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Prospective Analytical Role of Sensors for Environmental Screening and Monitoring

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Highlights

• Environmental analysis has become more important due to increasing pollution with growing population.

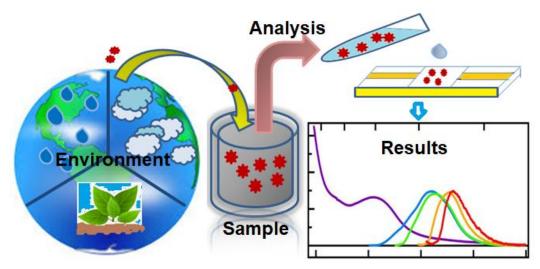
• Sensors are excellent analytical tool for monitoring and screening of large number of environmental pollutants.

• Different sensing platforms had been developed for environmental analysis using various transduction principle and biological elements for detection of various inorganic, organic, and biological analytes.

ABSTRACT

Presently, environmental analysis has become more important due to increasing pollution with growing population. Hence it is obligatory to safe environment from contamination and reduces the influence of hostile elements and procedures. For this purpose, sensors are excellent analytical tool for monitoring and screening of large number of environmental pollutants. They show a prominent potential to match laboratory-based analytical techniques for environmental analysis. Additionally, they are economical and simple to use for immediate or prompt determination of type and concentration of contamination present in the environment. Here is a brief insight into different types of sensors depending upon the transducing elements to detect various inorganic, organic, and biological analytes.

Graphical Abstract



Keywords

Sensors; Environmental; Contamination; Organic; Inorganic; Biological

1. Introduction

For the past few years, environmental monitoring has become more interesting topic for the scientific community. It has been found that about 22% worldwide diseases along with 23% deaths occurs as a result of pollution in environment [1]. Many inorganic and organic chemical impurities, discharged in water, air, and soil, yearly, causes serious health threats to animals, plants, and humans globally [2]. Also, the pollutant quantities that are discharged in environment are also increasing with growing population. Thus, the identification along with the regulation of environmental contamination has emerged as a main problem to the technological society of advanced and progressing countries of the world. Public interest and proper law are mandatory these days for improved environmental control [3, 4].

Numerous harmful waste products are produced by human actions as well as by industries. These compounds can pollute soil, water, or air in addition to effect the environment and public health. These pollutants may pass across different media (like, water to top soil) that indirectly or directly influence human health [5]. Regulating environmental pollution is essential and regarded as a critical component in evaluating quality of environment in rural and urban areas [6]. Therefore, in situ instantaneous controlling and managing numerous pollutants for instance metals, pathogens, radioisotopes, crude oil, volatile organic compounds, and agrarian chemicals

at very low concentration is urgently required in different domains concerning automotive technologies, industrial plants, air and water quality management, health and medicine, natural land/soil/sea etc. [7]. It is mostly granted by scientists, policy makers, and public that consistent technologies for sensing with extraordinary effectiveness are extremely required to solve these problems [8].

The proliferation in the analytes number needs more suitable analytical methods that includes a wide variety of actions, comprising of recognition and monitoring of different gases for instance NOx, CO, NH₃, and mostly perplexing situation of CO_2 [9]. In "off-site" analysis, samples are sent to laboratory for examining. Traditional approaches comprising of various chromatographic techniques (to be specific, HPLC (High performance liquid chromatography) or gas chromatography incorporated into mass spectrometry or capillary electrophoresis) are essentially getting the maximum precision with lower detection limits, but then again are time-taking, costly, and involve many skilled personnel [10, 11]. The invention of biosensors as novel investigative tools intended for "on-site" analysis provides quick, consistent, and complex measurements with lower price [12]. A sensor is a self-contained integrated device capable of giving precise semi-quantitative or quantitative investigative information consuming recognition element which is retained in direct spatial contact with transduction element [13]. Such sensors can be employed by both regulatory consultants and industries to control harmful compounds discharged by dumping of waste products in soil, water, or air but would not contest with certified diagnostic systems [14]. Different biosensors are established for providing adequate material aimed at repetitive sample testing as well as screening. They are integrated with biological analytes, a biological derivative, or biomimic, related with or incorporated in a transducing microsystem or physicochemical transducer [15, 16]. A bioanalytical system is perpetually fixed in construction and has multiple processing steps which differentiate it from biosensors [17]. Selectivity, sensitiveness in addition to limit of detection (LOD) are quite of few main constraints for assessing sensor efficacy [18].

Biosensors are fabricated by the combination of biology, biochemistry, nanotechnology, electronics, and physics, displaying all the preferred features like accurateness, rapidity, constancy, economic, immediate monitoring abilities that facilitated to solve environmental issues [19, 20]. They are designed for bioprocess and environmental management, agriculture, regulation of quality of food, military, along with biomedical applications [21, 22]. Mostly

biosensor systems are practical in pharmacological and medical markets. Consequently, a lot of investigations and progress has been made in this area. Additionally, they offer the opportunity of compactness and "on-site" analysis for estimating pollutants inside composite media following negligible formulation regarding sample. Conversely, sensors determine particular chemicals components along with biological impacts [23]. Nano-configurations also played a substantial role to modify electrodes to enhance their capacity as well as sensitivity regarding sensors. Having large surface area and exceptional catalytic characteristics, nanoparticles currently acted as appropriate candidates intended for sensing technology and expressively affected protocols aimed at detection of different environmental contaminants particularly metal ions, pesticides, and drugs [24].

The presence of emerging contaminants (ECs) including chemicals found in pharmaceuticals, personal care products, pesticides, industrial additives, etc. in environment is one of biggest concerns of our time due to the high potential risk posed to human health. Sensors represent powerful tools for rapid screening of particular chemical compounds (also in low accessibility sites) for highlighting the presence of emerging contaminations at levels where they become harmful in the form of pollutants and challenge environmental sustainability or human health [25]. Advancement of sensing technologies is required for accurate monitoring and control of such pollutants, which must meet strict necessities with reference to sensitivity, robustness, selectivity and precision, and should integrate into existing systems to enable decentralised, high-frequency analysis [4].

The objective of this review is to present significant scientific contribution to development and advancements in sensors and their analytical role in environmental pollution screening and monitoring. The topics cover various types of sensing platforms that had been developed for environmental analysis including using various transduction principle and biological elements for detection of various inorganic, organic, and biological analytes. The main purpose of this review is to highlight the design, functioning, and performance in the analysis of environmental contaminants using different types of sensors. In this perspective, this review presents a survey on latest literature on advances in sensors for a range of contaminants (metals, nutrients, organic compounds, pesticides), with some indication of performance (e.g. limits of detection) along with their potential applications.

2. Sensors types and their phenomenon

The biosensor production to monitor environmental pollutants, pathogens, and toxic elements has boosted the workable advancement of society because of the problems caused by pollution to the environment. Different sensors are described for detecting together with monitoring numerous environmental pollutants, summarized in Table 1. They are categorized into different types based on the signal transduction and biological elements. Many different biochemical reactions and phenomenon are exploited in sensors. The transducer possibly optical, physicochemical, or piezoelectric substance which is utilized for conversion of biological signals obtained from recognition elements to optical or electrical signals (Fig. 1) [26]. Biological elements include antibodies, enzymes, microorganisms, organelles, and tissues.

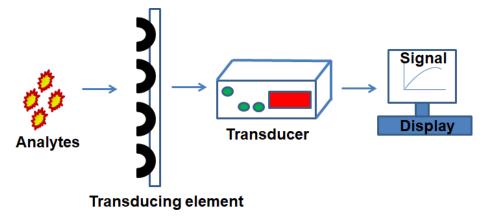


Fig. 1. Basic components and principal of biosensor.

Table 1

Types of sensors along with specification and applications.

Sensors	Transduction	Specification	Applications	Ref
	principle/Elemen	t		
Optical fiber and	Optical	Principle for emission of	Detecting and quantifying food	[27, 28]
surface plasmon		light where active	toxicants, heavy metal, water-	
resonance		bacteria reacts towards	along with foodborne pathogens	
biosensors,		any chemical, physical,	and monitoring environment	
Bioluminescent		or biological change OR		
sensors,		immobility of		
Colorimetric		biomolecules tagged		
sensors,		with fluorescent		
		molecules in the course		
		of reaction by analyte,		
		Observe modification in		

		optical density regarding	
		sample in reaction	
Amperometric,	Electrochemical	A current change	Estimation of urea, carbon [29
conductometric,		between standard and	dioxide, urea, pesticides, and
and impedance		functional electrode	heavy metals
biosensors		occurs due to redox	
		reaction, Evaluates	
		electric conductivity	
		change in medium that	
		depends on analyte	
		entry, consequently	
		alters ionic species	
		concentration through	
		assessing electric	
		conductivity while	
		reaction of analyte with	
		medium takes place,	
		Estimates changes in	
		resistance or	
		conductance after	
		biorecognition inside	
		medium	
Quartz crystal	Piezoelectric	Observes variations in	Sensing of nucleic acid and [30
microbalance		oscillating frequency that	cellular research
biosensors		occurs when analyte	
		absorbs or de-absorbs,	
		resulting in production	
		of current in	
		piezoelectric substance	
Immunosensors	Antibodies	Amplification and	Clinical chemistry [31
		detection of reaction	
		between antigen and	
		antibody	
Aptasensors	Aptamers	Signal amplification on	Detection of small toxic [32
		interaction with analytes	molecules used in agriculture,
		·	heavy metals, also aquatic

Genosensors	Nucleic acids	Produced through	Evaluating protein and non- [33]
		amplifying DNA via	macromolecular compounds
		PCR (polymerase chain	
		reaction)	
Enzymatic	Enzymes	Reversible oxidation or	Detection of herbicides and [34]
biosensors		reduction onto electrode	pesticides, and environmental
		through applying active	screening
		potential	
		(electrochemical)	

Environmental monitoring needs constant quantification of large number of products or analytes at various different sites, and thus work and cost involved is huge. Traditional examination indicates problems of typical sampling and following sample stabilization, transportation to laboratory, preparation for study, measurement etc., is awfully time taking and unsuited for continuous monitoring of certain analytes in environmental analysis. Sampling is the critical steps because of trouble in obtaining a representative sample. Furthermore, stabilization of few analytes, for instance sulphide, is not easy task and special care must be taken. This difficulty could be overcome by execution of on-situ analysis which would remove the requirement of representative sample and evade the risk of changes in chemical form and analyte concentration during transport and sample pretreatment. Sensors have made considerable and important impact to on-site pollution monitoring. Depending on the transduction principles, few sensors for detecting analytes via generating signal which is measurable are given below:

