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

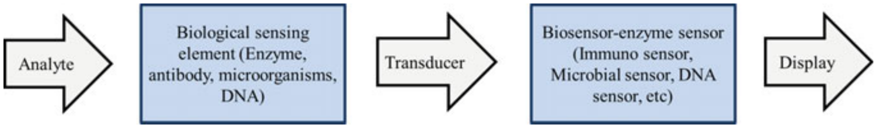

Fig. 1 Components of biosensor

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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