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REVIEW

Biosensors for toxic metals, polychlorinated biphenyls, biological oxygen demand, endocrine disruptors, hormones, dioxin, phenolic and organophosphorus compounds: a review

Madan L. Verma[1] · **Varsha Rani**[2]

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Abstract

The growing pollution by hazardous agents is a major concern due to pollutant transfer to water, air, soil and food. Since actual analytical methods are limited, there is a need for detectors that are more sensitive, more selective, faster and cheaper. For instance, advanced portable biosensors have better sensitivity compared to classical diagnostic devices. Here, we review ultrasensitive detection of pollutants by biosensors. In particular, nanobiosensors display remarkable nanomolar to picomolar detection of various pollutants including heavy metals, pesticides, endocrine disruptors, dioxin, biological oxygen demand and microbial pathogens.

Keywords Biosensor · Nanobiosensor · Pollutant · Environment · Detection · Selectivity · Sensitivity

Introduction

Biosensor technology is one of the emerging technologies that have produced a major impact in the diverse sectors ranging from healthcare, food, pharmaceutical, agriculture and environmental industries (Campana et al. 2019; Verma 2017a; Verma et al. 2010). According to a new market report published in 2020 by Allied Market Research "Biosensors market by product (wearable biosensors and non-wearable biosensors), technology (electrochemical biosensors, optical biosensors, piezoelectric biosensors, thermal biosensors and nanomechanical biosensors): Global opportunity analysis and industry forecast", the global biosensors market size was valued at $17,500 million in 2018 and is expected to reach $38,600 million by 2026, registering a compound annual growth rate of 10.4% from 2019 to 2026 (https://www.alliedmarketresearch.com/biosensors-market).

Biosensors are remarkable portable tools employed for the detection of chemical and biological components of clinical, food and environmental monitoring (Kalyani et al. 2020). Biosensors are endowed with unique properties like higher specificity, rapid response, compacted size, higher selectivity, higher stability, lower cost and user-friendly nature that make them the ideal sensing device. It combines a biologically derived recognition entity with a transducer for developing biochemical parameters quantitatively (Mishra et al. 2018; Verma 2017b). Biological elements can be an antibody, enzyme, cell receptors, nucleic acids and microbes, while the sensing element can be an electric potential and electric current (Jain et al. 2010). Different variants of the biosensors are based on the working mechanism of the transducer used. It can be resonant biosensors, electrochemical biosensors, thermal biosensors, ion-selective field-effect transistor biosensors and optical biosensors (Prasad et al. 2017; Verma 2017a).

Biosensors are being used in different fields such as food product quality control, environmental applications, medical applications, military and bioprocess control as depicted in Fig. 1. The role of biosensors in the food industry is to detect contaminants in the food products, content verification and freshness of the product as well as to monitor the conversion of raw material (Saravanan et al. 2020). The detection of hazardous substances is also a vital application of the biosensors in defence services (Kuswandi 2018; Verma 2017a, b).

✉ Madan L. Verma
madanverma@gmail.com; madanverma@iiitu.ac.in

[1] Department of Biotechnology, School of Basic Sciences, Indian Institute of Information Technology, Una, Himachal Pradesh 177220, India

[2] Department of Biotechnology, Shoolini University, Solan, Himachal Pradesh 173229, India

Environmental hazards can be monitored as well as controlled by using the specific data about the contaminated site provided via biosensors. Biosensors can also measure the pollutants and determine the biological effects of pollutants like endocrine-disrupting effects and toxicity levels (Rodriguez-Mozaz et al. 2004). Thus, the exceptional capabilities and performance of the biosensors provide the excellent services for the detection of chemical and biological components as well as monitoring the clinical, environmental and the food products (Malhotra et al. 2017; Amine et al. 2006).

This article reviews the role of biosensors in environmental monitoring like nitrogen compounds, heavy metals, phenolic compounds, biological oxygen demand, pesticides, insecticides, endocrine disruptors, hormones, organophosphorus compounds and polychlorinated biphenyls. This article is an abridged version of the chapter published by Rani and Verma (2020) in Environmental Chemistry for a Sustainable World (https://www.springer.com/series/11480).

