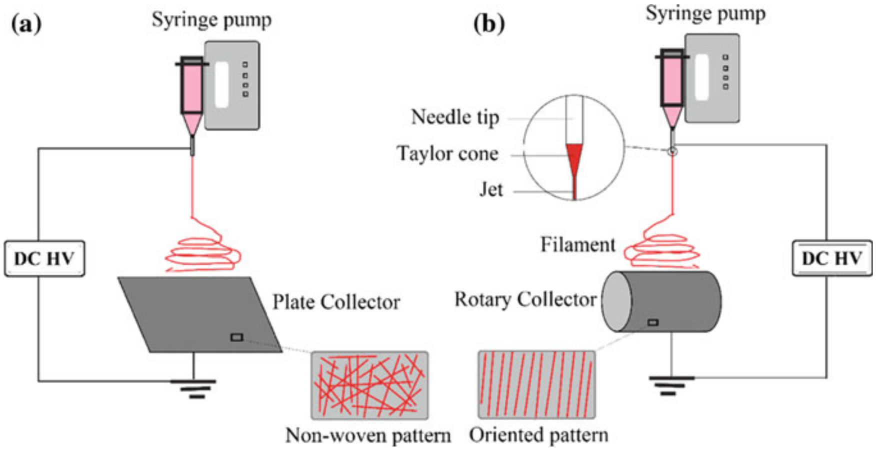

Fig. 1 Schematic of fabricating **a** Non-woven(mat) and **b** Oriented nanofibers by electrospinning. Reprinted with permission from Ref. [29]. Copyright license © under CC BY-4.0

3 Role of Nanofiber in Sensing Water Pollutants

In this section, we will discuss the role of different available nanofiber materials for detection of various water pollutants categorically depending on the pollutants. We have limited this review for the detection of three categories of pollutants, with nanofiber as the sensing material, irrespective of the detection methodology. The selected pollutant categories are heavy metals, organic impurities and biological contaminants.

3.1 Heavy Metal Ions Detection

Due to heavy industrialization and increased usage of electronic goods, heavy metal ions (HMI) induced pollution has reached a grave level. HMIs are one of the micro pollutants that can cause immense environmental problems [17]. Water pollution by heavy metal ions is significant issue also because long-term exposure to these metal ions can result in critical or chronic damage to the brain and the central nervous system, immune system, reproductive and gastrointestinal systems [31]. Major sources of these heavy metal ions are fertilizers and other chemicals produced from industrial or household electronic waste. These HMIs do not decay or degrade with time and have a tendency to accumulate in living organisms. Among different heavy metals, lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As) are considered extremely toxic [32–36]. Even small doses of these highly toxic metals can lead to severe problems on environment and on human health.

Human beings are mainly exposed to these metal ions from air, water and food. For example, the major source of mercury contamination in humans is due to infected fish consumption. Due to the severity of the consequences, it is of utmost importance to detect these heavy metal ions in natural and drinking water and to determine their quantities. It is also important to remediate the water after detection which can be dictated based on the analysis and type and range of contamination. Several international organizations like World Health Organization (WHO), the US Environmental Protection Agency (EPA) and the European Union have enlisted HMIs as the priority substances to be monitored and have set certain permissible limits for their concentrations in water. The permissible limits of contaminants in different water categories as per the Environmental protection agency (EPA), USA and World Health Organization (WHO) are given in Table 1.

The detection of HMIs in water is possible through various different techniques which include the spectroscopic techniques like atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), X-ray Fluorescence Spectrometry (XRF) and others [38, 39]. These techniques are extremely sensitive and can detect very low concentrations(femtomolar) of metal ions also. However, they are very expensive and require high end instrumentation and thus are expensive to manage. Other relatively less intensive techniques include

Table 1 Permissible limits of heavy metal contaminants in drinking and marine water [10, 37]

Heavy metal	Drinking water (μg/l)		Aquatic fresh water (μg/l) EPA
	EPA	WHO	
Lead (Pb)	15	10	82
Mercury (Hg)	2	6	1.4
Cadmium (Cd)	5	3	1.8
Arsenic (As)	10	10	–
Chromium (Cr)	100	50	570

the electrochemical sensing, Surface enhanced Raman spectroscopy, colorimetry and optical methods [35]. The role of nanofibers for sensor application using different techniques is shown in a generalized form in Fig. 2. Mostly nanofibers are used as carriers of sensing materials and in some cases as the sensor itself. Depending on the material the it can be a colorimetric or a florescence sensor. The scheme shown here is generalized and is extended for other types of sensors also.

