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Polymer based nanocomposites: A strategic tool for detection of toxic pollutants in environmental matrices

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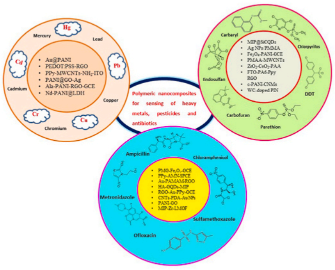
HIGHLIGHTS

- Different polymer/inorganic nanocomposites based sensors have been discussed.
- Polymer/inorganic nanocomposite as emerging tool for sensing environmental pollutants.
- Selectivity, accuracy and stability of nanocomposites based sensors have been reviewed.

GRAPHICAL ABSTRACT



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ABSTRACT

A large fraction of population is suffering from waterborne diseases due to the contaminated drinking water. Both anthropogenic and natural sources are responsible for water contamination. Revolution in industrial and agriculture sectors along with a huge increase in human population has brought more amount of wastes like heavy metals, pesticides and antibiotics. These toxins are very harmful for human health, therefore, it is necessary to sense their presence in environment. Conventional strategies face various problems in detection and quantification of these pollutants such as expensive equipment and requirement of high maintenance with limited portability. Recently, nanostructured devices have been developed to detect environmental pollutants. Polymeric nanocomposites have been found robust, cost effective, highly efficient and accurate for sensing various environmental pollutants and this is due to their porous framework, multi-functionalities, redox properties, great conductivity, catalytic features, facile operation at room temperature and large surface area.

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Synergistic effects between polymeric matrix and nanomaterials are responsible for improved sensing features and environmental adaptability. This review focuses on the recent advancement in polymeric nanocomposites for sensing heavy metals, pesticides and antibiotics. The advantages, disadvantages, operating conditions and future perspectives of polymeric nanocomposites for sensing toxic pollutants have also been discussed.

Abbreviations

SPCE	Screen-printed carbon electrode
ASPCE	Pre-anodized screen-printed carbon electrode
A-MWCNTs	Acid treated multi-walled carbon nanotubes
Hyalu	Hyaluronic acid
L-Ser	L-Serine
DMSA	Dimercaptosuccinic acid
NH_2-MIL-53(Al)	Metal-organic framework
MIL-53(Fe)	Metal-organic framework
PA	Phytic acid
ZIF-8@ZIF-67	Metal-organic framework
MnS_2	Manganese disulphide
afGQDs	Amino-functionalized graphene quantum dots
mMIP	Mesoporous structured molecularly imprinted polymer
SMIP	Silica molecularly imprinted polymer
MNPs	magnetic nanoparticles
PIN	Polyindole
WC	Tungsten carbide
FTO	Fluorine tin oxide
PMAA	Poly(methacrylic acid)
CNMs	carbon nanomaterials
HA	Hydroxyapatite
oxMWCNTs	Oxidized multi-walled carbon nanotubes
AMN	Silver manganite
$NiMoO_4$	Nickel molybdate nanosheets
APT	Kanamycin aptamers
β-CD	β-cyclodextrin
Fc	Ferrocene
CuMOF	Metal–organic framework
POAP-co-POPD	Poly(ortho-aminophenol-*co*-ortho-phenylenediamine)
G-DNAzyme	G-quadruplex DNAzyme
TC-Apt	Tetracycline-binding aptamer
Zr-LMOF	Luminescent zirconium metal–organic framework
$UPPy_{MIP}$	Ultrathin over-oxidized polypyrrole films
TiO_2–C	COOH functionalized TiO_2
PTh	Polythiophene
en	Encapsulated
Ti_3C_2	Titanium carbide
ITO	Indium tin oxide
IL	Ionic liquid
PA6	Polyamide 6
DPV	Differential pulse voltammetry
SWV	Squarewave voltammetry
CV	Cyclic voltammetry
DPASV	Differential pulse anodic stripping voltammetry
EIS	Electrochemical impedance spectroscopy
CI	Chemiluminescence

1. Introduction

Environmental pollution is a global issue and it is badly affecting the human development. The water quality has been deteriorated because of the direct release of wastes from agriculture, household and industries in water sources such as rivers, ponds, etc. Heavy metals, antibiotics, and pesticides present in aqueous system pose serious health issues (see Figs. 1 and 2). Regular monitoring of water sources may provide the evaluation about the toxicity of pollutants and also the efficacy of under practice pollution controlling methods (Kruse, 2018). Different analytical methods such as mass spectroscopy, high performance liquid chromatography, gas chromatography and spectrophotometry have been previously utilized to detect these pollutants, however, these techniques have few drawbacks of being expensive, bulky in size, laborious and require special technicians for their operation. Detection accuracy is quite low for spectrophotometry, while accuracy is good in case of gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) but these techniques cannot be used for *in-situ* detection (Chen et al., 2012).

Alternatively, sensors have been found promising because of their excellent inherent features like facile operation, flexibility, cost friendly, great selectivity, sensitivity and *in-situ* detection (Barsan et al., 2015). Sensors provide specific response with direct relation to the amount of specific chemical substance. Sensors are devices which are known as fast detection tools that exploit chemical reaction of target analyst and it mainly consists of transducer and receptor. Firstly, the receptor binds with analyte molecule and then transducer translates the reaction into detectable signal (Saleem and Lee, 2015). The efficacy of sensor is basically determined on the basis of its detection limit, selectivity, sensitivity and response time. Different types of sensors like field effect transistors, fluorescent sensors, surface plasmon resonance sensors, electrochemical and colorimetric sensors have been emerged (Rasheed and Rizwan, 2022). Sensors may also be classified on the basis of their specific features like mass, optical, thermal and electrical sensors. Miniaturization, portability and cost effectiveness are specific features related to the sensors which are making sensors more popular for the detection of pollutants.

Use of nanomaterials is well documented for designing ideal sensors for various toxic pollutants (Rasheed et al., 2019; Shakeel et al., 2022). Nanomaterials having 1–100 nm size range exhibit unique chemical and physical features such as optical, electronic, magnetic and chemical versatility (Khan et al., 2019) and these features render them excellent sensing platform in analytical chemistry discipline for the last two decades. Development in polymeric materials proved as a turning-point in sensing field. They have been pursued as signal promoting element in analytical operations because of their various tunable features and excellent potential to adhere to the electrode surface. However, there are some limitations as well associated to the polymeric materials such as poor selectivity, poisoning of surface and poor sensitivity because of adsorbed interferences (Shrivastava et al., 2016).