Application of biosensors in environmental monitoring

Pollutants are producing harmful effects globally. Thus, there is a pressing need to develop excellent portable tools which are user-friendly, cost-effective, fast to monitor and control these pollutants. Biosensors work like ultrasensitive tools for the environment impact assessment of ecological, biological and chemically monitoring of the inorganic as well as organic pollutants (Rogers 2006; Sharpe 2003; Rogers and Gerlach 1996).

Sulphur dioxide is a major contaminant of air, mainly produced by biological decay, oceans, forest fires and volcanoes. Anthropogenic sulphur dioxide pollutants are produced from the processes like sulphuric acid manufacturing, combustion of fossil fuels, coal burning and wood

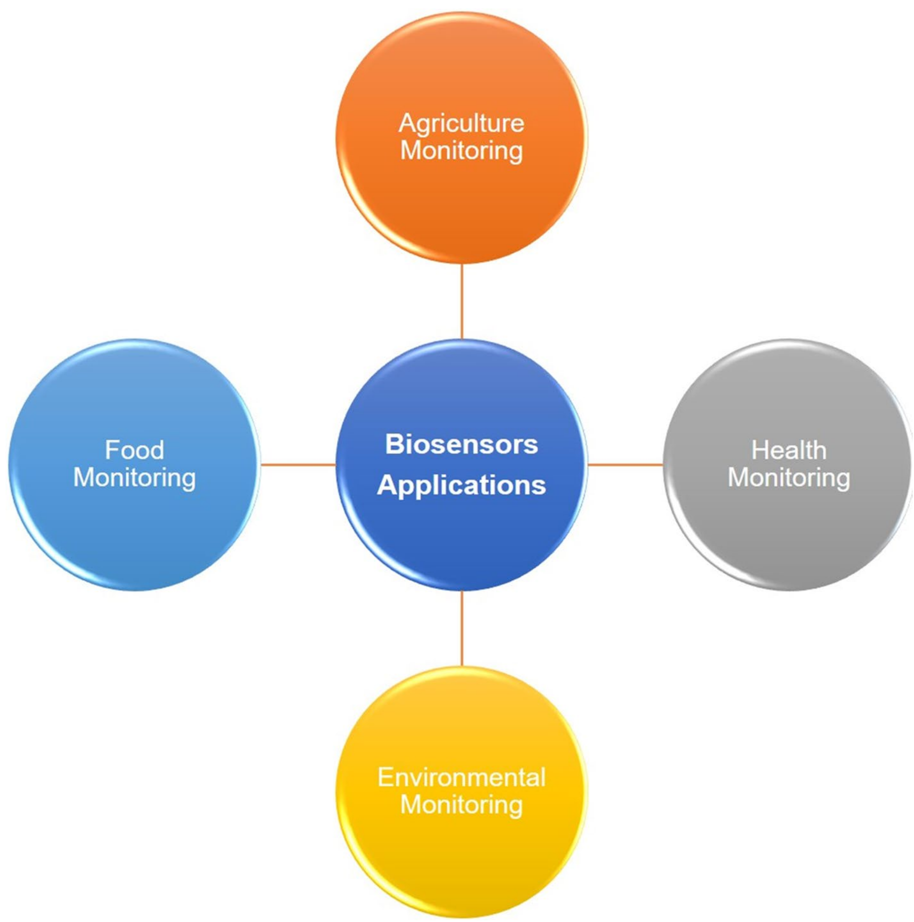

Fig. 1 Applications of biosensors in different fields. Biosensors can be used for the monitoring of various toxicants, pollutants and contaminants in various fields such as the environment, health, food and agriculture

pulp industry (Tayanc 2000). An amperometric biosensor based on sulphite oxidase and cytochrome c developed for the measurement of sulphur dioxide concentration in the flowing gas stream. Biosensor produced linear response of pollutant detection in the range of 4–50 parts per million at the low voltage (Hart et al. 2002).