In the following paragraphs, we will review the available nanofiber-based detection methodologies for different heavy metal ions. The role of nanofiber and

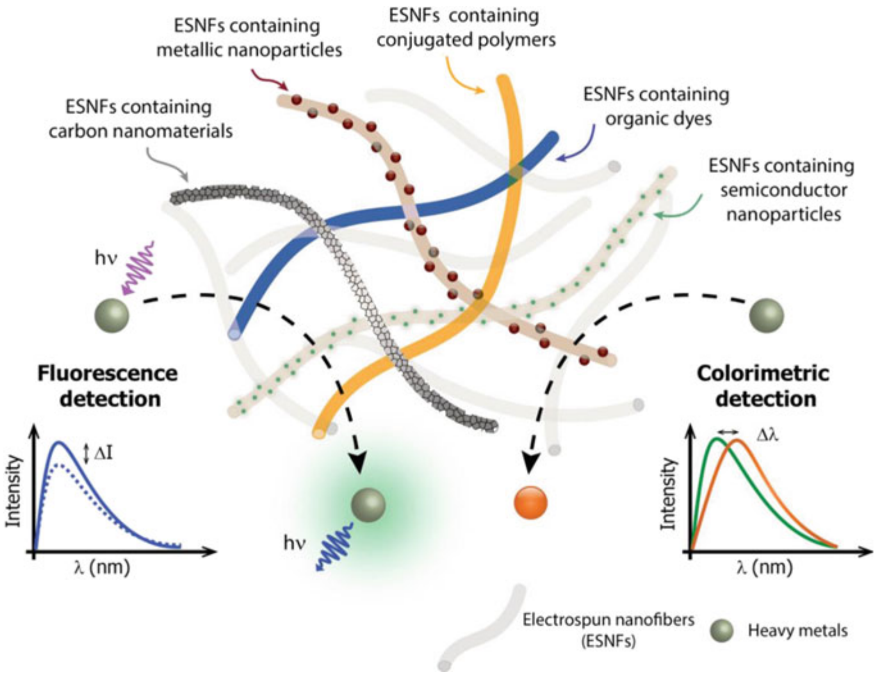

Fig. 2 Scheme of methodology of nanofibers for utilization as Fluorescent and colorimetric sensor for HMIs. Reprinted with permission from Ref. [40] Copyright license © under CC BY-4.0

the sensing material is discussed for detection and the methodology of fabrication of sensor. The level of detection is the key aspect of any developed sensor for heavy metals since they can be harmful even at extreme low concentrations. We have included lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As) for the current discussion since they happen to be most important among all HMIs.

3.2 Detection of Lead

Lead is one of the most common HMI contaminants due to its widespread utilization as battery electrodes and water pipelines. It is non-biodegradable and can continue to accumulate inside the body leading to disturbed immune, reproductive and neurosystem [31]. It is an essential pollutant to be monitored specially for drinking water. Some excellent review exist for detection of lead ions in water [36, 41–44]. There are a variety of ways in which it can be detected include colorimeter, electrochemical sensing, fluorescence spectroscopy and others [40, 42–44]. Some of them are detailed in the following paragraphs.

Colorimetric sensors for Pb detection are most useful due their applicability in field operations. Kim et al. [42] and Terra et al. [40] have provided a good review of different available techniques for fluorescent and colorimetric sensors. Nanofibers based colorimetric sensors have been reported by many researchers. One of the most commonly used material for colorimetric sensor is polydiacetylene owing to its unique optical property resulting from the delocalized π-electrons and the restricted conformational movements along the backbone [45, 46]. Since the biocompatibility of the nanofiber too plays a role during the detection process, Raj et al. [47] have reported a biocompatible curcumin based colorimetric sensor for lead detection. Electrospinning was utilized to fabricate Curcumin loaded cellulose acetate nanofiber membrane and a visual detection limit of 20 μM is reported with color changing from yellow to orange. The advantage of this method is the usage of a biocompatible material thus reducing the chance of secondary contamination of water.