Fabrication of polymeric nanocomposites has opened new horizons in the field of nanotechnologies. Polymeric nanocomposites are versatile materials with great functionalities and enhanced efficacy. Advanced polymeric nanocomposites are efficient to sense the environmental pollutants (Rizwan et al., 2022). Polymeric nanocomposites are hybrid materials, composed of polymer (as matrix) and nanomaterials (as nano-fillers) and these nanocomposites are multi-functional because of the integration of multi-components. Various polymers like nylon, polyester, polyaniline (PANI), polyethylene (PE), polypropylene (PP), Teflon and epoxy are used as polymeric matrix, while different inorganic components including metal based NPs (nanoparticles), carbon nanomaterials and nano-clays are incorporated in polymeric matrix to form polymeric nanocomposites with specifically enhanced properties (Jamróz et al., 2019). Polymeric nanocomposites possess power as great transducer in analytical sensors due to their synergistic effects coming from particular components in comparison of individual counterparts (Qi et al., 2018). Polymeric nanocomposites based sensors have been reported previously for the monitoring and detection of heavy metals, pesticides and antibiotics in various mediums (Mahmoudpour et al., 2020; Majumdar et al., 2021; Tajik et al., 2021). For instance, Prussian blue (PB) and graphitic carbon nitride based nanostructures possess excellent photo-catalytic potential and play great role in advanced oxidation processes for the removal of different environmental pollutants (Lam et al., 2020; Nayebi et al., 2021).

In this review, the applications of different polymeric nanocomposites (Fig. 3) for sensing heavy metals, pesticides and antibiotics in aqueous systems have been reported. Furthermore, the efforts have been made to discuss the limit of detection, linear range, recovery, advantages and disadvantages of polymeric nanocomposites in sensing heavy metals, pesticides and antibiotics.

2. Efficient sensing strategy in environmental sensors

Basically, sensing process and signal expression are the main features of sensing strategy. There are different approaches for sensing environmental pollutants such as the analytes are sensed through changes in response signal originated from the sensing units and samples in detection systems. The sensing may be electrochemical, colorimetric, fluorescent or may be of other types. Generally, the sensing approaches are divided into two types: (a) turn on mode and (b) turn off mode, according to the response signal alterations. The positive correlation between the intensity of signal response and the amount of analyte belongs to the turn on mode, which is carried out in many sensing approaches (i.e., glucose sensor). On the other hand, turn off mode is found in suppression sensing approaches (immune-sensor or enzyme sensor to inhibitors). Apart from sensing approaches, the main focus of ongoing research is to obtain the reliable and efficient sensing device.

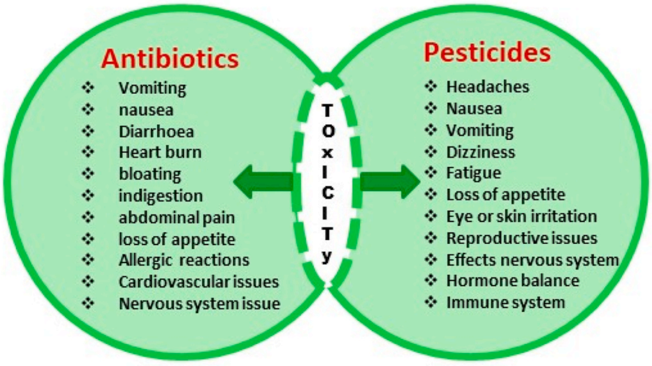

Fig. 2. Health hazards associated with pesticides and antibiotics.

Until the introduction of novel detection strategies, previous strategies are being modified such as an approach where a biomolecule is

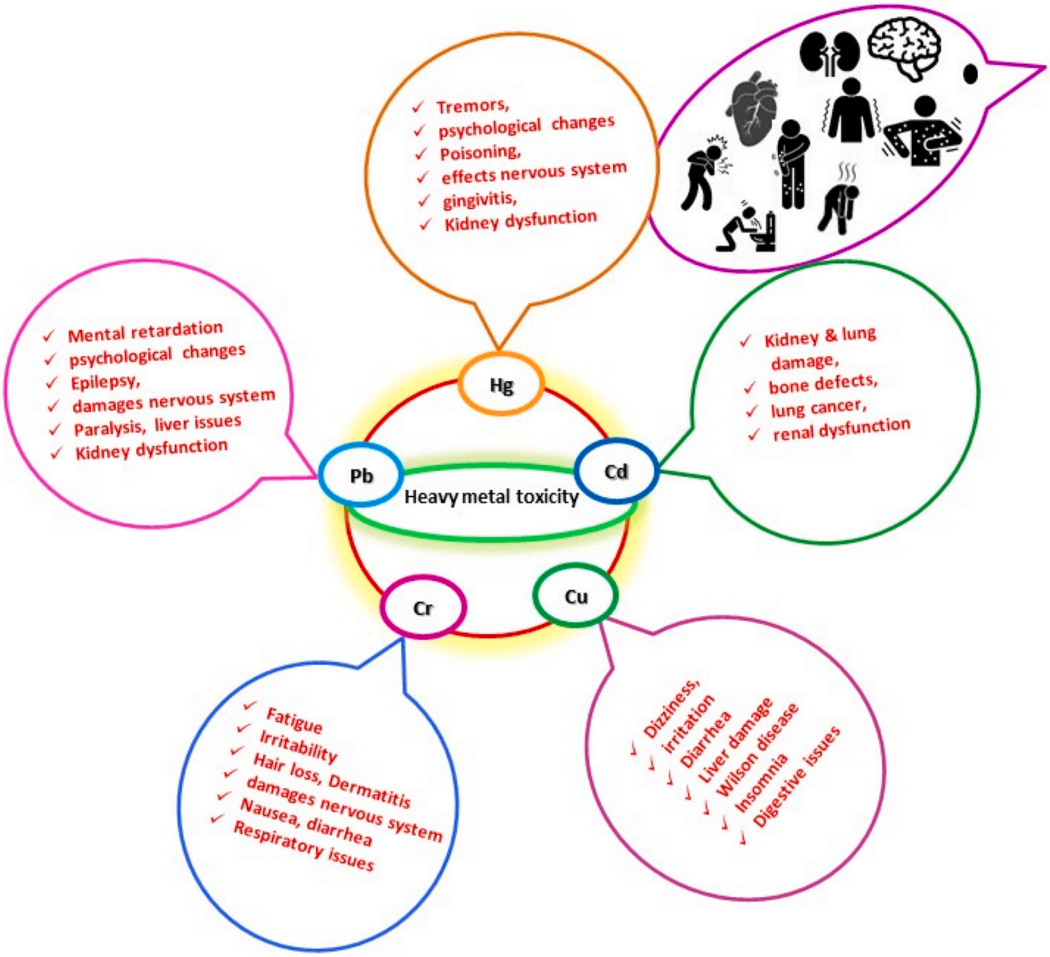

Fig. 1. Toxic effects of heavy metals on human health.