2.1. Optical sensors

The field of plasmonics has shown extraordinary capabilities in realizing highly sensitive and accurate sensors for environmental monitoring. Optical sensors are extensively used in many analytical practices, because of their easiness in preparation and signal attainment, economical, and rapid response time [35]. Modern optical sensors need no wire connections with detector or complicated and energy-consuming hardware, allowing development of wireless sensor aimed at in-field and online investigation. Optical sensors depend on the absorbance, reflectance, luminescence, refraction, and emission of light produced during a biochemical reaction [36]. The utilization of optical fibers in sensors is promising for environmental monitoring, by reason of benefits counting light weight, durability under extreme temperatures and pressures, resistance to electromagnetic interference, high transmission rate, flexibility, and small size [37]. The usage of optical fibers allows spectroscopic analysis for remote sensing and real time monitoring at site

of interest. They permit analyst to bring the laboratory to the sample instead of the sample to the laboratory as is usually the case. It might overcome or minimize above-mentioned problems of analyte instability [38]. Analysis is carried out employing interaction between analytes and optical field consuming fiber optics probes. These probes consist of at least two fibers. One fiber is connected to light source that produces excitation wavelength and the other one is connected to photodiode to measure optical density change at suitable wavelength. Signal produced is comparable to analytes concentration [39]. Employment relevant to optical sensors are favorable for environmental monitoring attributed to benefits for instance resistance to electromagnetic interference, light weight, stability under high pressures and temperatures, extraordinary transmission rate, flexibility, and small size [37]. Thus, these new analytical tools enable extensive and precise determination of wide variety of samples to analyze environment.

2.2. Electrochemical sensors

These sensors measure the signal produced due to the reaction between the sensing surface and the analytes. Electrochemical reactions taking place at electrodes in sensors transform this receptive information to quantitative and qualitative and electric signals which is also based on amperometry (change of current), potentiometry (change of potential), and conductometry (change of conductance) measurements [40]. These sensors are used for effective and sensitive detection of environmental contamination, such as pesticides, herbicides, heavy metals, dye compounds, and pharmaceutical compounds even at low sample volume. These sensor systems are selective, accurate, sensitive, speedy, and user-friendly diagnostic tools for environmental analysis [4].

2.3. Piezoelectric sensors

These sensors also called mass-centered biosensors including estimation regarding change in mass at the time of reaction between various analytes [41]. The mass change of modified piezoelectric surface due to accumulation of analyte produces mechanical vibrations and gets converted into electrical signals [42]. These sensors are applied to assess contamination rapidly with no pretreatment of sample at low cost [43].

2.4. Immunosensors

In recent years immunosensors made substantial growth, compelled by the requisite for quick, transportable, sensitive devices for the detection and monitoring of organic pollutants in environments [44]. They are affinity based simple and reliable diagnostic tool depending on the

chemical reaction between antibody/antigen as biological element which is immobilized in transducer surface. They are used for identifying antibodies specifically as well as precisely that indicates presence of toxic components [45]. Various attempts are made to attain a low detection limit by advancing different signal amplification approaches, eradicating the interferences, and reducing analysis cost [31].

2.5. Aptasensors

Aptamers possess improved functionality and constancy to detect and monitor environmental pollutants as compared to antibodies. Owing to enhanced chemical and synthetic simplicity, they are employed to fabricate sensors to be utilized for detecting dissimilar environmental contaminants including small toxic molecules used in agriculture, heavy metals, in addition aquatic bacterial pathogens [32]. Aptasensors utilizes the capability of aptamers of compacting into definite structures that permit them for binding with numerous analytes owning significant affinity along with specificity [46]. The particular sensors offer on-site, rapid, and single, in addition to complex recognition of analytes which is useful in pollution control, industrial waste management, and environmental toxicology.

2.6. Genosensors

Nucleic acids are the main influential and multipurpose element of genosensors. DNA probes or primers are the sensing materials in these sensors that display particularity concerning entire structure of DNA. Such DNA fragments (primers or probes) could be produced via nucleic acid amplification through PCR (polymerase chain reaction) [47]. They are further functionalized to enhance their stability and enable their introduction into biosensors to plays the role of receptor of specific biological and/or chemical species for environmental pollution monitoring [48]. Genosensors integral chemical and physical stability together with favorability for speedy screening along with high selectivity, sensitivity, simplicity, and reliability which is found to be very useful for detecting probably injurious pollution present in environment, inspecting food quality along with safety, in addition to recognition regarding toxins, allergens, contaminants, detergents, disease-causing microorganisms, etc. [49].

2.7. Enzymatic sensors

Among many biological elements utilized in sensor development, enzymes-based sensing have fascinated and recognized as an inventive technique for quantitative and qualitative environmental analysis. In these sensors, enzymes are used as biological element immobilized on transducer surface to sustain enzyme activity [19]. Enzymes specifically react and remove pollutants by precipitation or transforming them into other products which are more liable for treatment. Enzymes show extraordinary selectivity to substrates to detect a single analyte in composite matrices. These sensors present sensibility, high reproducibility, and selectivity for less time-consuming and cheap analysis including limited steps for sample preparation that is valuable for monitoring the negative environmental impacts [50].

3. Advantages of sensors over conventional approaches for environmental monitoring

Development in science and technology is a double-edged sword. It not only brings ease to people but also threatens the human environment. The environment pollution has extended to a point where it cannot be ignored. Conventional methods and processes for protection or monitoring of environment could no longer meet the increasing environmental pollution [51]. Traditional analytical techniques, for instance high-performance liquid chromatography (HPLC), UV-vis spectroscopy, atomic absorption spectroscopy, liquid chromatography-mass spectrometry, and others, have been extensively exploited to detect numerous analytes. Sometimes low concentration of these analytes could be sensed efficiently [52]. Though, these instruments are costly and require difficult operation. Additionally, recognition through these devices is time taking process. These aspects limited various usages of above techniques aimed at quick, easy, and trustable analysis and revealing of several toxic analytes. There are several challenges faced in employing traditional methods for instance such low concentration of analyte prior to identification, the presence of interfering species, and ingrained protocols for sample collection.

Progress in sensors lead to environmental monitoring lead to analysis in a more reliable manner with greater convenience, specificity, sensitivity, outcome reproducibility, speed, non-labor-intensiveness, automation, and cost-effectiveness [53]. Such sensing devices are lightweight and portable, have low limits of detection, require less amounts of sample, and can be refined to develop rapid, economical, and fast devices required for point-of care analysis.

With advancement in the field of nanotechnology and materials science, numerous functional nanomaterials particularly nanoparticles, quantum dots, carbon nanotubes, graphene, and other two dimensional nanomaterials, have been used to fabricate different sensing platforms for environmental applications [54]. For example, surface modification of GCE (glassy carbon electrodes) by nanomaterials helped their usage as electrochemical sensors for label-free

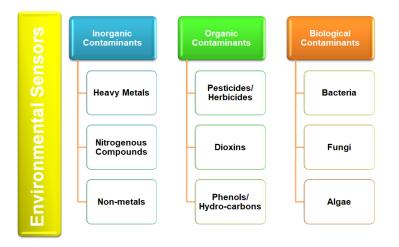
detection [55], consuming fluorescent quantum dots or nanoparticles in fluorescent sensors results in high-performance detecting via fluorescence quenching [56], and modification of active substrates based on metallic nanoparticle could affect surface-enhanced Raman scattering detection as low as single molecule level [57]. Though, detection of real environmental samples is still not easy through applying these fabricated sensors due to limitations in rapid and in-situ operation.

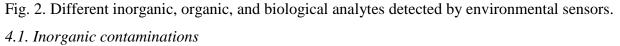
To deliver more wide-ranging, accurate and exact data sets regarding environmental monitoring, customary typical chromatographic practices have been integrated with various detectors in sensing technology [58]. Even though traditional identification techniques are still in use used to detect contaminating agents with high degree of reproducibility and sensitivity, but these techniques are not useful in a field-deployable platform. In addition to the complex instrumentation of traditional methods, they need highly skilled personnel, they are expensive and short shelf life of some reagents restricts their use in remote areas [11]. Some of conventional methods necessitate significant pre-sample treatments that results in long readout times, and ultimately delayed responses.

Consequently, latest systematic and scientific achievements should be used for improving our environment. Employing high-tech approaches along with unceasing sensing innovation, communication, and embedded technology has great research significance and need to be updated accordingly.

4. Environmental applications through sensors

The increase in disposal of harmful contamination into the environment urges the scientific community to develop more prompt and effectual approaches for analysis [59]. Therefore, it is essential to construct monitoring systems for continual observation of the environment. This necessitates the improvement of present techniques and suitable systems in the field of sensors. Such sensors could be used for prompt and immediate environmental control of contaminations produced by different human activities and industrial sectors. The most important characteristics of sensors are precision, accuracy, selectivity, sensitivity, drift, and response time [60]. Sensors employed in environmental applications to detect and measure particular inorganic, organic, and biological contaminants (Fig. 2) are described below:





Inorganic contaminants generally found in water occur naturally or produced by man by mining, industrial or agriculture activities. They include toxic metals, nonmetallic composites for instance nitrites, cadmium, lead, or phosphates in addition to different salts and nutrients [61]. Monitoring of inorganic contaminants, particularly heavy metals are potentially amongst the most significant uses of sensors for analysis of environment. Generally, biosensors based on paper, silicon, polymer, or glass are used to detect inorganic wastes electrochemically or optically (primarily calorimetrically) [62-64]. Environmental samples contain inorganic wastes in very low concentrations, therefore it is required to enrich or preconcentrate the sample to improve sensor diagnostic performance [65]. Some important inorganic contaminants are described below:

4.1.1. Heavy metals

Heavy metals ions had been discovered inside various sources comprising beverages, food, plants, soil, as well as in natural waters. Pesticides, combustion of fossil fuels, fertilizers, smelting, mining, and leakage from cookware or utensils cause heavy metal pollution [66]. Furthermore, activities by human, heavy metal natural resources for instance weathering of metallic rocks, volcanic explosions, plus wood fires. When they get released into atmosphere, through any sources, they get accumulated as they are biodegradable and turn out to be lethal at high concentrations [67]. Heavy metals pose a serious problem for human health and constant exposure for long period could cause prolonged poisoning, nephrotoxicity, growth abnormalities, cardiovascular ailments, encephalopathy, as well as cancer. Their exposure is also dangerous for

terrestrial and aquatic plants, in addition to animals even at low concentration [68]. As a result, prompt and consistent on-site recognition of such ions is critical. Sensors with biological elements for sensing are as well utilized to detect heavy metals. These biological elements are resistant to heavy metals, therefore used as receptors in sensors. The detection of heavy metals electrochemically is a very promising approach due to its high efficiency and sensitivity [69].