Li et al. [48] prepared a sensor strip utilizing electrospun polyamide-6/nitrocellulose nanofiber nets as membrane to assemble bovine serum albumin decorated Au nanoparticle (BAu probe) for colorimetric detection of Pb^{2+}. It was possible to have a naked eye detection of Pb^{2+} even at a concentration of 0.20 μM. Pb^{2+} could accelerate the specific leaching reaction, thus causing a color change from pink to white (fading gradually with the increasing concentration of Pb^{2+}) which could be observed by the naked eye. In another work, Li et al. [49] have also developed pink to purple chromatic strips wherein they have utilized electrospun nylon-6/polyvinylene fluoride nanofiber nets with l-glutathione-conjugated Au nanoparticle based probes. The sensor strips showed a response time of 10 min and detection range 10–500 μg/dL. In both these works, the large surface area provided by the nanofiber nets, high porosity and tree network structure of sensing material aided in better sensitivity and detection limits.

Zhang et al. [50] have reported amplified detection of picomolar concentration of metal ions by Plasmon-enhanced fluorescence. Similar to SERS, the substrate of polyacrylonitrile/noble metal/SiO_2 nanofiber mats were prepared. This enhanced the fluorescence intensity of conjugated polyelectrolytes which was further dramatically quenched in presence of the picomolar concentration of heavy metal ions including Pb^{2+}. Electrochemistry based approaches also find nanofiber as a suitable material for electrode fabrication/modification. Rafols et al. [51] have used Glutathione as a modifier for screen printed carbon nanofiber electrode for determining the heavy metal ion concentration using voltammetry (see Fig. 3). Glutathione immobilization on carbon nanofiber was achieved through aryl diazonium electografting. It was observed that the carbon nanofiber modified electrodes gave better level of detection as compared to normal screen-printed electrodes with LOD of 3.0 μg L^{-1} and 3.2 μg L^{-1} for Pb (II) and Cd (II), respectively.

3.3 Detection of Mercury

Mercury ions are more toxic than other elements and are non-biodegradable. The classic example of the havoc that can be caused by Hg^{2+} ions is the outbreak of the Minamata disease in Japan. The fish contaminated due to high amount of mercury in sea water was consumed by the locals and resulted in severe neurological and other disorders [52]. Its detection is extremely important for aquatic life as well as

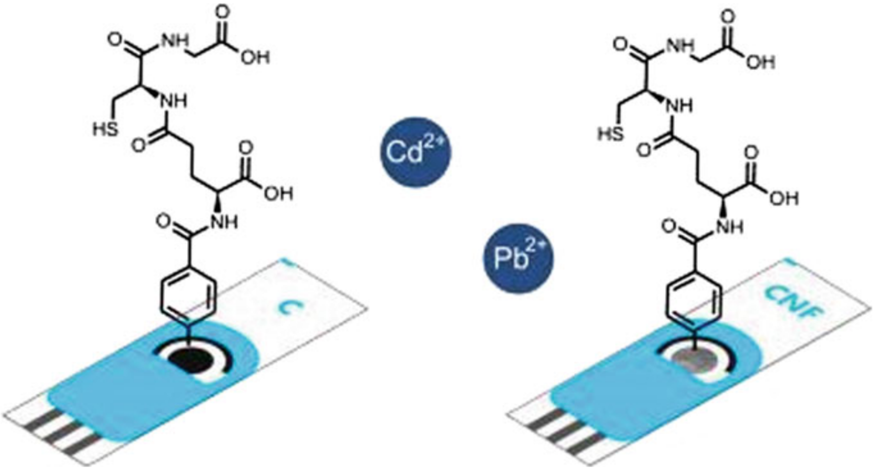

Fig. 3 Schematic of the voltammetric detection of modified screen-printed electrodes with carbon nanofibers. Reprinted with permission from Ref. [51] Copyright © Elsevier Publications

for our well-being. Trace level detection of mercury is reported by various different methodologies including Electrochemical, Florescence spectroscopy, Colorimetry, SERS, ICP-MS and others [38, 53–55]. Some excellent reviews exist in the field of detection of trace level mercury [53, 56]. As per the theme of this chapter, we will limit our discussion to nanofiber related sensors only.

A very interesting article by Senthamizhan et al. [57] offers real time selective visual monitoring of Hg^{2+} ions utilizing fluorescent gold nanoclusters decorated over polycaprolactone nanofibers. For immobilization, the nanofibers were kept immersed in a solution of bovine serum albumin (BSA) coated gold nanocluster for different time periods. The detection was extremely selective towards Hg^{2+} and exhibits stability of over four months. The nanofiber helped in avoiding Au nanoparticle aggregation and was used as a support matrix. Another article by Yu et al. [58] utilizes BSA nanofibers coated with gold nanoclusters and graphene oxide for fluorescence based detection of mercury. The LOD reported was 0.0238 nM. Ma et al. [59] have also reported a highly selective and sensitive fluorescent nanofibrous membrane for Hg^{2+} ions. The process followed was similar to others viz. preparation of electrospun nanofibers of PAN, and then introducing a fluorescent chemosensor dithioacetal-modified perylenediimide on its surface. The reported sensitivity was up to a concentration of 1 ppb of Hg^{2+} ions with excellent selectivity over other heavy metal ions. In general, the methodology followed by most Fluorescent based sensor with nanofibers is similar and is elucidated in Fig. 4.