An electrochemical biosensor was developed for the 30 nanogram detection of formaldehyde, an air pollutant (Herschkovitz et al. 2000). Smoke from exhaustion of automobiles, forest fires and tobacco contains formaldehyde compounds. Table 1 shows the list of some biosensors used for determining the pollutants.

Monitoring of environmental and food contaminants has been reported via sensors based on electrochemical aptamers. In the process of development of nucleic acid-based sensors, aptamers are small, stable and inexpensive biorecognition components. Due to the extraordinary design properties like better elasticity and expediency, aptamers showed excellent sensitivity and selectivity (Mishra et al. 2018). Pharmaceutical industry produces many contaminants whose concentration is ever-increasing and produces adverse effects on human health (Tijani et al. 2016). Although there is a lack of data about the actual concentrations of these pollutants, there is an urgent need to regulate and monitor the resources for sustainable development. The use of miniaturized enzyme-based biosensors is a promising way to tackle these pollutants of high concern (Campana et al. 2019). Monitoring of the environment is a key process to manage the pollution. The most promising approach to monitor the atmospheric pollutants is electronic noses which are made up of a sensor array. Electronic noses work on controlling the pollution as well as odour (Sayago et al. 2019). The role of biosensors in the detection of diverse environmental pollutants has been discussed as follows:

Detection of heavy metals

Heavy metals refer to metals having atomic weights in the range of 63.5–200.6 g mol^{-1} with a specific gravity greater than 5 g cm^{-3} (Srivastava and Majumder 2008). Heavy metals are polluting the environment at the concentration of more than 10 parts per million. It produces adverse effects on human health and environment (Abdu et al. 2017). Heavy metals are ubiquitously present in our biosphere (Verma and Singh 2005; Sharpe 2003). The genesis of heavy metals is due to the anthropogenic and natural sources. Being highly toxic, heavy metals are producing harmful effects on the environment (Dubey et al. 2018). Metal exposure to humans is damaging health including significant deaths. Commonly found metal environmental contaminants are mercury, lead, chromium, zinc, copper and cadmium (Barrocas et al. 2008). A range of heavy metals can be traced via nanotechnology-based electrochemical and optical sensors (Malik et al. 2019; Ion et al. 2010). Bacterial biosensors use resistant bacterial genes for the analysis of heavy metals present in the environment. Metal-resistant genes from the bacterial strains have been isolated as biological receptors (Rathnayake et al. 2009). Durrieu and Tran-Minh (2002) developed an optical biosensor for micromolar detection of cadmium and lead. Enzyme alkaline phosphatase was inhibited to develop this optical biosensor, which was present on the surface of microalga, namely *Chlorella vulgaris*. A biosensor was developed by using microalgae *Tetraselmis chuii* for the volumetrically measurement of 4.6×10^{-10} M copper ions (Alpat et al. 2007). Performance of an electrochemical

Table 1 Biosensors for the determination of pollutants in the real samples

Analyte	Matrix	Transducing and recognition element	References
Pesticides	River water	Optical and immunochemical	*Kalyani* et al. (2020), Rodriguez-Mozaz et al. (2004) and Mallat et al. (2001)
Phenols	Wastewater	Electrochemical and enzymatic	Mazhari et al. (2017) and Nistor et al. (2002)
Heavy metals	Wastewater	Electrochemical/optical and bacteria	De Benedetto et al. (2019), Philp et al. (2003) and Farre et al. (2001)
Biological oxygen demand	River water	Optical and bacteria	Jouanneau et al. (2014) and Chee et al. (2000)
Linear alkyl benzene sulphonate	River water	Electrochemical and bacteria	Borji et al. (2020) and Nomura et al. (1998)
Daunomycin, polychlorinated biphenyls, aflatoxin	River water	Electrochemical and deoxyribonucleic acid	Mishra et al. (2018), Ponomareva et al. (2011), Kara et al. (2008) and Marrazza et al. (1999)
Oestrogens and xenoestrogens	Lake and sewage water plant samples	Optical and human oestrogen receptor	Salehi et al. (2018), Bahadir and Sezginturk (2015) and Seifert et al. (1999)
Alkanes	Groundwater	Optical and bacteria	*Kuswandi* (2019) and Sticher et al. (1997)