Mercury Hg (II) ions are detected using potentiometric sensors inside different samples. SPE (Screen-printed electrode) fabricated with ionophore of zirconium antimonate is used to estimate ions comprising mercury (II) potentiometrically at 25 °C in 5×10^{-8} to 1×10^{-1} mol/L concentration range of Hg (II) with LOD equals to 5×10^{-8} mol/L. This modified sensing device was effectively employed for determination of these ions within diverse samples for instance in rivers, tap, and waste waters released from industries, dental amalgam waste, samples collected from tissues of fish, and evidenced as rapid, simple, and accurate method [70]. A simple, sensitive, and selective method was developed to detect Hg²⁺ ions exploiting fluorescent 2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1H)-one (TDHO) derivative based organic nanoparticles TDHQNPs. In optimum conditions, fluorescent investigations showed a selective interaction with only Hg²⁺ in the presence of coexisting species. The TDHQNPs interaction with Hg²⁺ leads to fluorescence quenching of TDHQNPs because of electrostatic metal-ligand interaction. The LOD was estimated to be 0.00329 µg/mL within concentration range varying from 0 to 100 µg/mL. Furthermore, fluorescence quenching results were used to develop an analytical technique for estimating Hg^{2+} in real samples [71].

Mercury (Hg(II)), Arsenic (As(III)), and lead (Pb(II)) can be detected electrochemically in water utilizing nanostars of gold (AuNSs) in addition to its nanoparticles (Fig. 3). The surface area of nanostars is four times greater when compared to nanoparticles that contribute to sensor functionality. SWSV has been employed to detect Hg (II), As (III), and Pb (II), and Ip, peak heights were recorded. Values of Ip exhibited an exclusive drift towards every analyte. Ip decreases for Hg (II) intensely at high loading of nanoparticles and negligibly with nanostars and nanoparticles have no substantial effect on values of Ip for Pb (II). This showed loading and shape, both have an influence on detection efficiency regarding heavy metal and can applied to detect ions in contaminated water of ground [72].

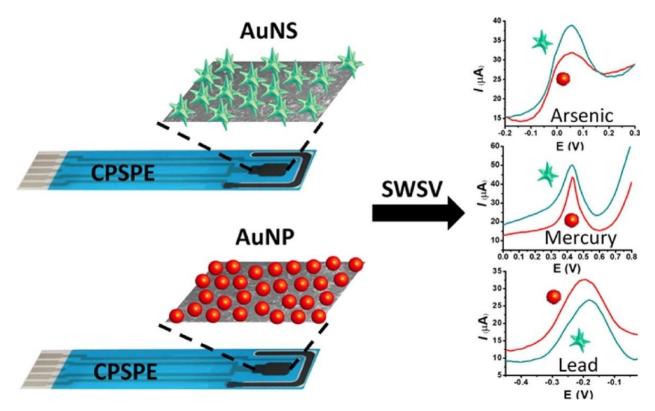


Fig. 3. Detection of mercury, lead, and arsenic employing electrodes of carbon modified with gold nanostars and nanoparticles electrochemically. Reproduced from reference [72], with permission from Elsevier 2022.

Electrochemical sensor was developed using graphene paste electrode modified by polyglycine (PGMGPE) aimed at Pb (lead) (II) and Hg (mercury) (II) quantification inside water. DPV (differential pulse voltammetry) and CV (cyclic voltammetry) had been utilized for investigating electrochemical performance concerning metal ions. Peak current changed with increasing concentration in a linear manner resulting in 0.8 μ M LOD for Pb (II) also with 6.6 μ M LOD for Hg (II). Thus established sensor displays better selectivity, stability, sensitivity, and low LOD, as well as was magnificently used for determining heavy metal ions in water [73]. Carbon electrode adapted by composites of chitosan and graphene oxide along with ion imprinting polymer (IIP) was used to fabricate sensor to detect Cu (II) with high sensitivity and selectivity. GO enhanced the electrode electrical conductance and intensify signal. Linear relationship was perceived starting from 0.5 to 100 μ molL⁻¹ in optimum situations. It showed 0.15 μ molL⁻¹ LOD and detection was barely obstructed by interfering cations of metal. Sensor exhibited exceptional reproducibility through repeated differential pulse anodic stripping and its efficiency was confirmed in river/tap water with satisfactory rates for recovery [74].

SPCE (Screen printed carbon electrode) consuming carbon black (CB) along with AuNPs (gold nanoparticles) had been used for electrochemical aptasensing of cadmium Cd (II) as shown in Fig. 4. On Cd (II) contact, the restrained 36-base thiolated ssDNA aptamer attached to SPCE-CB-AuNPs experienced configurational modification which alters the electrochemical response. This sensor measured Cd (II) within range of 1 to 50 ppb, having 0.14 ppb LOD measured by SWV (square wave voltammetry). This had also been used for analyzing samples containing real samples of water as well as established better reproducibility and exceptional precision to Cd (II), approving probable usage to evaluate Cd (II) present in environment [75].

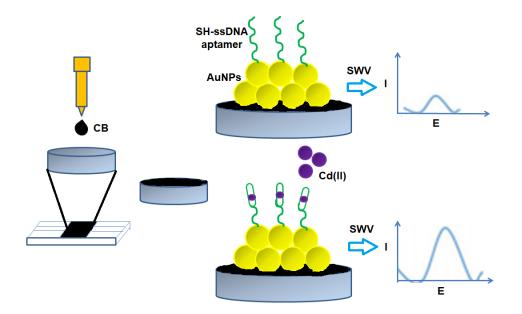


Fig. 4. Schematics of detection of cadmium by aptasensor.

As (arsenic) (III) recognition, in water had been performed by using electrochemical aptasensor. This sensor was developed by immobilizing hundred-base thiolated Ars-three aptamer on nanosystem consisting of carbon nanoparticles/gold nanoparticles along with modified GCE (glassy carbon electrode). This sensor identified As (III) present inside water with LOD equals to 0.092 ppb, being selective when interfering ions like Cd, Cu and Hg were present [76].

Cadmium Cd (II) ions in water were detected and adsorbed by an optical sensor (Sulphur with organic ligand attached on mesoporous silica monolith) with specific color formation. The sensor showed an improved sensitivity as well as distinctive spectral and color response to Cd (II) ions present in aqueous medium. The sensor provided an easy process for ultra-tracing of Cd (II) ions optically without consuming complex instrumentation. LOD of Cd (II) ions as well as their

adsorption capacity was $0.36 \mu g/$ and 167.33 mg/g, respectively under optimized conditions. The developed sensor has also the ability to sense ions of Cd (II); nevertheless different metal ions exist in high concentration. Furthermore, adsorbed Cd (II) ions were totally eluted by treating it with 0.30 M HCl and instantaneously redeveloped in original form after washing with water for next task. Consequently, the optical sensor is reusable and effective for numerous detection and adsorptive removal applications [77].

An ecological colorimetric with fluorescence turn-off sensor have been designed to recognize ions of copper (Cu²⁺) rapidly inside water consuming "*benzildihydrazone-N,N'-bis(2-hydroxy-4diethylamino-1-formylbenzene)* (L)" which is an organic Schiff base ligand. Fluorescent along with UV-Vis evaluation confirmed interaction between L and numerous ions of metal and displayed promising binding of both deprived of any interference of other ions of metals. Due to binding yellow color changes to slightly red. Acquired complex of L-Cu²⁺ could be utilized to detect cyanide anion (CN⁻). The corresponding LODs for Cu²⁺ was estimated as 7.3×10^{-10} M and for and CN⁻ was 1.5×10^{-7} M. Concentrations of these ions measured inside samples of real water evaluates diagnostic ability of established system (Fig. 5) [78].

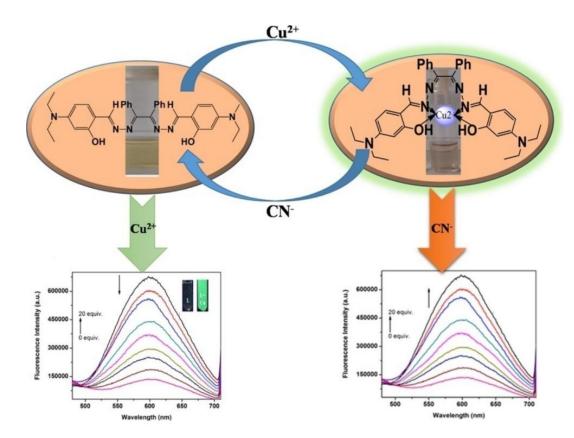


Fig. 5. Fluorescent spectra regarding L (10 μ M) obtained by adding Cu²⁺ ions (approximately 20 equiv.) inside methanol (MeOH)-water (H₂O) (2/1, volume percent). At room temperature, on exposure to 420 nm L displays significant release at 600 nm. On consecutive addition of ions of Cu²⁺ to L, intensity of emission corresponding to L presented continuous reduction. Intensity decreases by 90%, when 0-20 equiv. ions of Cu²⁺ were added. The emission intensity reduction is because of interaction of L with Cu²⁺ ions. At room temperature, fluorescent spectra regarding L-Cu²⁺ (having volume equal to 10 μ M) on adding CN⁻ ions (approximately twenty equiv.) into MeOH-H₂O (2/1, volume percent). The results validate that obtained complex of L-Cu²⁺ possibly are employed for effective sensing of ions particularly CN⁻. Reproduced from reference [78], with permission from Elsevier 2021.