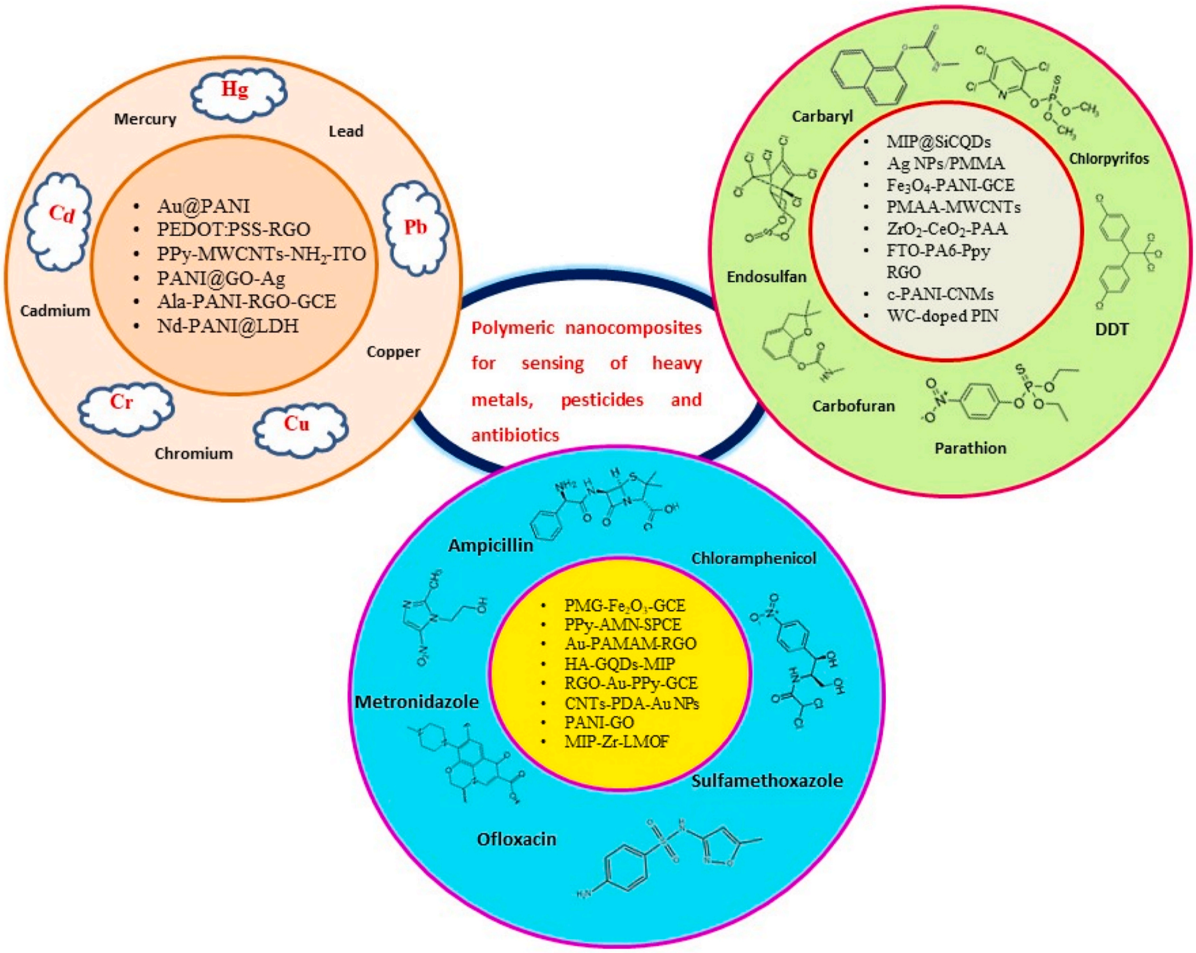

Fig. 3. Polymeric nanocomposites for sensing heavy metals, pesticides and antibiotics.

modified on a sensing unit with the help of nanomaterials, in order to enhance the reliability and sensitivity for specific target analyte. Paramagnetic materials usually enable the facile assembly of sensors and also reduce the energy barrier produced due to various modifiers. The paramagnetic nanomaterials (i.e., laccase) may coat upon carbon paste electrode (CPE) through the magnetic force for sensing hydroquinone (Zhang et al., 2007). Nano-configured three dimensional structures also play important role in enhancing the sensitivity of sensors by providing many binding reactive sites and spatial reaction field. For example, the electrodeposition of gold based nanoclusters on the electrode to accumulate mercury specific oligonucleotides for sensing mercury traces (Zhang et al., 2014). A triboelectric sensor was synthesized by covering the gold nanoparticles with the poly-dimethoxysiloxanes and 3-mercaptopropionoc acid for sensing mercury (Lin et al., 2013). Colorimetric sensing approach is a qualitative method which operates on the principle of color difference. Recently, the visual-distance based sensing technique, based on a V-Chip, is anticipated for the quantitative sensing by translating the analyte recognition into the visual-length signal. Gold based nanoparticles enfolded into the hydrogel would be released in the existence of a target like Pb^{2+}, UO_2^{2+}, cocaine, etc. for catalyzing hydrogen peroxide to produce oxygen, which eventually push the ink-bar moving into the V-Chip. The ink bar distance may visually quantify the concentration of the target (Huang et al., 2016). Hence, the diverse approaches have been constantly evolving either on the basis of previous work or novel emerging ideas in order to match the great sensing capacity.

2.1. Signal indicator and amplification

The signal indicator choice and amplification approach directly influences the performance of a sensor and it also affects the response signals. Electrochemical and optical indicators are the two general categories of signal indicators. Optical indicators include fluorescent indicators such as carbon quantum dots (CQDs), fluorescein isothiocyanate (FITC), etc. (Silvi and Credi, 2015). On the other hand, colorimetric indicators include gold nanoparticle solution, starch iodine solution (blue coloration), few enzymes (laccase, glucose oxidase, etc.), electroactive species (ferrocene, potassium ferricyanide) and thionine (Abdolmohammad-Zadeh and Rahimpour, 2016). Signal amplification approach may enhance the sensitivity of a sensor up to a certain level. Utilization of nano-carriers is an effective approach for signal amplification in the sensors. Nano-carriers like carbon nanotubes (CNTs), mesoporous carbons, etc. have been evolved as suitable materials for designing sensors with increased sensing accuracy through strengthening of response signal (Zeng et al., 2016).