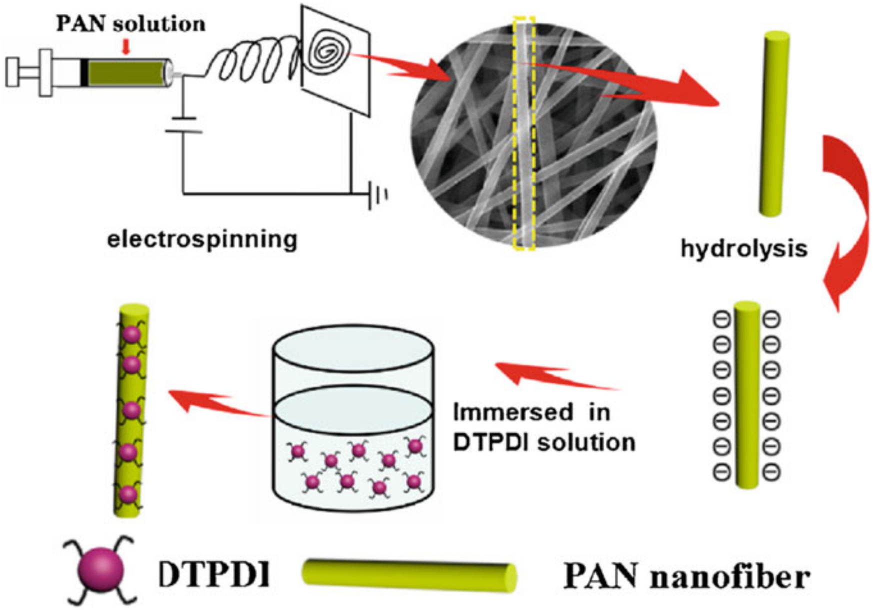

Fig. 4 Generalized Scheme of fabrication of fluorescent sensor for heavy metal ion detection. Reprinted with permission from Ref. [59] Copyright © Elsevier Publications

Another much explored category of sensors for heavy metal ion detection are the electrochemical sensors. Tang et al. [60] reported a reusable electrochemical biosensor based on a platform of ordered mesoporous carbon and self-doped polyaniline nanofibers. DNA was immobilized on these platforms and in the presence of Hg^{2+} ions, the folding was induced which resulted in the increased electrical signal. The conductive nanofibers efficiently transmit these signals resulting in a highly sensitive detection with an LOD of 0.6 fM of Hg^{2+}. Ghosh et al. [61] have demonstrated a highly sensitive precise detector fabricated using Au@BSA coated on Nylon-6 nanofibers which were already precoated with a green emitting fluorophore fluorescein isothiocyanate. The Hg^{2+} ions quench the red emission completely and the same was observed as a signal in the sensor. The authors claim that the sensor can sense as low as 80 counts of ions of mercury. Kacmaz et al. [62] reported an optical chemical sensor device for Hg^{2+} ion detection using ethyl cellulose nanofibers. The nanofibers were fabricated with an azomethine flouroionophore as an additive dye. In the presence of the heavy metal ions the optical absorption spectrum of the fiber changes much more as compared to thin films and it has been demonstrated to detect Hg^{2+} ion concentration as low as 0.07 nM. Another novel approach by Parsaee [63] was to use bio-ultrasound assisted fabrication of Au-NPs using algae and immobilized over PAN nanofibers. The detection was based on colorimetry and fluorescence in presence of the dye Rhodamine-B(RhB). The catalytic reduction of RhB by Au-amalgam causes a color change which could be mapped to the amount of Hg^{2+} present in the solution. The LOD of this method was reported to be 1.10 nM of metal ion concentration. Another interesting work by Sanchez-Calvo et al. [64], reports fabrication of paper based electrochemical sensor for Hg^{2+} detection. The electrode was modified by AuNPs-carbon nanofibers and rGO-AuNPs which increased their selectivity and sensitivity. While nanofibers provided larger surface area, the AuNPs with their affinity towards Hg^{2+} helped in more sensitive recordings. The sensor was able to detect up to 30 nM with CNFs/AuNPs chemistry.