An isolation technique is suggested to develop innovative electrochemical sensor for evaluating toxicity of ions including Cd²⁺, Cu²⁺, Zn²⁺, Ni²⁺ Fe³⁺, as well as Cr³⁺ present in four real water samples. The testing outcomes achieved from this method, values of IC_{50} (half maximal inhibitory concentration) of Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , also Cr^{3+} were 3.7, 21.3, 4.4, 26.7, and 10.7 mg/L, correspondingly. Inhibition value of Fe^{3+} is 25 mg/L that was approximately identical by further increasing Fe³⁺ concentration to 250 mg/L .These results for detection proposed that this technique can also be used for complex samples [79]. The relative investigation of N, N'-(ethane-1,2-divl)bis(4-methoxybenzene sulfonamide) [EDBMBS] /Nafion/ glassy carbon electrode (GCE) as well as N,N'-(ethane-1,2-divl)bis(3,4-dimethoxybenzenesulfonamide) [EDBDMBS] was carried out to detect ions of Ni⁺² electrochemically. EDBDMBS/Nafion/GCE cationic-sensor showed better selectivity, wide ranges for concentration starting from 1 nM to 1 mM, durability, in addition to enhanced respond to nickel ions. LOD and sensitivity are approximately 0.78 nM and 2.3417 µA.µM.cm⁻² respectively. This unique effective cationic sensor is used for quantification of toxic pollutants in environment and proposes an economical approach for sensing and eliminating toxic Ni²⁺ from water samples [80]. Steric paper based electrochemical sensor was used to monitor zinc (Zn) ions in environment within range of 0.1 to 7,000 nmol/L. This device offers a new methodological approach for on-site environmental monitoring [81].

Nanoparticles of gold adapted by L-cysteine along with nanocomposite of reduced graphene oxide were layered on GCE aimed at Cd^{2+} and Pb^{2+} immediate determination (Fig. 6). Under optimum conditions, increase in concentration from one to ten nanomolar results in progressive

rise in peaks. LOD are 0.06 and 0.04 nM for Cd^{2+} and Pb^{2+} , respectively. Sensitivity attained was 2.2 μ AnM⁻¹ and 3.2 μ AnM⁻¹ for Cd^{2+} and Pb^{2+} . Hence the fabricated device was appropriate to synchronous determine target ions present inside samples of water [82].

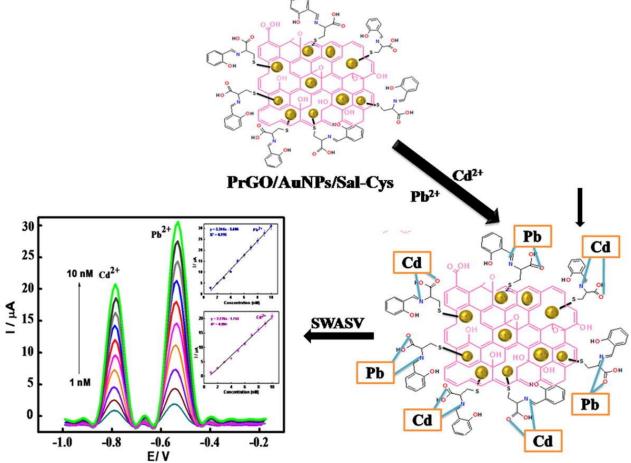
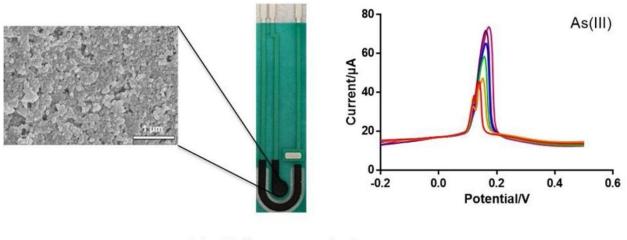


Fig. 6. Cadmium (II) and lead (II) determination with GCE modified by with nanoparticles of gold , L-cysteine, along with reduced graphene oxide. Reproduced from reference [82], with permission from Elsevier 2022.

A sensor with deposition of composites of iron-chitosan on screen-printed carbon electrode was employed to detect arsenic As (III) inside water from mining wastes and soil leachate using SWASV (square wave anodic stripping voltammetry) (Fig. 7). At potential of +0.15 volts clear As (III) peak was detected for both samples of water. 1.12 ppb and 1.01 ppb LOD for mining wastewater and soil leachate was estimated, respectively. Low relative standard deviations (RSD) showed improved constancy concerning detection of As (III) to be applied for real application regarding wastewater. The intervention out of metal ions of copper, zinc, lead, and cadmium was insignificant to detect As (III) in composite water medium. Results validate sensor suitability applicability to monitor As (III) pollution in wastewater having satisfactory characteristics range [83].



Fe-Chitosan-coated carbon electrode sensor

Fig. 7. Iron-chitosan coated carbon electrode to detect arsenic inside water from mining wastes and soil leachate using SWASV (square wave anodic stripping voltammetry). Reproduced from reference [83], with permission from Elsevier 2022.

In another research work, new functional ligand was developed and immobilized on inorganic silica successfully to fabricate solid-state sensor aimed at immediate adsorption and detection of cadmium (Cd(II)) ions in water samples. The developed sensor was formed optical color on adding Cd(II) ions in trace amounts at experimental conditions. The data explained that the materials was able to detect ultra-trace level of Cd(II) ions with LOD of 0.88 μ g/L based on false positives and false negatives with escalation of uncertainties. The competing ions did not affected adversely the detection and adsorption of Cd(II) ions. Additionally, signal was only observed for the Cd(II) ion. The maximum adsorption was found to be 176.19 mg/g that was analogous to other forms of materials. The developed solid-state sensor exhibited high possibility to be used in real wastewater [84].

4.1.2. Nitrogenous compounds

Similarly nitrogenous compounds in the form of nitrites are frequently used as fertilizers to protect or treat crops and plants. These compounds are poisonous and not safe for human health leading to irreparable consequences. Potentiometric, enzyme based or optical sensors are generally used for evaluating NO³⁻ and NO²⁻ ions in environmental waters. Bacteria-based

sensors have also been widely employed for environmental analysis to detect NO_x - (NO^{3-} + NO^{2-}), NO^{2-} , and SO_4^{2-} [85]. An automatic and transportable optical sensor was established to on-site investigation of nitrate and nitrite present inside natural waters in 3 min. The aforementioned system was installed at different sites for different periods examining discharge through waste-water treatment plant, infected tank water, along with stream water. Statistics produced via this method was like sample data collected by recognized laboratory instrumentation [86].

An innovative electrochemical sensor depending on composite comprising of $Cu_2O/CNTs$ has been produced through modifying CNTs consuming reduced Cu₂O spheres to detect nitrite ions selectively and sensitively. The developed Cu₂O/CNTs electrochemical sensor displays better sensitivity towards sensing nitrite ions having 0.018 nM LOD within concentration range of 0.1 nM to 1 mM. This sensor exhibits cost-effective anti-interfering capability, stability, and excellent reproducibility along with functionality. The acquired outcomes demonstrate that developed sensor possess inclusive usage for water quantification [87]. Hydrazine (N2H4) being extensively utilized for manufacturing agrarian chemicals, artificial catalysts, as well as pharmacological products produced irreversible contamination to water, air, and soil. Its immense use has highly toxic effect on environment. Furthermore, it gets released (for instance isoniazid (INH)) during few drug metabolism processes that is harmful for human body and contributes to suppression regarding metabolism of molecules, oxidation of mitochondria, and damage to DNA. Consequently, selective and sensitive sensing methods are urgently desired for *in-vitro* and *in-vivo* detection of hydrazine. Fluorescence sensors being influential device evaluates it in environment in addition to living structures efficiently along with negligible perturbation [88].

4.2. Organic contaminations

In developed countries, urbanization and industrialization resulted in an extensive use of environmental resources that led to a destruction of ecological systems. An important source of environmental pollution is industries which discharge their wastes in the form of harmful organic compounds in soil, air, or water [89]. In addition to industrial wastes, organic contamination includes pesticides, herbicides, and animal and plant tissues that adversely affect the environment. Such organic pollutants are largely destructive to humans and aquatic organisms; hence, it is obligatory to detect and monitor their concentrations by means of sensitive and reliable sensors [90].

4.2.1. Pesticides and herbicides

Organophosphorus compounds are frequently used in agriculture industries as pesticides and herbicides to control wide range of plant diseases. Organophosphate pesticides (OPs) are widely consumed pesticides because of their low cost and high efficiency for eliminating pests. Many sensors based on acetylcholinesterase (AChE) inhibition assay have been developed to detect OPs. These sensors were quite sensitive, user-friendly and still the most employed strategy that not only detect OPs, but also by carbamates pesticides, heavy metals and natural toxins, however low selectivity and accuracy remained challenges for their real applications. Therefore, AChE based sensors provides information on a total level of AChE inhibitors in one sample instead of on one individual target OP [91]. Organophosphate pesticides were analyzed by using impedimetric e-tongue (electronic tongue) that was free of enzymes displayed as Fig. 8. It consists of four units for sensing built on graphene hybrid nanocomposites. Each sample was analyzed thrice by taking impedance measurements and Principal Component Analysis (PCA) was performed for electrical resistance, indicating that the system has ability to differentiate pesticides at nanomolar concentrations. This system could also be used to detect pesticides in real samples with concentrations lower as 0.1 nmol/L. This sensor has precision, stability, as well as reproducibility besides being used for quick analysis of pesticides lower than the range of concentration allowed by law in some countries [92].

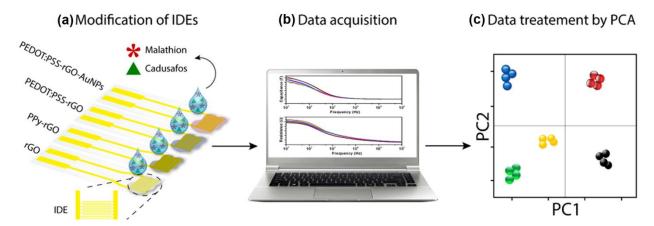


Fig. 8. a-b) Diagram of e-tongue device established on hybrid nanocomposites of graphene to detect pesticides at trace amounts, c) Illustration of PCA, statistical method for manipulating electric resistance data gained by e-tongue. Reproduced from reference [92], with permission from Elsevier 2021.