The spectacular applications of different types of biosensors is increased multifold in situ environmental samples testing for nanomolar to picomolar detection of different pollutants such as phenols, biological oxygen demand, alkanes, oestrogens, microbial contaminants and pesticides biosensor was optimized by using a chemometric tool (De Benedetto et al. 2019). The performance of this amperometric biosensor for detecting metal ions was based on the robust design of the facile methodology. The model prepared was validated and employed for micromolar detection of different metal ions such as Bi^{3+}, Al^{3+}, Ag^{+} and Ni^{2+} ions. This biosensor was efficiently used as an amperometric detector in the ion chromatographic system (De Benedetto et al. 2019). Thus, biosensor has significantly improved the detection limit of heavy metals.

Detection of biological oxygen demand

Biological oxygen demand is a vital parameter used for validating the water quality. More the value of this parameter indicates the less suitability of drinking water. The method for biological oxygen demand determination is a slow process which is not suitable for online monitoring (Farre et al. 2001). However, biosensor-based methods are the best one for the fast monitoring of biological oxygen demand (Rodriguez-Mozaz et al. 2004; Chee et al. 2000). Biological oxygen demand-based sensors are the most commonly used biosensors for environmental monitoring. A Japanese company, "Nisshin Electric", had developed first commercial biological oxygen demand sensor in 1983, and a number of biological oxygen demand biosensors based on the microbial cells are marked by Medingen GmbH, Dr. Lange GmbH in Germany and Autoteam GmbH; Kelma (Belgium); US Filter (USA) and Bioscience, Inc. (Rodriguez-Mozaz et al. 2004, 2005). A bacterium named *Pseudomonas putida*, isolated from river water, was used for development of biological oxygen demand sensors (Chee et al. 1999). *Vibrio fisheri* genes lux AE and *Escherichia coli* recombinant cell-based biosensors were used for measuring the biological oxygen demand (Nakamura and Karube 2003). An optical biosensor was reported to measure the biological oxygen demand of multiple samples (Kwok et al. 2005). Biological oxygen demand also provides information about the biodegradable organic load of water (Jouanneau et al. 2014). Organic matter of water is being oxidized by the amount of dissolved oxygen in water. The value of biological oxygen demand of surface water ranges from 0.5 to 4 mg per cubic decimetre due to different values in different seasons. Thus, it is vital to monitor the water bodies at regular intervals. Biological oxygen demand determination via biosensors is a step towards the biotechnology advances (Ponomareva et al. 2011).

Kara et al. (2008) reported a biological oxygen demand sensor based on an immobilized *Pseudomonas syringae* in a microcellular polymer. Biosensor showed the detection linearity over the range of 5 to 100 mg per litre at a flow rate of 0.6 millilitre per minute. *Pseudomonas syringae* containing microcellular disc of polymer made this biological oxygen demand biosensor long shelf life and highly stable. Thus, with the aid of the whole micro-organism or its bioactive sub-part used in the development of the biological oxygen demand sensors, they have provided the early detection of water quality in the various natural and storage water systems.

Detection of nitrogen compounds

Nitrites are the widely used compounds as fertilizers as well as food preservatives. Continuous consumption of these compounds is causing serious health problems in human beings. Nitrites compounds react adversely with the haemoglobin component of the red blood cells, thereby impairing oxygen carrying capacity to the human body (Moorcroft et al. 2001). Increased levels of nitrites in water bodies are also affecting aquatic life (Rodriguez-Mozaz et al. 2004). A biosensor has been employed for the amperometric determination of nitrites using cytochrome c nitrite reductase enzyme of *Desulfovibrio desulfuricans.* Biosensor demonstrated a response time of 5 s with a linear range between 0.015 and 2.35 micromolar (Chen et al. 2007). An enzymatic conductometric biosensor was developed for the micromolar determination of nitrites in water samples (Khadro et al. 2008). Electrochemical biosensors have been reported to detect the degradation of DNA and purine metabolites in nanomolar concentrations. This electrochemical biosensor is also used to check the DNA damage and the DNA interaction with an anticancer drug, 6-mercaptopurine (Shpigun and Andryukhina 2019). Thus, biosensors have improved considerably the detection limit of nitrites in the water bodies. It also provides the stability status of biological macromolecules of high importance.