3. Applications of polymeric nanocomposites for sensing heavy metals

3.1. Sensing of mercury (Hg)

Heavy metal ions are playing a major role in creating environmental pollution particularly related to water and soil due to their hazardous, non-biodegradable and non-biocompatible nature along with very long half-life time (Tian et al., 2020). Among these metals, mercury is one of the most hazardous environmental pollutants. Mercury is released into the atmosphere via various sources including cement kilns, thermal power plants, trash incinerators (regular garbage, medical waste, etc.), gold mining, chlor-alkali plants, metal smelting plants, coal combustion, etc. (Ait-Touchente et al., 2020; Singh and Singh, 2020). Mercury or mercury ions possess harmful effects on human health such as severe nervous system problems, organ damage (brain, kidney, etc.), Alzheimer, Hunter-Russell, and Minamata (Katowah et al., 2020a). Furthermore, mercury can also impart serious effects on aquatic animals and plants, wildlife and microorganisms. The release of mercury into the environment is prohibited by European Union (EU), World Health Organization (WHO) and United States Environmental Protection Agency (USEPA). The maximum permissible limit of mercury, set by WHO, is 5 nM. However, the maximum allowable content of mercury in drinking water is 10 nM and 30 nM set by USEPA and WHO, respectively (Tian et al., 2020; Sayyad et al., 2021b). Hence, the development of sensitive, reliable and selective methods to determine minute concentrations of mercury in drinking water, food, soil, etc. is of paramount importance.

For instance, Al-Zahrani and Khan reported the characterization of ion selective CNTs reinforced PANI@Zn–CuO composite membrane prepared by sol-gel method. The fabricated membrane was found to be suitable for preparing ion-selective membrane electrode for detecting Hg^{+2}. The results showed the excellent properties of fabricated electrode including lower limit of detection (1×10^{-6} M), higher working concentration range (1×10^{-1} M to 1×10^{-6} M), smaller response time (17 s), and suitable working pH range (3–6) along with the room temperature stability of about 2.5 months. Moreover, the practicality of the prepared sensor was determined by the titration of heavy metal ions using EDTA, which is a typical material used for removing heavy metals from water on site (Al-Zahrani and Khan, 2021).

In another study, Sayyad and colleagues investigated the incorporation of reduced graphene oxide into poly (3,4-ethylenedioxythiophene):poly (4-styrenesulfonate) (PEDOT:PSS) and the utilization of resultant composite material for preparing organic field-effect transistor (OFET) sensor for Hg^{+2} detection (Sayyad et al., 2021b). The morphological, structural and electrical properties of PEDOT:PSS was observed to be enhanced by adding RGO. The sensor platform showed satisfactory results within the linear concentration range of 1–60 nM along with the lower detection limit of 2.4 nM. The sensor displayed the significant selectivity towards Hg^{+2} after the exposure of various heavy metal ions such as, Cd^{+2}, Cu^{+2}, Pb^{+2}, Zn^{+2}, Fe^{+3} and Na^{+} within 2–3 s. In addition to this, the fabricated sensor offered lower cost, user-friendliness, high performance, better sensitivity, high stability and portability. All these characteristics of the prepared OFET sensor suggest an incredible option for utilizing these gadgets in different fields including environmental monitoring, health care, manufacturing, biomedical diagnostics and military applications.

A unique electrochemical sensor based on biomimetic ion-imprinted polymer (IIP) for sensing Hg^{+2} was reported (Ait-Touchente et al., 2020). The sensor was synthesized by using a two-step procedure: (i) surface functionalization of gold electrode with diazonium salt and the growth of ZnO nanorods (Fig. 4a), (ii) electro-polymerization of pyrrole in the presence of L-cysteine (L-Cys) as a cross-linker and Hg^{+2} as a template (Fig. 4b). These two preparation steps enhanced the performance of composite sensor (Au-diazo-ZnO/IIP) along with the lower limit of detection (1×10^{-12} M) and sensitivity (0.692 μA.pM^{-1}). This enhanced performance was verified by comparing the results with the bare gold electrode having IIP in the absence of ZnO nanorods and without any surface modification. The prepared sensor (Au-diazo-ZnO/IIP) showed the excellent selectivity towards Hg^{+2} in the presence of different competitive ions (Cu^{+2}, Pb^{+2} and Cd^{+2}) even at lower concentrations. Hence, the developed sensor can be effectively used to identify mercury in laboratory or in field using a portable potentiostate.

Katowah and colleagues reported the development of ternary nanocomposites based on copper oxide-poly-methylmethacrylate and (CuO-PMMA) carbon nanofillers based thin film sensors for Hg^{+2} detection (Katowah et al., 2020a). The incorporation of carbon nanofillers into the PMMA matrix resulted in improved thermal properties. The sensor was fabricated by coating a thin layer of composite film (CuO-PMMA-SWCNTs, CuO-PMMA-MWCNTs or CuO-PMMA-G) onto a glassy carbon electrode (GCE) using a conductive chemical binder. The electrochemical results showed the maximum response for CuO-PMMA-SWCNTs towards Hg^{+2} as compared to the MWCNTs and graphene based nanocomposites in a buffer medium. Moreover, the fabricated sensor exhibited fast response time, good reproducibility, large linear range and good stability. Therefore, the nanocomposite sensor based on SWCNTs offers a unique way to produce sensors for detecting heavy metal ions for health care and industrial applications. The sensing performance of different polymeric nanocomposites for mercury ions has been provided in Table 1.

3.2. Sensing of lead (Pb)

Lead is another member of the toxic heavy metals family, which causes severe effects on human health and environment. Lead poisoning can severely impact human health including behavioral and learning

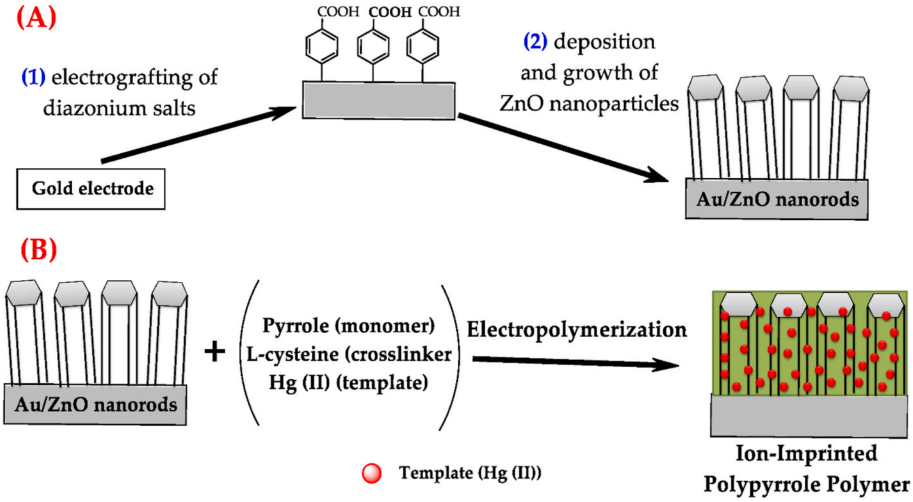

Fig. 4. Schematic representation of: (a) surface modification of gold electrode and deposition of ZnO nanorods on modified surface, (b) electro-polymerization of pyrrole in the presence of L-cysteine and Hg^{+2} for preparing ion-imprinted polymer electrode. This figure is opted from an open access article distributed under CC BY license (Ait-Touchente et al., 2020). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Literature survey on the sensing performance of polymeric nanocomposites for mercury ions (Hg+2).