(rGO-reduced graphene oxide, Polypyrrole and PEDOT:PSS- conducting polymers, AuNPsgold nanoparticles, malathion and cadusafos-pesticides)

A colorimetric nanozyme sensor was fabricated utilizing heteroatom-doped graphene to detect aromatic pesticides. The adsorption of various pesticides on graphene led to mask active sites of nanozymes and as a consequence there is a reduction in peroxidase-mimicking actions. Using same concept, 5 dissimilar pesticides (for instance fluoroxypyr-meptyl, bensulfuron-methyl, diafenthiuron, lactofen, and fomesafen) were effectively distinguished by sensor having concentration ranging from 5 to 500 μ M. The sensor was also used for further usage to distinguish pesticides present in samples containing soil. The aforementioned study offers simplistic as well as economical process for detecting pesticides, in addition to contributing to protection of environment [93].

An appropriate colorimetric sensor comprising of six metal nanoparticles was established to detect pesticides in vapor phase. To reduce the leaching of nanoparticles after exposure to pesticides, 3D-origami design was employed to develop paper-based sensor. The agglomeration of nanoparticles led to change in color after exposition to pesticides. The color change delivered an effective way to detect pesticides quantitatively such as malathion, chlorpyrifos, parathion, and diazinon even at low concentration. In addition to this, the developed sensor also distinguishes between aromatic and aliphatic thions as well as separate amine-comprising compounds from other considered analytes. Results are evidently verified by both multivariate statistical approaches and visual detection. The LOD of parathion, malathion, diazinon, and chlorpyrifos were 103.0, 58.0, 117.0, and 81.0, correspondingly. Furthermore, sensor possibly applied for analyzing four samples instantaneously. This device is used as a diagnostic kit to observe the pollution caused by pesticide in agriculture environments [94]. Direct electrochemical detection of pesticides is an efficient method to monitor pesticide residues in environment. DPV (differential pulse) as well as CV (cyclic voltametric) methods have been employed for detecting 2 pesticides independently or instantaneously, i.e., PQ (paraquat) and CR (carbaryl), out of natural apple juice and acetate buffer solution. BDDGR (boron doped diamond electrode functionalized by graphene) identified pesticides PQ as well as CR simultaneously, with 31.83 a μ M⁻¹ cm⁻² sensitivity towards PQ plus 33.27 a μ M⁻¹ cm⁻² sensitivity towards CR. Therefore, BDDGR incorporated with DPV method display significant potential to detect pesticides within various natural frameworks [94]. A surface based resonance based senor was

developed to detect DDT (dichlorodiphenyl trichloroethane), its metabolites and analogues in real water samples. A reusable immunosurface is made through covalent attachment of analyte derivative to a self-assembled alkanethiol monolayer formed on SPR gold-thin layer. The sensor surface regeneration permitted 270 assay cycles (20 min for each assay cycle). Low LODs, in the sub-nanogram per litre range, were attained for DDT-selective (15 ng/L) and DDT group-selective immunoassays (31 ng/L). Both assays were performed in river water samples. SPR measurements were confirmed by gas-chromatography-mass spectrometry. The SPR DDT analysis of DDT was 3 times more sensitive than colorimetric ELISAs and a much lower time of response [95]. An ultrasensitive sensor was established to detect an organophosphorus compound using unmodified silver nanoparticles (AgNPs). An indirect enzyme-based detection of malathion with acetylthiocholine (ATCh) and acetylthiocholine (ATCh) in AgNPs presence using fluorometric method. The addition of malathion to the system decreased enzyme hydrolysis and thiocholine generation. The developed system displayed linearity within range of 2-100 fM, with an exceptional LOD of 0.556 fM by fluorescence spectroscopy. The possible application of system was established by measuring malathion in real samples like lake water, agricultural runoff water, cabbage, and apple samples using fluorometric method. The obtained results were further authenticated with HPLC [96].

The voltametric investigation of Aclonifen (ACF) herbicide in real samples of water and soil was performed by a sensor consuming glassy carbon electrode coated by $g-C_3N_4/GCE$ (graphitic carbon nitride) (Fig. 9). SWV (square wave voltammetry) technique had been utilized to identify ACF even at low levels. Linearity of 0.01 μ M - 1.2 μ M was observed with LOD of 1.28 nM of analyte under observation. The given methodology detected ACF effectively present within natural samples to reveal significance of fabricated sensor for agro-toxicology. High stability, low limit of detection, better reproducibility, as well as exceptional accuracy for ACF proposed the analysis of ACF along with other evolving environmental contaminations [97].

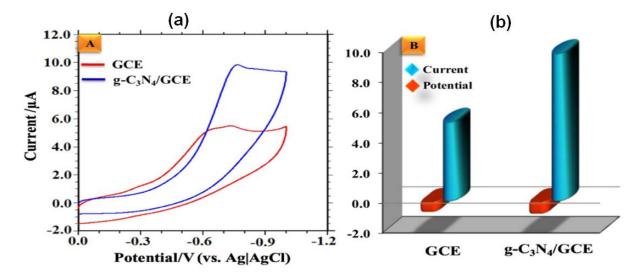


Fig. 9. a) Improved influence of $g-C_3N_4/GCE$ upon voltametric performance of ACF (0.1Mm) at value of pH 8, b) Deviation in peak voltage and peak current at GCE and $g-C_3N_4/GCE$. Reproduced from reference [97], with permission from Elsevier 2021.

Bentazon (BTZ) is toxic herbicide when exposed to humans. It is highly soluble within water that led to its diffusion and contagion of marine environment. Hence it is important to make easy and effectual diagnostic methods to detect this herbicide accurately in environmental samples. For this purpose, GCE, fabricated by carbon nanospheres cross-linked with film of chitosan, was used to detect BTZ herbicide voltametrically. Sensor repeatability and voltametric signal was improved by integrating surfactant (cetyltrimethylammonium bromide) in supportive solution comprosing of electrolytes. Direct range of concentration from 1.99 μ mol/L till 65.4 μ mol/L had been attained, possessing 1.4 μ mol/L LOD along with 6.22 A/mol L/cm² sensitivity in optimized conditions. Enhanced electroanalytical method was productively used for bentazon quantification in water samples [98].

A novel, sensitive, and reproducible sensor was established based on Pencil Graphite Electrode modified with cellulose to investigate Atrazine (ATZ) inside Britton-Robinson buffer having 4.3 pH. Electrochemical measurements were made by using SWV and CV. Adapted sensor showed an exceptional catalytic reaction to ATZ reduction with dropping peak at 880 mV as well as straight calibration line over concentration range of 5-320 ng/mL for ATZ, with 0.008 ng/mL LOD. This was able for detecting ATZ effectively having 3% accuracy devoid of interference from interfering metabolites. Aforementioned sensor exhibit high sensitivity for voltametric quantification of herbicide ATZ [99].

Anthropogenic copper (Cu) contamination discharged from antifouling paints, drainage of acid mines, in addition to wastes from industries is hazardous to humans including their environment. An optical sensor, formed by integrating self-assembled PEI-GA-PEI (glutaraldehyde-cross-linked bi-layered polyethylenimine) functionalized with interferometers consisting of NAA (nanoporous anodic alumina), was used to detect ionic Cu qualitatively and quantitatively inside environmental waters. Copper solution displays 1 to 100 mg/L range that is linear besides lower LOD that is equal to approximately 0.007 ppm. Sensor selectivity and specificity related to copper ions are confirmed via monitoring dissimilar six ionic solutions of metal having Cd^{2+} , Al^{3+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , as well as Zn^{2+} interfering ions. This work offers a different prospect to advance economical, movable, and sensitive systems for real environmental uses [100].

GLY (glyphosate) is widely used as herbicide and listed as a cancer causing agent by International Agency for Research on Cancer (IARC). Their stability is risky for various matrices, particularly food (typically heritably adapted crops) and environmental (water and soil). Being a toxic pollutant, electrochemical detection minimizes the consumption concerning contaminating chemicals, spending reasonable device [101]. Extreme usage of GLY adds contamination to environment. A simple, low-cost, and effective electroanalytical system was developed utilizing GrO-PE (graphite oxide paste electrode) to detect traces of GLY directly in samples of ground water, extracts from soybean and lettuce (Fig. 10). This sensor showed a linear relationship between peak current and concentration for GLY, ranging from 1.8×10^{-5} to 1.2×10^{-3} mol /L. 1.7×10^{-8} mol /L LOD and 5.6×10^{-8} mol /L⁻¹ LOQ were estimated. The developed system possesses strong analytical efficiency, reproducibility, precision, and repeatability. No interference regarding additional species has been observed, presenting its extreme selectivity. They are applied to determine GLY in real samples 98% to 102% rate for recovery. Results made it a favorable device to analyze environment without any difficult fabrication and complex handling [102].

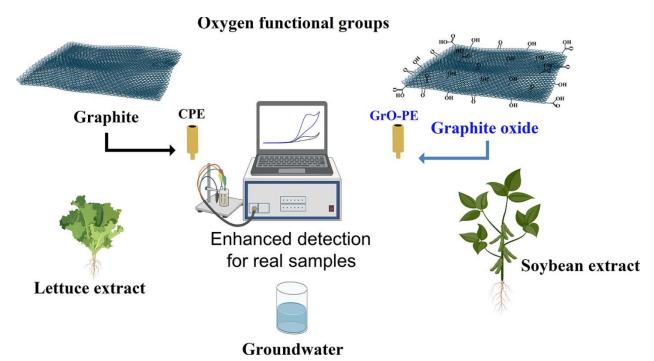


Fig. 10. Effective electroanalytical system utilizing GrO-PE (graphite oxide paste electrode) to detect traces of GLY directly in samples of ground water, extracts from soybean and lettuce, Reproduced from reference [102], with permission from Elsevier 2022.