3.4 Detection of Cadmium

Cadmium is another heavy metal which has serious human health hazards and it badly affects renal function and the respiratory tracts [65]. It is present not only in industrial effluents, but also in the electronic wastes like mobile phones and their batteries, computer circuit boards etc. [66]. Many researchers have reviewed the detection of Cadmium using different techniques like SERS, colorimetry, Fluorescence etc. [38, 39, 67].

Promphet et al. [68] have utilized graphene/polyaniline/polystyrene electrospun nanoporous fibers modified electrode and a voltammetry study for simultaneous determination of lead and cadmium. The developed electrochemical sensor reported a detection limit of 3.30 μg/l and 4.43 $\mu g\ L^{-1}$ for Lead and Cadmium, respectively. They also reported reusage of the electrode after simple washing up to ten times.

Migliorini et al. [69] have also studied the effect of polyamide-6/chitosan nanofibers and AuNPs modification of fluorine doped tin oxide electrodes for Cd^{2+} detection. The voltammetry study revealed a linear response in 25–75 μg L^{-1} concentration of Cd^{2+} and a detection limit of 0.88 μg L^{-1}. One dimensional phytic acid doped polyaniline nanofibers were utilized as a modifier for glassy carbon electrode for simultaneous detection of Cd^{2+} and Pb^{2+} using differential pulse anodic stripping voltammetry by Huang et al. [70] group. The reported detection limits were 0.02 and 0.05 μg L^{-1} for Cd and Pb, respectively.

Zhang et al. [71] have reported a green synthesis scheme for the fabrication of AuNPs/CNFs over glassy carbon electrodes by electrospinning for detecting Cd^{2+}, Pb^{2+} and Cu^{2+} metal ions. Square wave anodic stripping voltammetry was used and detection limits reaching up to 0.1 μM. Mishra et al. [72] have deposited graphene oxide nanofibers on screen printed carbon electrodes for the fabrication of HMI sensor. The GO dispersed in PVA was electrospun over SPCE followed by alkaline phosphatase immobilization over these composite fibers. There was an inhibition of ALP activity in presence of HMIs which was used as a scale for monitoring the level of pollutants in water. The detection limit reported was 0.0075, 0.015 and 0.0312 ppb for detecting Hg^{2+}, Pb^{2+} and Cd^{2+} metal ions. CNFs in three dimensional networks were used as a voltammetric sensors by Qin et al. [73]. CNFs were prepared from bacterial cellulose by carbonization at 800 °C, wrapped with Nafion polymer and cast on GCE for trace level determination of Cd^{2+} and Pb^{2+} metal ions. The detection limits are 0.38 and 0.33 μg L^{-1} for Cd^{2+} and Pb^{2+}, respectively.

Microfluidic based sensors are also reported for cadmium detection. Shen et al. [74] have reported a low-cost microfluidic electrochemical carbon based sensor without any modifier and a novel design for heavy metal ion detection. The miniaturized design has a paper flow channel with all three electrodes (working, reference and counter) arranged over it as shown in Fig. 5. The analyte flows through a capillary action and is detected as soon as it comes in contact with the

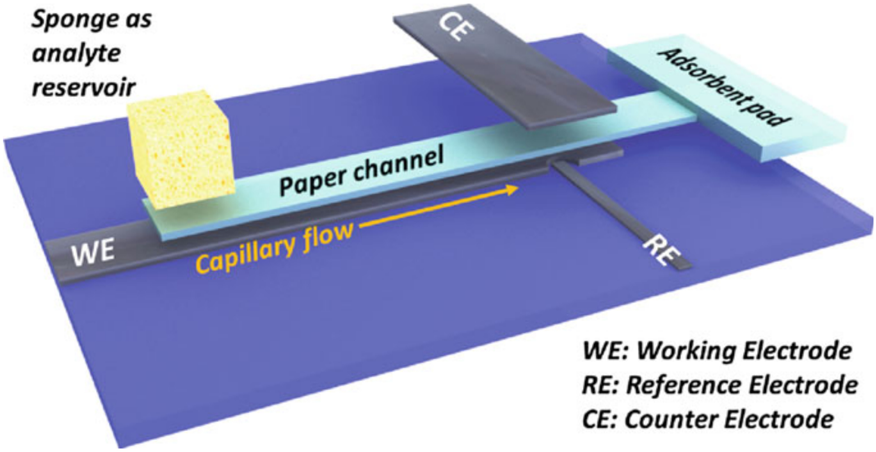

Fig. 5 Schematics of a microfluidic sensor device for heavy metal ion detection. Reprinted with permission from Ref. [74]. Copyright © American Chemical Society

electrodes. The device is quite robust and demonstrates up to 10 repetitive measurements stably. The detection limits achieved were as low as 1.2 μg L^{-1} and 1.8 μg L^{-1} for Cd^{2+} and Pb^{2+} ions, respectively.