Sensing material	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
Ag–MnS_2-Ch-PVA	9.0 nM	20–100 nM	Sewage water Tap water	Excellent sensitivity and selectivity	Colorimetric	100.3–101.8%	Eskandari et al. (2020)
Pt-g–C_3N_4–PANI-GCE	0.014 nM	1–500 nM	Laboratory waste water	High selectivity and sensitivity	DPV	98.9%	Mahmoudian et al. (2020a)
CNTs-PANI@Zn–CuO	1×10^{-6} M	$1 \times 10^{-1} - 1 \times 10^{-6}$ M	–	Room temperature stability of about two and half months	Potentiometric	–	Al-Zahrani and Khan (2021)
Pt-g–C_3N_4–PTh	0.009 nM	1–500 nM	Waste water	–	DPV	98.0%	Mahmoudian et al. (2020b)
Au-ZnO-IIP	1 pM	$1 \times 10^{-12} - 1 \times 10^{-6}$ M	–	Highly selective	SWV	–	Ait-Touchente et al. (2020)
CuO-PMMA-SWCNTs-GCE	55.76 pM	0.1 nM–0.01 mM	Tap water Sea water Mineral water	Higher sensitivity, reproducibility, and stability	Electrochemical	98.5–99.3%	Katowah et al. (2020a)
PEDOT:PSS-RGO	2.4 nM	1–60 nM	–	Good selectivity, higher sensitivity, lower cost, user-friendly, and portable	OFET	–	Sayyad et al. (2021b)
Au@PANI	0.014 ppm	0.01–0.1 ppm	–	Good reproducibility	SERS	–	Singh and Singh (2020)
GCE-PTn-afGQDs	0.6 pM	1 pM–1 μM	River water	Good selectivity	CV	97.0–103.0%	Tian et al. (2020)

problems, growth disorder, kidney injury, lower intelligence quotient (IQ), nervous system failure, anemia and hearing problems (Wang et al., 2020b; Pathak et al., 2021). Higher concentrations (≥70 μg/dL) of lead can cause disruption in brain, coma and even death (Sayyad et al., 2021a). The permissible limit of lead in drinking water is 10 ppb and 15 ppb set by WHO and USEPA, respectively (Pathak et al., 2021; Sayyad et al., 2021a). However, no safe limit of lead has been defined in the blood particularly for infants. Therefore, it is important and urgent to develop a cheap, simple and fast method for selective and sensitive detection of lead in the environment.

Nguyen and colleagues developed a glassy carbon electrode modified with nanocomposite based on poly (vinyl alcohol)-chitosan-thermally reduced graphene nanosheets (PVA-Ch-TRG) for the detection of lead in aqueous samples (Nguyen et al., 2021). The incorporation of TRG nanosheets resulted in enhanced mechanical, electronic and electrochemical properties along with the large surface area while the presence of PVA-chitosan blend imparted excellent adsorption capacity of lead and electro-catalytic properties for sensitive determination of lead. The experimental outcome revealed that the experimental conditions such as pre-concentration time, buffer pH, content of graphene and pre-concentration potential significantly influenced the detection process. The fabricated composite electrode showed a linear detection range of 1–50 ppb and a lower detection limit of 0.05 ppb, at a pre-concentration time of 5 min. As compared to the conventional sensors, there is no requirement of novel ligands for complexation for the developed sensor, which may cause environmental issues and also a time consuming process. The results further showed that the existence of other metal ions did not influence the detection of lead, instead the prepared sensor can be used to simultaneously detect lead and cadmium without overlapping peaks. Hence, this study suggested a novel approach for producing lead sensors due to the environmental friendliness and economical production of bulk quantities of sensor components (TRG, PVA and chitosan).

Pathak and colleagues reported the fabrication of a novel flexible sensor consist of chitosan and copper nanocomposite with an integrated reference electrode based on Ag/AgCl for the sensitive detection of lead ions in water samples (Pathak et al., 2021). The results showed the formation of Cu-chitosan nanocomposite which decreased the electron transfer resistance as compared to the bare carbon electrode or only chitosan modified electrode. Consequently, the developed sensor offered a lower limit of detection as compared to the already reported sensors while providing the mechanical flexibility. For instance, the lower limit of detection for as-fabricated sensor was 1.12 ppb, 0.72 ppb, and 1.01 ppb in mining wastewater, drinking water, and soil leachate, respectively. Likewise, the fabricated sensor showed quite good reproducibility of the sensing results, i.e., relative standard deviation (RSD) values for 10 consecutive measurements were 1.93%, 0.65% and 8.75% in mining wastewater, drinking water and soil leachate, respectively. The fabricated sensor also displayed a minimal interference for the detection of lead ions in the presence of other heavy metal ions. Therefore, the reported sensor based on copper and chitosan nanocomposite offered a reliable and sensitive detection of lead ions in different water samples.

Fall and colleagues fabricated a nanocomposite sensor for highly sensitive detection of lead ions in water samples (Fall et al., 2021). The glassy carbon electrode (GCE) was first modified by drop-casting carbon nanotubes (CNTs), iron oxide (Fe_2O_3) and reduced graphene oxide (RGO) as a composite. The resultant modified electrode was then used as a scaffold for electro-synthesis of polypyrrole, which eventually led towards the design of a novel conductive composite material. The fabricated nanocomposite films showed excellent conductivity and stability as compared to the GCE modified with only polypyrrole. The experimental results displayed a linear concentration range of 0.02–0.26 μM along with the lower detection limit of 0.1 nM and sensitivity of 162.8 $\mu A^{\circ} \mu M^{-1}$. Furthermore, the developed composite sensor showed higher repeatability, lower interference for other metallic ions, and better reproducibility for the sensing of lead ions. The applicability of the prepared sensor was further verified by detecting the lead ions in tap water. Hence, the reported functional nanocomposite material suggested a suitable platform for the preparation of sensitive sensors for the detection of trace amounts of lead ions in water.