Detection of polychlorinated biphenyls

Polychlorinated biphenyls, a group of manmade persistent organic compounds, are the environmental pollutants (Borji et al. 2020). Such toxic persistent organic compounds are present ubiquitously (Centi et al. 2006). Due to the lipophilic nature, polychlorinated biphenyls get accumulated in the food products easily and affect human health (Gavlasova et al. 2008; Centi et al. 2006). Gas chromatography coupled mass spectrometry is the generally employed method to detect polychlorinated biphenyls in micromolar concentrations (Gavlasova et al. 2008; Centi et al. 2006). Immunoassay-based sensory platforms, particularly enzyme-linked immunosorbent assays, are commonly used for the determination of polychlorinated biphenyls in fields and laboratories in the range of 0.2–0.5 mg per litre (Gavlasova et al. 2008). Pribyl et al. (2006) reported the determination of the polychlorinated biphenyls by a novel piezoelectric immunosensor. Extracts were directly employed without any purification steps for the determination of polychlorinated biphenyls. Lower-cost sensors had been constructed successfully for the monitoring of soil for polychlorinated biphenyls in the range of 1–100 parts per million (Pribyl et al. 2006). Genetically engineered rhizosphere bacterium, namely *Pseudomonas fluorescens* F113Rifpcb, has been employed to degrade the polychlorinated biphenyls (Power et al. 2011). Thus, whole-cell- and immunoassay-based biosensors have shown the efficient methodology for the detection of toxic and persistent organic polychlorinated biphenyls.

Detection of phenolic compounds

Phenolic compounds are the organic pollutants that are present in the polymers, plastic, industrial effluents, pesticides, dyes, resins, drugs, paper, detergents, oil refineries and disinfectants (Luong et al. 2008). Chloro- and nitro-phenols are the highly toxic compounds for aquatic life as well as for human beings (Lin and Juang 2009). Phenolic compounds produce adverse effects in animals and plants because they can easily penetrate in the cell membrane of plants and skin of the animals. Processes like photosynthesis, respiration, biocatalysed reactions, mutagenicity and hepatotoxicity are affected by phenolic compounds (Rodriguez-Mozaz et al. 2006). The US Environmental Protection Agency and European Commission have put phenols in the list of hazardous compounds due to the highly toxic and persistent environment. Scognamiglio et al. (2012) developed a biosensing system for micromolar detection of catechol and bisphenol-A by using laccase enzyme from *Trametes versicolor* and tyrosinase enzyme from *Agaricus bisporus*, respectively.

Effluents of paper, wine and plastic industries had detected the presence of phenols by using a paper biosensor. A bioconjugate of tyrosinase sourced from *Streptomyces tuirus* DBZ39 and gold nanoparticles was used to develop the paper biosensor. Paper-based biosensor was very efficient in the micromolar detection of phenols (Mazhari et al. 2017). Phenolic compound detection from the effluent of the textile industry has been reported from a polyphenol oxidase biosensor. Jenipapo (*Genipa americana* L.) fruit had been used for the development of polyphenol oxidase enzyme-based biosensor, and this biosensor was found very effective for the micromolar detection of the phenolic compounds (Antunes et al. 2018). Thus, biosensors based on enzymes (laccase/tyrosinase) and antibodies are the prominent players employed for the detection of the phenolic pollutants.