A sensor consuming nanocomposites of graphene nanoprobe doped by copper-aluminum metal hydroxide (CuAl–LDH/Gr NC) was fabricated to evaluate traces of GLY. Nanocomposites offer good conductivity with large surface area and enrichment ability for GLY. Linear range of detection was measured as 2.96×10^{-9} to 1.18×10^{-6} mol/L with 1×10^{-9} mol/L LOD. Sensor showed outstanding repeatability, stability, besides anti-interfering capability. More, sensor attained acceptable rates of recovery in spiky surface water, ranged from 97.64 to 108.08%, representing pronounced accurateness and expediency [103]. A microsensor employing molecularly imprinted (MI) chitosan (CS) grafted onto 4-aminophenylacetic acid has also been used to detect GLY. The analysis was done by means of mathematical models derived from physical concepts. GLY interaction with imprinted sites of films comprising CS-MIPs had been perceived at high frequency with LOD of 1 fg/mL. Transfer resistance of charges is directly proportional to logarithmic concentration regarding GLY. There is a decrease in capacitance with the increase in GLY concentration that clarified by discharging of charged sites on electrostatic interaction of GLY with sites [104].

Gly is a serious problem that frequently occurs within drinking water. Constant on-site recognition regarding Gly within supplies of water offers timely cautioning in cases of pollution,

before reaching of pesticides to drinking water. Gold electrodes were employed for detecting GLY electrochemically within water from taps with no need of secondary electrolyte, pretreatment of sample or modifications of electrode. Amperometric estimations measure Gly with 2 μ M LOD that is lower to limit for allowable pollution of drinking water in United States. There was a linear relationship between Gly concentration and signal. This sensor was also applied to estimate AMPA, metabolite of Gly, and omethoate, a pesticide having same structure as of Gly. This research results in direct and on-site Gly estimation in sources used for drinking water [105].

4.2.2. Dioxins

Dioxins are produced by industries as toxic byproducts and are considered as organic pollutants. Dioxins have a vital influence on environment, as contaminating resides in water and soil. The emissions of dioxin by industries can be transmitted by rivers, winds, and sea currents. Dioxins take years to decompose and are constantly reprocessed in environment. For prospective application, a selective and an efficient 1, 4-dioxane chemical sensor had been developed using nanocomposites of PAni (polyaniline) and SiO₂ (silicon dioxide) on GCE (Fig. 11). The sensor shows LOD of $16.0 \pm 0.8 \text{ pmol L}^{-1}$, $0.5934 \,\mu\text{A}/\mu\text{mol}/\text{L}^2/\text{cm}^2$ sensitivity, and quantification limit (LOQ) equals to $53.3 \pm 1.5 \text{ pmol L}^{-1}$ over a range starting from 0.12 nmol/L upto 1.2 mmol/L. Additionally, suggested sensor demonstrated extraordinary precision in 1, 4-dioxane sensing present inside real samples. It's an easy way that guarantee sustainable nontoxic green environment [106].

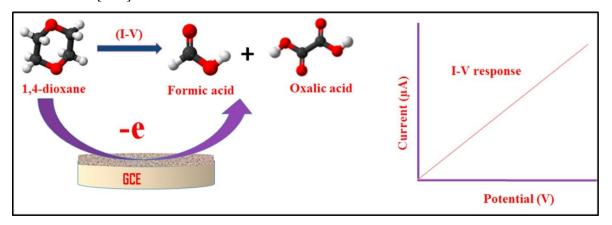


Fig. 11. Representation of suggested recognition device for 1,4-dioxane via using probe of PAni-SiO₂ NCs/binder/GCE inside water medium. Reproduced from reference [106], with permission from Elsevier 2021.

Hydrogenated graphene (graphane) are one of the favorable sensors for detection of molecules comprising of TCDD (2, 3, 7, 8-tetrachlorodibenzao-p-dioxin). Employing DFT (density functional theory), adsorption of TCDD molecules adsorption onto pure, Nickel/Copper modified graphane, and H-defected showed that the TCDD adsorption stability onto graphanehad been enhanced through H-vacancy. After introducing Cu and Ni, charge transfer and energies for adsorption of TCDD molecules were amplified. Hence Cu and Ni upgraded sensitivity of graphane towards TCDD molecules. Additionally, band gaps changes in substrates of graphane due to TCDD adsorption alters conductance of substrates, that produces electric signal for TCDD molecules detection [107].

4.2.3. Phenols

Many organic pollutants discharged in environment possess phenolic structures and are toxic in nature. They are the byproduct released during the production of pulp, paper, plastics, dyes, drugs, polymers; oil refinery etc. which makes it important for monitoring concentration of phenol in range of sub-ppm having extraordinary accuracy along with low LOD.

Bis-phenol (BPA) chemical sensor was developed by utilizing nanoparticles of $Fe_2MoO_4 \cdot Fe_3O_4 \cdot ZnO$ aimed at ecological environment. The developed sensor shows better sensitivity (2.2468 $\mu A \mu M^{-1} cm^{-2}$) and durability with lower LOD (42.25 ± 2.11pM) with improved electrochemical response. The fabrication of this sensor consuming nanoparticles is favorable strategy for consistent I–V method. It leads to fabricate chemical sensor to identify more harmful toxins effectively inside environment and also in health sector [108]. A photoanode was prepared by bismuth vanadate (BiVO₄) / polyoxometalates (POM) composite films and explored for photo-electrochemical phenol sensing. The results of BiVO₄/POM sensor composite film electrodes displayed their responsiveness to phenol concentration present in solution exhibiting linear relationship of about 99.16%. The response of BiVO₄/POM composite film electrode to phenol solution was greater about 3.6 times when compared to pure electrode of BiVO₄ demonstrating the effectiveness regarding photo-electrochemical sensing technique for detection of phenol [109].

A quantifiable real time sensor was introduced to detect phenol inside wastes discharged by industries by SWV. During this method, phenoxyl radicals formed due to oxidation of phenol get converted into hydroquinone as well as catechol to recognize. Phenol is reliably detected in sub-ppm range over an extensive range of pH. Pre-concentration of phenol before screening enhances

the sensitivity of the sensor and delivers LOD of 0.1 ppb for phenol. In conclusion, in a millifluidic device, 3 electrodes of graphite worked as working, reference, and counter electrodes. They were used for constant detection of phenol in wastewater discharged by industries. Owing to its selectivity, this sensor could be manufactured as well as positioned for large scale monitoring of phenol present inside wastewater from industries [110].

Poly (methyl orange) (PMO) on GCE had been utilized as an electrochemical sensor to determine 4-nitrophenol (4-NP). Excellent electrocatalytic activity of PMO-modified GCE (PMO/GCE) was revealed by cyclic voltammetry for 4-NP oxidation in phosphate buffer solution (0.5-M). Moreover, the fabricated sensor displayed a linear correlation with concentration of 4-NP ranged within 600 nM to 10 μ M, in addition to 170 nM LOD. The sensor established exceptional selectivity for 4-NP detection in real water samples [111]. A phenol gas sensor was developed consuming semisolid, alkaline sodium polyacrylate and commercial screen-printed electrodes. In ambient conditions, sensor showed excellent sensitivity in the low ppbv (μ g /m³) range, with good linear operation within range of 0.1–1.0 ppmv for up to 105 min accumulation, and low sensitivity toward examined interferences. The sensor specified an opportunity to discriminate between several phenolic compounds depending on their oxidation potential. Providing favorable electroanalytical performance, a strong usage is intended in topical field's for instance cultural heritage preservation, environmental monitoring, and occupational health and safety [112].

4.2.4. Hydrocarbons

Hydrocarbon contamination is also one of the major environmental problems caused by sharp increase in industrial sector. Therefore, it is crucial to detect and quantify environmental pollutants in various water sources [113]. An electrochemical immunosensor was established to sensitively detect an aromatic hydrocarbon BaP (benzo[a]pyrene). In this sensor, biocompatible layer of Fe₃O₄/PANI/Nafion (magnetite/polyaniline/Nafion) was used for sensing alon with labeling with highly-carbonized spheres modified by multi-enzyme-antibody (multi-HRP-HCS-Ab2). Fe₃O₄/PANI/Nafion stable layer restrain biomolecules and reduces hydrogen peroxide representing an enhanced path for transfer of electron on platform. The change in current is directly proportional to log of BaP concentration ranging from 8 pM and 2 nM with 4 pM LOD. The suggested immunosensor revealed satisfactory reproducibility and constancy and has potential to detect aromatic in environment [114]. Reflectometric sensor was developed aimed at

enzymatic detection regarding halogenated contaminant in samples of water. A substrate made of microspheres of polyacrylate decorated by functional groups of succinimide was used for bonding enzyme (haloalkane dehalogenase (DhlA)) covalently. Dye (ETH5294 Nile Blue chromoionophore-NBC) gets bonded to microspheres physically and work as optical proton sensor. A halogen and proton were released by hydrolytic dehalogenation of halocarbon. DhlA catalyze the dehalogenation process that protonated NBC proton indicator. The color of sensor changes from violet to blue. Reflectance spectrophotometer was used to measure concentration of halogenated hydrocarbons. This evaluated with diverse concentrations of dicholoroacetic acid (DCA) at pH value of 8.0, within 1-100 mg L⁻¹ range. When concentration of DCA increases after 1 mg/L up till 30 mg/L, continuous increase regarding comparative reflective behaviour had been perceived (Fig. 12). This sensor presented 0.3 mg L⁻¹ LOD over a range within 1 to thirty mg/L for DCA. Proposed sensor, at wavelength of 662 nm, responds in 2 min to detect fifty mg/L of DCA. Hence short time concerned to sensor for responding is effective in detecting hydrocarbon pollutants in wastewater investigation in industrial sectors [115].