In another study, a novel electrochemical sensor based on iron oxide (Fe_3O_4), polydopamine (PDA), and manganese oxide (MnO_2) core-shell magnetic nanoparticles was developed for detecting lead ions (Wang et al., 2020b). In short, the magnetic Fe_3O_4 nanoparticles were first prepared by the solvothermal reaction. PDA-Fe_3O_4 nanoparticles were then produced by the polymerization of dopamine (DA) in Tris-HCl buffer at 25 °C. Finally, PDA-MnO_2-Fe_3O_4 core-shell nanoparticles were prepared by the redox activity between $KMnO_4$ and PDA. In the end, PDA-MnO_2-Fe_3O_4 core-shell nanoparticles were magnetically separated and rinsed with water and ethanol followed by drying at 50 °C in vacuum for 12 h (see Fig. 5a). The prepared core-shell nanoparticles were dispersed in ultrapure water by ultra-sonication to prepare a homogeneous suspension. In order to capture the lead ions, the nanoparticle suspension was added to the HCl solution containing different amounts of target ions. After magnetic separation and rinsing with

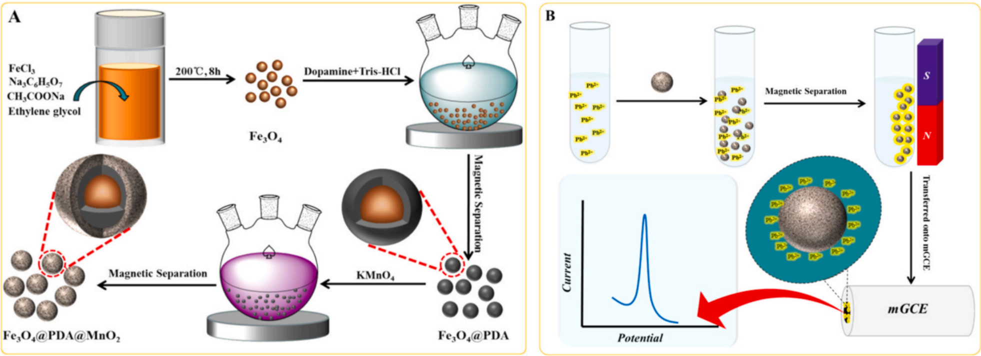

Fig. 5. (a) Schematic representation of the synthesis of PDA-MnO$_2$-Fe$_3$O$_4$ core-shell magnetic nanoparticles and (b) capture, isolation and detection of lead ions in sample solution. Reprinted with permission from (Wang et al., 2020b), Licence number: 5282050640614.

ultrapure water, the obtained mixture was transferred into the magnetic glassy carbon electrode (mGCE) for electrochemical measurements under strong magnetic force (Fig. 5b). Hence, the prepared nanoparticles acted as a pre-concentrator to effectively, selectively and sensitively capture and identify lead ions. Moreover, the suggested methodology offered several other advantages such as cheap, simple operation, good reproducibility and good selectivity. The sensing performance of different polymeric nanocomposites for lead ions has been presented in Table 2.

3.3. Sensing of cadmium (Cd)

Cadmium is one of the most hazardous water pollutants because of its high toxicity and increasing industrial usage (Priya et al., 2020). Cadmium is released into the environment through various industries including mining, metal plating and smelting, pesticides, electroplating, chemicals, etc. (Wu et al., 2020). Cadmium ions can be easily ingested, absorbed and accumulated in the human body via food chain and can cause serious health implications such as renal dysfunction, osteomalacia, bone degeneration, osteoporosis, lung cancer, proteinuria and cancer (Wang et al., 2020a; Li and Feng, 2021). The maximum permissible amount of cadmium in drinking water is 3–5 μg L^{-1} specified by WHO (Wu et al., 2020; Eswaran et al., 2021). Therefore, it is necessary and urgent to develop a sensor that can rapidly and efficiently monitor and detect trace amounts of cadmium in the complex water medium and food samples.

Eswaran and colleagues fabricated an efficient and low cost nanocomposite based on polymelamine-graphitic carbon nitride (PM-gC$_3$N$_4$) modified electrode for simultaneous electrochemical sensing of lead and cadmium ions in water samples (Eswaran et al., 2021). The modified electrode was prepared by simultaneous electrochemical deposition of polymelamine (PM) and g-C$_3$N$_4$ on the electrode surface in H$_2$SO$_4$ medium. The developed nanocomposite network acted as a ligand due to the presence of porous cavity in g-C$_3$N$_4$ to bind metal ions and also due to the amine functional groups present in polymelamine to create complex with metal ions. The developed sensor displayed a linear concentration range from 0.1 to 1.0 μM along with a lower detection limit of 0.02 μM for sensing cadmium ions. Moreover, the prepared modified electrode offered other advantages including facile preparation, low cost, easy to operate, long term stability and good reproducibility.

Table 2
Literature survey on the sensing performance of polymeric nanocomposites for lead ions (Pb^{+2}).

Sensing material	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
PVA-Ch-TRG-GCE	0.05 ppb	1–50 ppb	River water Lake water	Cost-effective, easy-to-use, and environmentally friendly procedure	SWV	–	Nguyen et al. (2021)
Cu-Ch	0.72–1.12 ppb	2.5–60 ppb	Tap water Mining waste water Soil leachate	Higher response towards lead ions	SWV	94.8–98.1%	Pathak et al. (2021)
Fe$_3$O$_4$@PDA@MnO$_2$-mGCE	0.03 μg L^{-1}	0.1–150 μg L^{-1}	Lake water	Excellent performance in sensitivity, selectivity, and long-term stability, lower cost, lower toxicity, and good reproducibility	DPV	98.0–100.8%	Wang et al. (2020b)
RGO@MWCNTs@Fe$_2$O$_3$-PPy-GCE	0.10 nM	0.02–26 μM	Tap water	Good reproducibility, repeatability and stability	SWV	99.2–100.4%	(Fall et al., 2021)
PEDOT:PSS-RGO-L-Cys-GCE	0.09 ppb	1–70 ppb	–	Good sensitivity, selectivity, reproducibility, and repeatability	DPASV	–	Sayyad et al. (2021a)
PPy-MWCNTs–NH$_2$–ITO	2.9×10^{-9} mol L^{-1}	$1 \times 10^{-8} - 3 \times 10^{-7}$ mol L^{-1}	–	Improved stability and higher conductivity	DPV	–	Lo et al. (2020)
Fe$_3$O$_4$@PDA-DMSA-mGCE	0.1–0.2 μg L^{-1}	0.5–50 μg L^{-1}	Lake water	High sensitivity and good anti-interference ability	DPV	94.7–101.4%	Wang et al. (2021a)
NH$_2$-MIL-53(Al)-PPy	0.315 μg L^{-1} 0.244 μg L^{-1}	1–400 μg L^{-1}	Tap water	Highly sensitive, strong anti-interference ability and good stability	DPV	96.8–101.2% 99.2–100.7%	Wang et al. (2020c)
PA-PPy-ZIF-8@ZIF-67-GCE	2.9 nM 14.8 nM	0.02–600 μM	Lake water Orange juice Honey	–	DPV	98.3–106.0%	Zhang et al. (2020)

Therefore, the reported PM-g-C_3N_4 modified electrode can be used for the real-time sensing of cadmium ions in real water samples.