3.5 Detection of Arsenic

Measuring arsenic in the aquatic and drinking water is imperative for protecting human health. Drinking water and wastewater treatment facilities are already subject to arsenic regulations to protect human exposure and environmental contamination. There are different methods of determining the arsenic mostly common with the above mentioned heavy metal ions like Colorimetry, Fluorescent spectroscopy etc. [38, 75–78] Some notable ones wherein nanofibers were used are detailed below.

Nellaiappan et al. [79] fabricated AuNPs decorated carbon nanofiber-chitosan modified electrodes for flow injection analysis of As(III) species. The electrochemical detector showed excellent stability, reproducibility and workability with a limit of detection value of 38.3 33 μg L^{-1}. Saikia et al. [80] have reported the use of PANI nanofiber with carbon dot derived from green synthesis route for fluorimetric detection of As^{3+} in water with a detection limit of up to 0.001 ppb. Kempahanumakkagari et al. [81] have provided a review of nanomaterials based electrochemical sensors for arsenic.

3.6 Detection of Chromium

Chromium is another element which can be very harmful for human and aquatic health. It is considered a carcinogen and causes genotoxic effects. It can cause maturity onset, cardiovascular disease and inhibit DNA replication [82]. Its infection in water is mainly due to anthropogenic activities and industrial effluents [83]. It occurs most stably in trivalent and hexavalent states. Many researchers have detected its presence using variety of techniques, most of which has already been detailed above.

Electrospun PVA nanofiber membranes modified with spirolactum-rhodaminene derivatives exhibited high selectivity and sensitivity towards Cr^{3+} ions as demonstrated by Wei et al. [84]. The membrane showed a detection limit of 1 μM for Cr^{3+} in aqueous solutions with excellent adsorption capacity. Wang et al. [85] have utilized a fluorophore, 1,4-Dihydroxyanthraquinone doped cellulose nanofiber film fabricated by electrospinning and deacetylating for Cu^{2+} and Cr^{3+} detection. Interestingly, once utilized for Cu^{2+} sensing the Chromium ion reverses the phenolate-Cu^{2+} reaction thus leading to recovered fluorescence which is proportional to Cr^{3+} ion concentration. The detection range for Cr^{3+} ion reported is 2.5×10^{-9} to 2.5×10^{-8} M in aqueous solution.

3.7 Organic Contaminants

Organic contaminants are released in the water resources mainly from industries. Gasoline and aromatic hydrocarbon solvents are produced and used in large quantities. Many incidents of oil spillage in ocean have been reported. The environmental impact of these spillage often results in loss of aquatic life as well as ground water contamination [86]. To ensure remediation, there is a need for monitoring of these toxic compounds. The common organic contaminants as per the EPA include volatile organic compounds (VOC), pesticides, insecticides, aromatic and chlorinated hydrocarbons [87–89]. Almost all the chlorinated hydrocarbons like chloroethylene pose severe kidney and liver problems while aromatics can harm our nervous system [3].

Surface enhanced Raman spectroscopy-based sensors for organics monitoring has been studied by many researchers. These sensors have the advantage of being extremely specific and sensitive to the analyte being monitored. Wei et al. [90] provide an extremely exhaustive review of the application of SERS sensing technique for environmental monitoring. Though SERS phenomena is observed in many nanomaterials, this section will limit its discussion on role of nanofibers in SERS sensors for organic contaminants. Nanofibers offer the optimum size for the surface plasmon resonance to occur and the SERS sensor to be effective. Chamuah et al. [91] have demonstrated the application of this technique with nanofibers in a simple way by coating PVA fibers with gold and utilizing it as a substrate for SERS sensor (see Fig. 6). They were able to detect the presence of three different pesticides using this platform namely deltamethrin, quinalphos and thiacloprid. Doping is also used by some groups to increase the sensitivity of nanofibers towards SERS. Singh et al. [92] report Ta doped TiO_2 nanofibers with enhanced SERS activity for organics detection.