Detection of endocrine disruptors and hormones

Glands secreting hormones make up the endocrine system that controls growth, development, regulation and maturation of humans by binding with specific receptors. Hormone mimicking compounds bind the hormonal receptors, and thus, blocking the normal passage for hormones is called endocrine-disrupting chemicals (Tijani et al. 2016). Ovaries in the female reproductive system on maturation produce oestrogen hormone. An example of endocrine-disrupting chemicals is xenoestrogens which bind the receptor of hormone oestrogen and mimic its activity (Badihi-Mossberg et al. 2007). A novel impedance biosensor had been developed to monitor the endocrine disruptors (Granek and Rishpon 2002). Normal homeostasis has been altered via endocrine disruptors (Moraes et al. 2008). The presence of endocrine disruptors in the environment is increasing the incidences of a variety of tumour formation such as breast, testicular and thyroid cancers. Waring and Harris (2005) reported an immunosensor for the determination of estrone, testosterone, progesterone and some organic pollutants. Oestrogens are affecting the reproductive system of the aquatic animals from the last decade. Rapid response action of monoclonal and polyclonal antibodies has been used for nanomolar detection using a biomacromolecular interaction analyser-based chip immunosensor (Samsonova et al. 2004).

An electrochemical biosensor has been developed for the detection of progesterone in the cow milk (Xu et al. 2005). Salehi et al. (2018) had developed a Rapid Adaptable Portable In vitro Detection (RAPID) biosensor platform to detect the chemicals interacting with the human oestrogen receptor. Increasing population and intensive farming has increased the harmful xenohormones in the environment. The use of such compounds has been prohibited by the European Council (Muller et al. 2008). The analysis of hormones exploiting the binding ability of natural receptors for oestrogen had been performed via several electrochemical biosensors (Bahadir and Sezginturk 2015). Thus, immunoassay-based biosensors are predominantly employed for the detection of estrone, testosterone, progesterone and some organic pollutants.

Detection of pesticides

Pesticides are used as insecticides in agricultural practices (Mulchandani et al. 2001). These pesticides contain toxic substances and therefore produce ill effects on human health as well as the environment. Toxic substances present in the pesticides are polluting the water and accumulates in the fruits, vegetables, grains and soil (Simonian et al. 2004; Aspelin 1994). Pesticides contain organophosphates which interfere with the functioning of acetylcholinesterase enzymes causing the failure of the human central nervous system. So, it is crucial to monitor the presence of these compounds in different sources and the environment. The detection of organophosphate compounds had been performed using anhydrolase enzyme sourced from *Altermonas* bacterium (Cock et al. 2009; DeFrank et al. 1993). Dhull et al. (2013) reported enzymatic biosensors for analysing the organophosphorus compounds.

Graphene-based electrodes have been used to monitor organophosphates by using Inkjet Maskless Lithography technique. Biosensor had rapidly quantified the paraoxon insecticide residues present in the soil samples in the nanomolar concentration (Hondred et al. 2018). Tunesi et al. (2018) developed an indium tin oxide-based biosensor for micromolar detection of chlorpyrifos, fenthion and methyl parathion.

Electrochemical biosensors are the most preferred for the determination of different classes of pesticides (Kalyani et al. 2020; Compagnone et al. 2010). A bi-enzyme biosensor has been developed to discriminate between the non-organophosphorus and organophosphorus pesticides (Zhang et al. 2015). Paraoxon has been detected in field analysis using an amperometric biosensor in the micromolar concentration (Arduini et al. 2006). Czech Republic developed a biosensor for micromolar detection of the cholinesterase inhibitors (Matejovsky and Pitschmann 2018). Thus, the enzyme organophosphorus acid anhydrolase-based biosensor is predominately used for the detection of a range of organophosphorus compounds.