Li and Feng proposed a reflective fiber-optic surface plasmon resonance (RFSPR) sensor based on Ag-PVA-TiO_2 composite membrane for detecting cadmium ions (Li and Feng, 2021). Ag film provided the excitation of resonance effect while PVA-TiO_2 acted as a sensing material for cadmium. The experimental outcome showed a red shift in resonance spectra as a function of increasing concentrations of cadmium ions. The composite film (Ag-PVA-TiO_2) showed highest sensitivity towards cadmium sensing as compared to the Ag-PVA and Ag–TiO_2 films, with the sensitivity values of 315.2 nm/μM and 48.2 nm/μM for the concentration ranges of 0–0.04 μM and 0.1–1 μM, respectively. Furthermore, the sensor offered several other benefits such as high selectivity, easy fabrication and good stability, which makes it a potential candidate for the sensing of cadmium ions in environmental water samples.

Wang and colleagues reported the development of an electrochemical sensor based on poly (*o*-phenylenediamine) (PoPD) and electrochemically reduced graphene (ERGO) composite for sensitive and selective detection of cadmium ions in water (Wang et al., 2020a). The glassy carbon electrode was modified by electrochemical deposition of ERGO to amplify the electron transport at the electrode surface. The ion imprinted polymer (PoPD) was then electro-polymerized on ERGO through cyclic voltammetry scanning by using oPD as a functional monomer and cadmium ions as template, followed by the removal of template via electrochemical peroxidation route. The results displayed that under optimum conditions, the fabricated sensor exhibited a linear concentration range of 1–50 ng mL^{-1}, along with the lower limit of detection as 0.13 ng mL^{-1}. Moreover, the composite sensor showed a higher selectivity towards cadmium ions. The sensing ability of the proposed sensor for detecting cadmium ions in real water samples confirmed its potential for sensitive and selective determination of cadmium ions in water.

Likewise, an electrochemical sensor platform based on chitosan, gold nanoparticles and graphene was developed for detecting cadmium ions in milk and drinking water samples (Wu et al., 2020). The fabricated composite sensor displayed higher sensitivity for detecting cadmium ions, which was attributed to the excellent conductivity and enhanced electron transfer induced by gold nanoparticles and graphene. The linear concentration range of the composite sensor for cadmium ions was 0.1–0.9 μM along with the lower detection limit of 1.62×10^{-4} μM. Furthermore, the developed platform showed good stability, higher selectivity, and better repeatability in the detection of cadmium ions. In the end, the prepared sensor was used for detecting cadmium ions in real samples and the experimental results verified the potential of fabricated sensor as a promising platform for quantitative determination of cadmium ions in water and food samples. The sensing performance of different polymeric nanocomposites for cadmium ions has been described in Table 3.

3.4. *Sensing of copper (Cu)*

Copper has been widely used in a variety of products including pesticides, electrical appliances and wood preservatives and in several processes such as dye manufacturing, lithography, electroplating, engraving, pyrotechnics and petroleum refining. This prominence use of copper throughout the human history is associated to its ductility and malleability as a metal or alloy, excellent electrical and thermal conductivities, and antimicrobial characteristics (Fernando et al., 2021). Copper ions are also crucial as a trace element for several biological functions in humans including tissue development, blood formation, functioning of enzymes, and transcriptional events (Li et al., 2021). However, the excessive intake of copper ions can cause several diseases such as diarrhea, nausea, vomiting, stomach cramps, kidney diseases, liver damage, Wilson and Alzheimer's diseases (Echabaane et al., 2021). Due to these concerns, the maximum allowable concentration of copper ions in drinking water is 20 μM and 30 nM specified by USEPA and WHO, respectively (Echabaane et al., 2021; Fernando et al., 2021). Accordingly, a convenient, effective and feasible method for detecting copper ions is required for human health and environmental protection.

Li and colleagues developed an electrochemical sensor based on thin-layer nanostructured polyethyleneimine (PEI) decorated black phosphorus (BP) for sensitive detection of copper ions (Li et al., 2021). The results showed a wide linear concentration range of 0.25–177 μM and a lower detection limit of 0.02 μM for the composite sensor, which was far below than the permissible limit for drinking water. The fabricated sensor also displayed a faster response time (1.5 s) along with the simple operation as compared to the conventional tiresome stripping voltammetry. The enhanced sensing response of the nanocomposite sensor was attributed to the synergistic effect of BP and PEI, i.e., BP offers the reactivity while PEI splits the thick BP layer to thin-layer PEI-BP structured composite with larger reaction area (see Fig. 6). Moreover, the rich N atoms in PEI provided strong adsorption of copper ions for chelation, which was the main reason for higher reduction current of copper ions. A flexible nanocomposite sensor was further prepared and used to detect copper ions in real water samples, which verified the applicability of developed sensor in monitoring the water quality.

Fernando and colleagues fabricated and analyzed an electrochemical

Table 3
Literature survey on the sensing performance of polymeric nanocomposites for cadmium ions (Cd^{+2}).

Sensing material	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
PANI@GO-Ag	1×10^{-5} M	$1 \times 10^{-1} – 4 \times 10^{-4}$ M	Municipal waste water	Cost effective material	CV	–	Eltayeb and Khan (2020)
Ag-PVA-TiO_2	0.006 μM	0–1 μM	–	High sensitivity, simple fabrication, good stability and strong selectivity	RFSPR	–	Li and Feng (2021)
PoPD-ERGO-GCE	0.13 ng mL^{-1}	1–50 ng mL^{-1}	River water Lake water	Good selectivity and sensitivity, good repeatability and stability	SWV	94.0–106.4%	Wang et al. (2020a)
CS-AuNPs-G-GCE	1.62×10^{-4} μM	0.1–0.9 μM	Tap Water River water Milk	High selectivity, good stability, and repeatability	DPV	98.5–109.2%	Wu et al. (2020)
PM-g–C_3N_4–ASPE	0.008 μM 0.02 μM	0.1–1 μM	River water Lake water Tap water	Superior stability, selectivity, and repeatability, good anti-interference, low-cost, efficient	DPV	92.5–106.4% 90.0–102.6%	Eswaran et al. (2021)
A-MWCNT-Hyalu-L-Cys-GCE A-MWCNT-Hyalu/L-Ser-GCE	0.032–0.057 μg L^{-1} 0.015–0.034 μg L^{-1}	0.4–4 μg L^{-1}	Honey Cocos nusifera Egg white	Good linearity, very simple and selective protocol with higher sensitivities	SWV	90.1–96.2% 90.2–95.0%	Priya et al. (2020)
Ala-PANI-RGO-GCE	0.03 nM 0.045 nM 0.063 nM	0.08–100 nM	Tap water	Enhanced repeatability, improved selectivity, and reproducibility, and good practical applicability	SWV	98–104.0%	Akhtar et al. (2020)