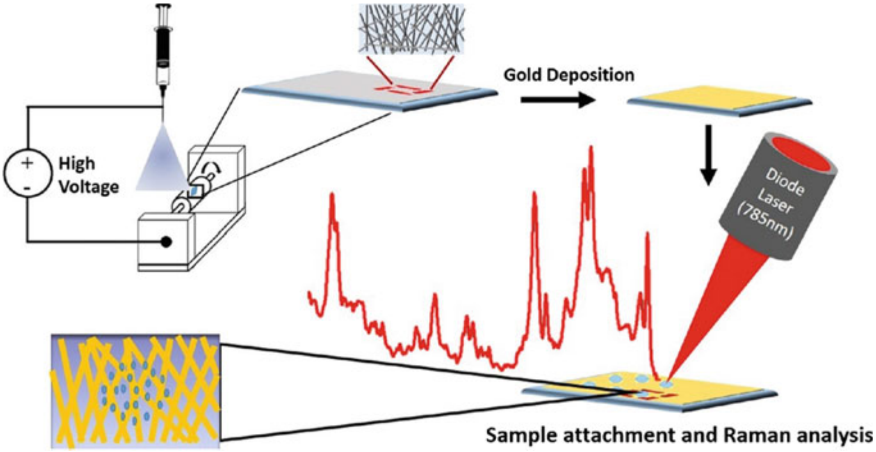

Fig. 6 Schematics of a typical method of utilizing Nanofibers for SERS applications. Reprinted with permission from Ref [91]. Copyright © Elsevier Publications

Gas chromatography is also used for organochlorinated pesticide detection. Vojtech et al. [93] have used polyetherimide nanofibers as sorbents or solid phase microextraction tool and these fibers were then tested in gas chromatograph. They claim that fast sorption and ease of production along with their ability to be utilized for detection of organochlorinated pesticide make these nanofibers a choice material for SPMEs.

Electrochemical sensors also see great potential in nanofibers due to their shape and size. An amperometric biosensor for determining the organophosphate pesticides(parathion) in aqueous system was developed by Bao et al. [94] The biosensor utilizes TiO_2 nanofibers and multiwalled carbon nanotubes along with other entities as sensing platform and is able to detect organophosphate pesticides with a wide linear range, less than 5 s response time and detection limit as low as 10 nM for parathion. Dai et al. [95] have also used the electrochemical technique for determining methyl parathion concentration using electrospun zirconia-embedded carbon nanofiber. The reported detection limit is 3.4 g L^{-1}, which is much lower than many other reported non-nanofiber-based electrodes [95]. Another example of utilizing nanofiber as template for active material is the work of Oliveira et al. They have modified nylon nanofibers with layer-by-layer deposition of polypyrrole and poly(o-ethoxyaniline) and assembled it over the graphite interdigitated electrode. A flow analysis system was developed and it was able to distinguish between contaminated and clear water. The electronic tongue apparatus, as they call it, was able to detect paraoxon, a pesticide in water up to 2.5 ppb concentration. Malathion is another organophosphorus pesticide which can be detected using a polyaniline nanofiber and single carbon nanotube composite modification of graphite interdigitated electrodes. The reported minimum detection limit is 2×10^{-7} M [89]. We can see that Carbon nanotubes have been extensively used as a modifier for the nanofibers and the fabrication of electrode for pesticide sensing using electrochemical sensors [89].

3.8 Biological Contaminants

The microbial world consists of a plethora of different types or classes of microbial agents which can be potentially present in water [96]. The biological contaminants like virus, bacteria, protozoans, fungi, and algae are widespread in the environment around us and are harmless until they get access to the internal sites in a body in sufficiently high concentrations. This access is often through drinking contaminated water and those with immunodeficiency due to some reason are more susceptible to it. Therefore, recognition and identification of a possible waterborne pathogen is extremely important and there are a variety of ways to achieve this [8]. As mentioned earlier, the microbes present in the environment are fully capable of infecting, colonizing, and initiating illness in humans, provided they are able to enter our body and multiply within it. As per the EPA standards, total coliforms should be less than 5% in drinking water. There are a variety of techniques available for the detection of harmful pathogens like Fluorescence detection, Polymer chain reaction(PCR), Electrochemical method, Raman based and microfluidic sensors [9, 97–101]. Nanofibers are an important class of material and can be utilized for not only detection but also for water remediation from pathogens.