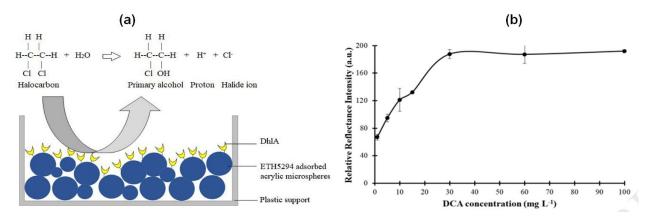
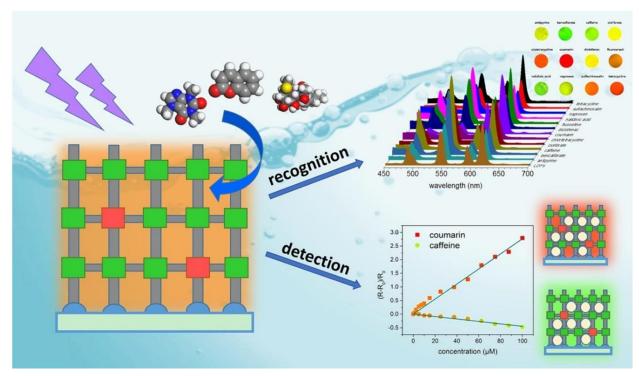


Fig. 12. a) Optical reflective biosensor comprising bioreceptor (DhlA), polyacrylate matrix for immobilization, and pH indicator (Nile Blue chromoionophore) to detect aliphatic halocarbons, b) The reflection curve of enzymatic halocarbon sensor for different DCA concentrations at 662 nm. Reproduced from reference [115], with permission from Elsevier 2021.

4.2.5. Active molecules

Active molecules present in, wastewaters or other environmental samples contained within several complexes for instance antipyretics, antibiotics, analgesics, antimicrobials, antiinflammatories, as well as hormones [116]. Such complexes along with biologically active metabolites being constantly introduced to water at concentration of ng/L or pg/L via different ways comprising of release out of fabrication sites, discarding of drugs by hospitals and households directly, excretion later to administration of drug to animals or humans in addition to water managements inside fish farmhouses. They pose a dangerous problem towards environment as they resist biological decomposition [117]. They are toxic and their accumulation inside living organism is life threatening even at trace concentrations. Release of active molecules to environment complicate environmental problem [118]. They are being mostly consumed in livestock, human, as well as agriculture, backing its intensification in environment and holds substantial influence on animal and human health. Hence to detect these bioactive molecules utilizing different modified and unmodified electrodes in a simple and reliable manner has been a great concern [119].

Antibiotic, Ciprofloxacin is a toxic drug, triggering difficulties if released to environment via different routes for instance disposal of extra drug, human excreta, improperly treated or untreated wastewater from pharmacological industries as well as wastes from hospitals [120]. Azomycin, highly soluble and non-biodegradable is consumed as an oral antibiotic medication to treat protozoal infections. It can cause genotoxic, mutagenic, carcinogenic, ataxia, and peripheral neuropathy due to long time use due to accumulation in water and soil [121]. GCE modified by polypyrrole (PPy) polymer-incorporated silver molybdate (Ag₂MoO₄) nanocomposite had been for detection of the drugs, azomycin and ciprofloxacin. The nanocomposite acts as effective photocatalyst for degradation of CIP drug (99.8%) in ten minutes. Additionally, modified GCE confirmed excellent electrocatalytic reactivity with regard to greater cathodic peak current along with low peak potential in comparison to other unmodified and modified GCEs to detect azomycin. Developed electrode exhibited low LOD of 65 nM with wide linear range of 0.5 to 499 µM. Furthermore, there is no effect of co-interference complexes, for instance biological substances having same functional groups and inorganic molecules to azomycin detecting [122]. Some drugs are not completely absorbed by body and excreted through urine and entered into environment, airs a danger to nature. A sequence regarding mixed-crystal Ln-MOFs (lanthanide metal-organic frameworks) were fabricated for forming nanocrystals and make thin films of luminescent Ln-MOF on ITO substrate (Fig. 13). Variations concerned to ratio of radiation intensity enabled films to sense diverse pharmacological molecules. Furthermore, ratio intensity was directly proportional to pharmaceuticals concentration. Such thin films produced more steady and precise luminescent signals. They are exceptional candidate for self-calibrating



luminescent sensor aimed at numerous uses [123].

Fig. 13. Luminescent sensor based on thin films of metal organic framework to detect various pharmacological compounds. Reproduced from reference [123], with permission from Elsevier 2022.

Methotrexate (MTX) and Doxorubicin (DOX) are commonly used to treat cancers. It is important to retain raight concentration of drug in body to prevent their side effects. However, some of the anticancerous drugs get excreted through urination or faeces and causes contamination of water environment that is dangerous for the health even at low concentration [124]. Considering this, a sensor was proposed to determine electrochemically MTX and DOX simultaneously. Sensor was fabricated by modifying modified GCE utilizing nanoparticles of copper cooper (CuNPs), CB (carbon black), along with Nafion (Fig. 14). Sensor revealed enhanced electrochemical enzymatic activity towards oxidation in SWV, at 0.93 and 0.69 volts for MTX and DOX, correspondingly., Linear range equals to 2.2×10^{-6} to 2.5×10^{-5} mol/L and 4.5×10^{-7} to 5.1×10^{-6} mol/L with and 9.0×10^{-8} mol/L and 2.4×10^{-8} mol/L LODs were attained for MTX and DOX, respectively in optimum conditions. In conclusion, this sensor could be effectively used to estimate MTX and DOX inside biologic matrix like samples of human urine and additionally in surroundings for instance samples of river water, with 100% recovery [125].

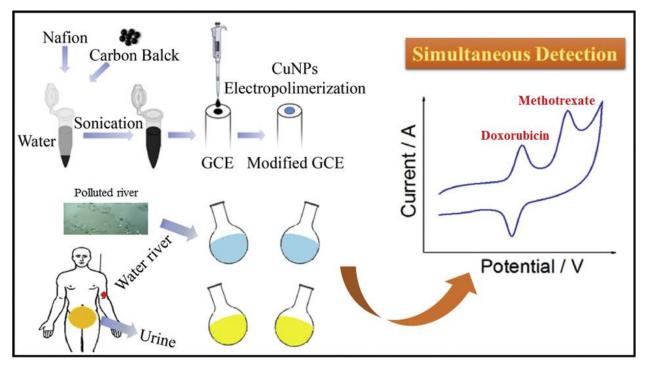


Fig. 14. Estimation of MTX and DOX in samples of biological matrix and river water using modified GCE by CB, CuNPs, along with nation. Reproduced from reference [125], with permission from Elsevier 2022.

Prohibited drugs ingestion and drug marketing is spreading globally and exists as a serious issue for local establishments. Forensic drugs are the latest source of evolving pollutants because of dumping of wastes from underground laboratory into sewage systems. These drugs with metabolites get discharged in wastewaters through excretion from humans after illicit drug consumption [126]. Henceforth, there is a need to develop effective as well as precise approaches for detecting such compounds within detained samples collected from biologic fluids, streets, in addition to wastewaters. This aimed at reducing and preventing drug trafficking besides consumption as well as negative impacts on water systems. Electrochemical methodologies propose a rapid, transportable, economic plus exact substitute for spectrometric and chromatographic techniques, to analyze forensic drugs along metabolites inside diverse matrices [127]. Inhalers used for asthma is also one of the major cause of pollution. Everyday exposition to numerous pollutants has been linked to regular asthma medication usage in the form of inhaler uses and related air pollution exposition [128, 129]. A speedy and extremely sensitive flow injection chemiluminescence immunoassay was established to sense ractopamine (RAC)

residues in pork products. Palladium nanocubes having exceptional catalytic performance for traditional luminol–PIP–H₂O₂ chemiluminescence system were utilized as active carriers for connecting a ractopamine antibody and horseradish peroxidase (HRP). Double amplification of a chemiluminescence signal was realized because of palladium nanocubes and HRP. Chemiluminescence intensity of an immunosensor possesses linear negative correlation with logarithmic value of ractopamine concentration. In optimum conditions, range of detection regarding ractopamine was found to be 0.005–1000 ng/mL, and LOD was 1.7 pg/mL. The projected immunoassay had suitable accuracy, high specificity and reproducibility and RAC was estimated in pork and pig feed. Outcomes provided a better prospect to detect small molecules in food and environment analysis [130].

4.3. Biological contaminations

Biological pollutants emerge from different sources and are responsible for environmental contaminations. They include bacteria, viruses, parasites, algae, and insects etc. that not only effect environment but also cause fatal diseases in humans [8]. Therefore, sensitive biosensors have been required to recognize biological impurities to protect environment especially aquatic environment and human illness.

4.3.1. Bacteria

A paper chips made up of polydimethylsiloxane (PDMS) are utilized for visible immunoassay to detect bacteria (*Escherichia coli*). An antibody was immobilized on paper chip on detection regions to capture *E. coli*, whereas antibodies labeled by gold nanoparticles (AuNPs) are used for detection (Fig. 15). AuNPs on paper chip reduces the silver ions effectively after immunological reaction, producing a result visible to the naked eyes. *E. coli* density in water samples was estimated by standardizing grayish value concerned to silver marked dots by logarithmic value of bacteria. Grayish detective region exhibits direct correlation with logarithmic value of *E. coli* with LOD of 57 cfu/mL. Sensitivity of this assay and ELISA is comparable; however less reactants and time were utilized in this assay. This technology suggested a pronounced potential for in-situ investigation of water quality [131].

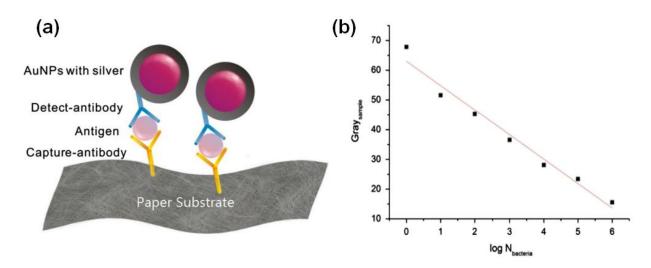


Fig. 15. a) Principle of paper chip based on gold nanoparticles labeled with silver nanoparticles. Capture-antibody gets absorbed on porous structure of chip to capture antigen, followed by bonding with gold nanoparticles, b) Calibration curve to detect *E.coli* using 0.97as calibration coefficient. Reproduced from reference [131], with permission from Elsevier 2021.

Field effect transistor (FET) founded on rGO (Reduced graphene oxide) functionalized by Al_2O_3 was employed to detect *E.coli*. This developed sensor was able to sense one *E. coli* cell in fifty seconds within 1 µL of sample. Antibodies specific to *E. coli* specific attached to gold were used as probes to capture *E. coli* selectively. The negative charges of *E. coli* cells modify the charge carriers' concentration present in rGO monolayer, thus permitting immediate *E. coli* detection in a sample. A range of about 1 to 100 CFU within sample (1 µL) with better selectivity was observed regarding *E. coli* identification inside water of rivers. This method offers cheap method for instantaneous revealing regarding extensive pathogens within water as well as in other fluid media [132].