Detection of herbicides

Vital process of photosynthesis in plants is inhibited by the triazine- and phenylurea-based herbicides (Singh et al. 2018). The detection of these herbicides can be performed via biosensors which are designed with membrane receptors of thylakoids, chloroplasts, photosystem and reaction centres employed by optical and amperometric transducers (Velasco-García and Mottram 2003). The determination of simazine, an herbicide, has been reported in nanomolar concentration by using an immunosensor based on ion-selective field-effect transistor (Starodub et al. 2000). Kim et al. (2018) had established a direct competitive immunoassay method which is based upon thermistor enzymes for the rapid detection of atrazine, an herbicide. Pollutants like heavy metals and herbicides can be detected by microalgae. These photosynthetic micro-organisms are able to detect the traces of pollutants and are highly sensitive towards the changes in the environment. Cyanobacterial and diatoms are important groups for the detection of pollutants. Sensitivity of diverse pollutants detection was enhanced when bacterial biosensors were introduced with bioluminescence genes (Vismara and Garavaglia 1997). The determination of mycotoxins and herbicides has been performed by electrochemical enzymatic biosensors based on enzyme peroxidase of plant origin. The preparation of modified electrodes with reduced graphene oxide is an advanced option for developing third-generation biosensors, and the limit of detection was 1400-fold better than the conventional immunoassay (Fernández et al. 2017). Thus, biosensor has shown multifold higher sensitivity over the conventional immunoassay.

Detection of dioxins

Dioxins are organosoluble, teratogenic and carcinogenic compounds. It has produced adverse effects on the environment, contaminating food, water, soil and food chain. Dioxins can be transported to longer distances through air and water all over the globe (Yulaev et al. 2001). The use of biosensors is extremely helpful for the monitoring of dioxins. Centi et al. (2007) developed immunosensors for detecting polychlorinated biphenyls in the milk samples. Nanomolar detection of 2,3,7,8-tetrachlorodibenzo-p-dioxin in the ash samples has been reported by Kurosawa et al. (2005). Biosensor immunosensor has shown a quick detection system for the dioxins.

Nanobiosensors

Nanotechnology involves the synthesis and application of the nanoscale materials (Verma et al. 2020). Application of nanomaterials in the integrated part of biosensor covers a vast and diverse array of devices which are employed in different fields ranging from the food to agriculture sectors (Chamundeeswari et al. 2019; Verma et al. 2019; Srivastava et al. 2018; Verma 2017a, b). Nanobiosensor is highly efficient in monitoring the processes of sustainable agriculture in terms of food safety and indiscriminate inputs of excessive herbicides. Due to unique properties of nanoscale materials, nanobiosensors enables the rapid detection of contaminants of soil and water (Kuswandi 2018; Prasad et al. 2017). Nanobiosensors exhibit the excellent detection limit of environmental pollutants in the range of nanomolar to picomolar level (Verma 2017a). Xu et al. (2005) developed electrochemical biosensors for the determination of hydrogen peroxide, xanthine and glucose, respectively. Plant/microbial mediated synthesis of nanomaterials follows the principles of green chemistry that are safe as compared to toxic chemically synthesized route of nanomaterials (Prasad 2014). The use of renewable resources for the construction of nanomaterials is targeted for the monitoring of the environmental pollutants (Srivastava et al. 2018; Prasad et al. 2014,2016). Nanobiosensors are routinely employed for the detection of pathogenic bacteria present in the environment (Jyoti and Tomar 2017). Gas biosensors are employed for monitoring and diagnosing a wider range of diseases in human beings. Highly sensitive and specific nature of gas biosensor provides rapid and accurate monitoring of diseases (Nasiri and Clarke 2019). Quantum dot-based bioluminescence resonance energy transfer sensor was developed for monitoring the target molecules changes and bioimaging in vivo (Hwang et al. 2019). Nanobiosensors are expected to be integrated into small devices for quick real-time monitoring of a plethora of environmental pollutants (Kuswandi 2019).

Conclusion

Extensive agrochemical usages to enhance the agricultural yield not only resulted in pollution of the upper layer of soil, but also caused the pollution of underground water. To meet the needs of increasing population, agricultural produce should be enhanced in an eco-friendly and sustainable way. Safe ecosystems and healthy lifestyles can be maintained by monitoring the toxicants and pollutants present in the environment. Biosensors are the best tools for monitoring various sectors such as food, healthcare, pharmaceutical as well as agricultural industries. Nanotechnology is becoming an integral component of the biosensing system for monitoring various pollutants in the environment. Thus, the performance of nanobiosensors, a reinvigoration of conventional biosensors, has been improved considerably with the intervention of advanced functional nanomaterial.

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