The most classical approach of utilizing nanofibers for pathogen detection is the florescence spectroscopy. Most commonly, the fluorescent markers are either grafted in the nanofibers or doped in the polymer solution before fiber spinning. The nanofiber morphology provides the added advantage of trapping the bacteria as well as provide large surface area for the interaction of bacterial cells with the sensing molecules. Zhao et al. [102] have utilized electrospun nanofibers mats of polystyrene-*co*-maleic anhydride with conjugated mannose and tetraphenylethylene as a fluorescent sensor for Escherichia Coli (*E. Coli)*. The sensor, in the test strip format, was able to provide visual sensitivity for concentration as low as 100 CFU/ml of the bacteria. Another recent report by Yu et al. [103], demonstrates an ultrafast and sensitive platform for bacterial concentration detection. They utilize a novel fluorescent molecule with a dynamic layer by layer film on nanofibers of polyvinyl alcohol-co-polyethylene as the platform for immobilizing the bacteria. The bacteria concentration showed a linear relationship with surface fluorescence and detection time as low as 5 min. There are other reports also which use Boronic acid, as dopant for fluorescence based detection of biological contaminants [104].

Luo et al. [105] have demonstrated a nanofiber biosensor based on conductometric immunoassay. The fabricated sensor demonstrated a detection time of 8 min and a limit of 61 CFU/ml and 10^3 CCID/ml for bacterial and viral cells, respectively. Colorimetry is another method wherein the pathogen detection is achieved by color changes when exposed to the bacteria. Yapor et al. [101] have utilized

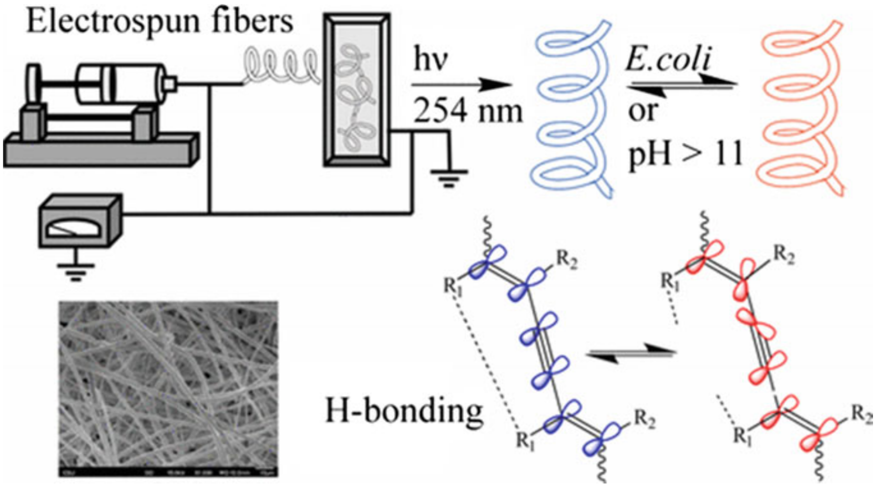

Fig. 7 Colorimetric response of PDA nanofibers in presence of E. Coli bacteria. Reprinted with permission from Ref. [101]. Copyright © American Chemical Society

Polydiacetylene mixed poly(ethylene oxide) and polyurethane nanofibers in mat form to fabricate a colorimetric sensor for E. Coli Bacteria. The detailed schematics is shown in Fig. 7. The color of the nanofiber mat changed from blue to red immediately on exposure to bacteria.

4 Conclusion

Water is of utmost importance for the existence of our ecosystem on earth and hence it is of utmost importance to monitor its purity and save it from being contaminated. In order to enact efficient remediation technique, it is imperative to assess or diagnose the pollutant concentration in water as well as the type of pollutant. The role of material is extremely important for water pollutant monitoring. Amongst multiple available alternatives, nanomaterials offer greater potential to be applied as a sensor material. In the present chapter, we have reviewed the application of Nanofibers as a sensing material for water contamination. Nanofibers have been utilized for fabricating different kinds of sensor like electrochemical, fluorescent, colorimetry, SERS etc. Different aspects and variety of nanofibers have been presented vis-à-vis the type of contaminant which they can detect in water. The nanofibers provide advantage in the form of a high surface area and surface-active material, easier and economical fabrication, as well as field utilization of sensors. They are an attractive and viable material for the fabrication of futuristic sensing devices for water pollutant monitoring.

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