A magnetic nano sensor was established to detect *Salmonella* (foodborne pathogens causing harmful disease). The senor possesses extraordinary reactivity towards visual recognition of pathogen named "*S. Enteritidis*" quantitatively present in water, cheese, and milk. These samples were tested consuming magnetic beads functionalized with anti *S. Enteritidis* streptavidin along with antibody tagged with biotin (to capture). They are incorporated to nanocomposite that is inorganic nanoflower and detecting antibody-HRP enzyme. Amplification of signal is improved by nanoflower action depending on HRP enzyme. A color produced was visually sensed through smartphone even in lower concentration. This sensor detected

S. Enteritidis present in milk, tap water, and cheese having LOD equals to 1.0 CFU/mL and 1.0 CFUg⁻¹, correspondingly. The effectual device usage in cheese and milk demonstrated opportunity to be utilized for numerous foodstuff [133].

A complex label-free interdigitated capacitive sensor had been fabricated to detect different concentrations of Cryptosporidium (protozoan) with substantial sensitive. The developed sensing platform revealed an enhancement in efficacy and LOD of Cryptosporidium in comparison to other detection methods. The results presented a linear detection range for Cryptosporidium concentrations with LOD of 40 cells/mm². This sensor displays a significant potential to directly detect the Cryptosporidium oocysts presence inside samples of water in reliable and real time manner. Development of such portable, adjustable, low cost and rapid detection method leads towards personalized and point-of-care (POC) applications [134].

Graphene film composite biosensor was devised to detect microcystin-LR (MC-LR). It acts as per substitute to laborious, costly, and non-portable orthodox approaches to monitor and assess water quality assessment. The established sensors can precisely identify MC-LR inside various aquatic sources maintaining significant sensitivity and 2.3 ng/L LOD. Developed sensor was effectively applied to determine MC-LR within numerous ecological samples like water, along extraordinary detection recovery. This suggests prospect for extensive manufacturing of sensor because of accessible fabrication method and easily tunable size [135].

4.3.2. Fungi and algae

A WGS (whole-genome shot-gun sequencing) system was designed to detect main pathogens out of samples collected from fields. This DNA sequencing device was used for wheat leaves infested by fungal pathogens. By mapping of data, all fungal diseases were detected existing in the diseased samples containing stripe rust (by Puccinia striiformis f. sp. tritici), septoria tritici blotch (by Zymoseptoria tritici), yellow leaf spot (by Pyrenophora tritici repentis), in addition to Septoria nodorum blotch (via Parastagonospora nodorum). The obtained results proposed that this portable device possess substantial probability to diagnose variety of crop contaminations as well as monitor atmosphere at field environments [136].

Aflatoxin is highly toxic and carcinogenic for human and animals, naturally produced by Aspergillus fungal species. An extremely selective, sensitive, reusable plasmonic sensor was established to detect aflatoxin B1 (AFB1) depending on enhance-SPR (surface plasmon resonance). First, N-methacryloyl-l-phenylalanine and AFB1 were combined according to per template particle and functional monomer. Gold chip surface was coated by MIP (molecularly imprinted polymers) in addition to AuNPs. The imprinted sensor had range starting from 0.0001 up till 10.0 ng/mL, with 1.04 pg/mL LOD. Furthermore, detection of AFB1 was done consuming numerous food samples [137].

Multi microsensor platform was developed to carry out instantaneously optical and electrochemical sensing in algae metabolism frame for monitoring. This platform aims to make estimation of microalgal fluorescence variation and production of oxygen by 3 dissimilar algae: Pseudokirchneriella subcapitata, Chlamydomonas reinhardtii, as well as Chlorella vulgaris. No sample preparation is needed for this dual sensor system and can be utilized for on-site analysis [138].

5. Challenges and limitation of using sensors for environmental monitoring

The effect of anthropic activities on environment and their harmful impact on human health have pushed researchers, all over the world, to monitor and screen the environment [139]. Growing trends aimed at technological growth and its influence on environment necessitates better understanding regarding relationship between components within it. Sensors play a vital role in developments necessary for meeting social demands, for instance pollution harms, hazard detection, environmental remediation, energy production, storage, and biomedical treatments [140-142]. Still, selectivity and specificity remain their main shortcomings. Social demands need an improvement in sensor performance that includes selectivity, sensitivity, stability, as well as usability. Consequently, research is now being focused on preceding the design regarding mechanism for sensing and evolving novel active sensing materials. Nanotechnology and material science play a key role in this regard and are continuously pursuing innovations for improved sensor devices. Recently, safe, smart, biocompatible, and environmentally "clean" sensor devices and instruments have been designed and developed. Because of advanced features of many sensor devices, counting their small dimensions, low weight, economic, and consistency, they are intensely aligned with numerous markets [143]. The limitation of sensing devices with reference to selectivity, sensitivity, accuracy, resolution, and precision are constantly being upgraded. Simultaneously, their possibility relative to manipulation and usage is also speedily growing [144].

The water analysis regarding quality, environmental and pharmaceutical compounds is elementary subject meant for human health. The existence of biological toxins, low-quality drugs, and chemical compounds in environment results in irreversible complications within human society [145].

Different sensing tools depending on analytical approaches are necessary to identify and quantify various inorganic, organic and biological contaminants. Applying sensors for immediate detection and on-site detection and monitoring of pollutants possess a big challenge in real samples [146]. In real samples, the presence of chemical and biological species has severe interference on sensing signals. In few cases, transducer of sensor having organics or inorganics fouling results in malfunctioning [147]. Unfortunately, most of real samples have various kinds of contaminating agents. However, many previously-described sensors in literature are only able to detect some polluting agents that can be organic, inorganic, or biological [35].

On-site recognition capability and sensor transportability are advantages over old-style analytical approaches for environmental monitoring. For reducing partiality and making fast decision-making broaden usefulness of sensors [148]. If the pretreatment of samples are executed in laboratories, this will limit the application of sensor for on-site detection. For this point of care (POC) sensing devices constituting microfluidics chips could be an effective solution in future [149].

In past few years estimation and detection of numerous pollutants in environment becomes analytically significant because of their extensive usage in ecosystems [19]. Specificity, sensitivity, cost-efficiency, reliability, and possibility of on-line usage are critical factors to design and construct sensor for environmental monitoring [150]. Most of the developed sensors for environmental monitoring do not compete with customary methods with regard to reproducibility or precision.

One limitation about sensors for environmental analysis is probability of immediate detection of multiple pollutants. More than a few studies have been successfully conducted to that end [151]. Carbon screen-printed electrodes had been employed for parallel identification of paracetamol, estradiol, and hydroquinone present inside tap water [152]. The main challenge to develop such dual sensor system was to combine two detection mechanisms because of their different responses towards the analytes. However, electrochemical and optical sensors presented promising perceptions for simultaneous identification of multiple pollutants within water samples [138]. The sensors developed for environmental monitoring necessitates in situ and real-time monitoring of multiple pollutants with new sensing systems and even their integration with

aircraft systems [153].

The summary of conventional and modern approaches exposes that it is impossible to accomplish immediate detection of pollutants by employing one type of sensor only. Hence, new instrumentation needs to be introduced which are more influential and specific than ever and permit the detection of little amounts of analytes with high assurance and minimum sample preparation. With the existing necessity for inexpensive, sensitive, quick, and consistent devices aimed at environmental monitoring, the major challenge is the gap between academic research results and the execution of these sensors as marketable products.

6. Conclusions

Over the years, novel sensors have been established for environmental analysis for improving our lives as well as world a better place to live. Despite the enormous prospective sensors, there is a lot of space in the field of sensing to develop fast and economical sensors having little or no impact on environment. Even though several sensors are used commercially, but their usage is restricted because of limited sensitivity, response time, and lifetime. The development of portable sensors replaced critical sensing process along with improved accessibility. Research is mainly focused on improvement of immobilization techniques of biological element, because of well-established transduction technology. Miniaturization, nanotechnology, and multisensory array determinations play a substantial role for enhancing selectivity, sensitivity, in addition to stability regarding sensors. Advancement of sensor technology exhibits a significant potential for understanding and exploring of the environment.

Sensitivity, consistency, specificity, cost-effectiveness, and probability of on-line usage are critical aspects to design and fabricate sensor for monitoring and analysis of environment. Different transduction principle along with various functional biological elements determines the specificity (low interference), affinity (low detection limit), response time, dynamic range, and lifetime of sensing system.

Still, most of the sensors do not contend the conventional methods in respect of reproducibility or accuracy; however, they permit constant immediate on-site monitoring of a contaminations as well as deliver appropriate evidence regarding environmental pollution. Even with the noteworthy potential, sensors are still in initial phases of applications concerning the recognition of pharmacological complexes, pesticides, besides much additional vulnerable dangers within applications of real world. Pharmacological and self-care commodities are developing organic pollutants. It enters and risks our aquatic system by human use that gains attention of environmentalist. It has been detected employing conventional as well as advanced methods; still it is essential to establish novel detection techniques for enhancing such pollutant detection. Advancement in recognition methods integrated with nanotechnology could sense very less concentration even, with substantial sensitivity in less than no time. Such approaches would considerably escalate decomposition of damaging compounds for environment. Moreover, majority of sensors have need of substantial enhancements, specifically regarding selectivity as well as capability intended for instantaneous exploration, before commercial employment. An effective and productive research is prerequisite to attain extremely enhanced methods of fabricating new materials along with suitable immobilization protocols that increases the selectivity, sensitivity, stability, as well as catalytic activity of the systems involved. In Future, an attention should be paid to develop sensors having capability in prospect of employment in every environmental situation sustaining lowest promising LOD, specificity, and precision to detect various environmental analytes in one platform.

Authors contribution statement

Sumera Khizar: Writing original draft, Nadia Zine, Nicole Jaffrezic-Renault, Abdelhamid Elaissari: Review and Editing, Abdelhamid Errachid: Approved the final manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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