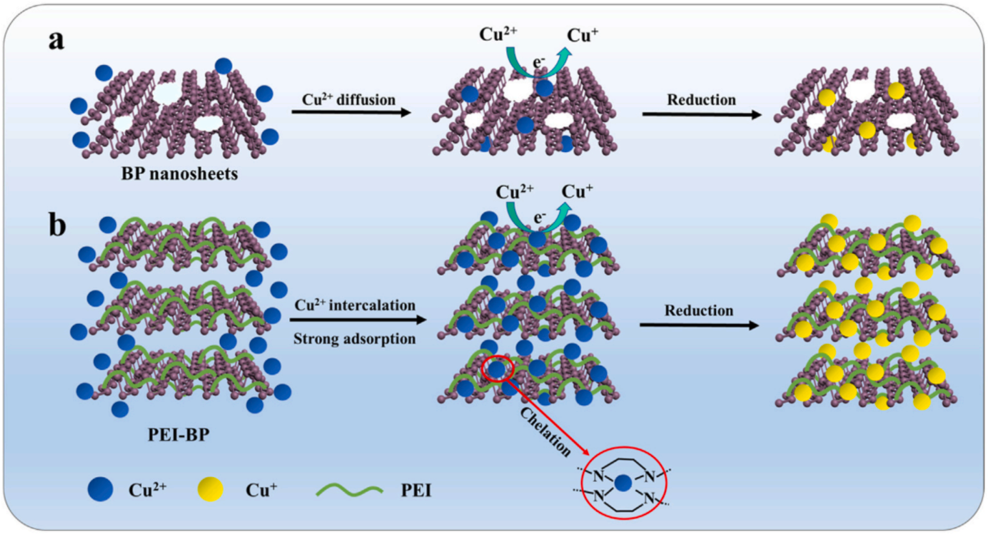

Fig. 6. Schematic representation of the reduction of copper ions (Cu^{2+}) by (a) black phosphorus nanosheets and (b) thin-layer nanostructured polyethyleneimine decorated black phosphorus. Reprinted with permission from (Li et al., 2021). Licence number: 5282361059340

sensor based on poly-4-vinyl pyridine (P4VP)-wrapped MWCNTs attached to a poly (ethylene terephthalate) (PET)-modified gold electrode for sensing copper ions (Fernando et al., 2021). The incorporation of P4VP resulted in the pre-concentration of copper ions next to the electrode surface for analysis through cyclic voltammetry due to its strong interactions with copper ions (i.e., complexation/chelation). The proposed sensor displayed a linear concentration range of 1.1–13.8 ppm, detection limit of 0.5 ppm and a RSD value of 4.9% for 1.3 ppm. The sensing results for ocean water, tap water, deionized water and lake water were quite similar, which highlighted the applicability of pre-concertation strategy for different real samples. Hence, the development of an electrochemical sensing platform by exploiting the polymer chelation behavior presents an effective strategy for continuous monitoring of water quality.

Likewise, a novel impedimetric sensor, based on glassy carbon electrode modified with chitosan and carbon dots (CDs) nanocomposite, was developed by (Echabaane et al., 2021) for faster and sensitive detection of copper ions. The carbon dots were simply prepared by heating an aqueous acidic solution of glucose. The resultant CDs exhibited a graphitic structure with hydroxyl and carboxyl groups on the surface, average size of 3.2 nm, and peculiar optical properties. The experimental outcome for the fabricated nanocomposite sensor displayed a linear concentration range of 10^{-9} M to 10^{-5} M along with a detection limit of 5×10^{-10} M. Moreover, the proposed impedimetric nanocomposite sensor showed good conductivity, large surface area and enhanced charge transfer at electrolyte/film interface, which eventually resulted in good selectivity towards copper ions, better reproducibility, good stability and lower detection limit. All these features of the developed nanocomposite sensor justify its application in quality control of water.

Chakraborty and colleagues reported the fabrication of a conductive nanocomposite sensor based on polylacetic acid (PLA) and exfoliated graphene (EG) in the presence of different additives such as silk nanocrystal (SNC), EDTA and albumin for sensing copper ions (Chakraborty et al., 2021). The addition of different fillers resulted in a decrease in thermal stability and mechanical strength of the composite films. The composite film without any additive displayed a sensitivity of 0.36 μA/ppm for detecting copper ions in the concentration range of 5–100 ppm, which confirmed its possible utilization as a future material for electrodes. The hysteresis loop of current-voltage response was found to be significantly influenced by different parameters such as type of cation/anion, scan rate, and type of electrode. For composite films modified with EDTA or albumin, a reduction peak of copper ions was observed, which suggested that the target ion binding with additives is dependent on the availability of ligand site. Moreover, the detection limit of composite films with or without the additives was observed to be similar to the already reported values for the polymer based sensors. All these results verified that the modification of nanocomposite film with EDTA or albumin resulted in higher metal ion selectivity without much affecting the sensitivity and detection limit. However, the sensitivity of the modified composite films can further be enhanced by playing with the concentration of exfoliated graphene. The sensing performance of different polymeric nanocomposites for copper ions has been described in Table 4.

3.5. Sensing of chromium (Cr)

Hexavalent chromium ions typically exist in water as $HCrO_4^{-2}$, $HCrO_4^-$ or $Cr_2O_7^{-2}$ at different concentrations and pH. These ions are identified as priority pollutants because of their higher mobility in water along with harmful effects on human health (Truskewycz et al., 2020). Chromium ions are released into the environment through various industries or processes including refractory and metallurgical industries, cement industry, chrome plating, fuel combustion, pigments manufacturing, leather tanning, corrosion inhibition, wood preservation, dyeing, steel production, cooling towers, textile industries, etc. (Motaghedifard et al., 2021; Wani et al., 2021). This release results in devastating effects on the human and aquatic life because of its carcinogenic, corrosive, mutagenic, and teratogenic properties (Truskewycz et al., 2020). The maximum permissible limit of chromium ions in drinking water is 50 μg L^{-1} according to the WHO (Ebrahim et al., 2020). Therefore, for quantitative and convenient detection and removal of chromium ions from the environment, economical, simple and sensitive methods are of paramount importance.

Motaghedifard and colleagues modified the surface of glassy carbon electrode with polyaniline (PANI), sulfated zirconium dioxide (ZrO_2–SO_4^{-2}) and MWCNTs based nanostructures to fabricate a sensing platform for chromium ions in industrial waste water (Motaghedifard et al., 2021). The incorporation of PANI resulted in higher selectivity and enhanced electron transfer while the sulfated zirconium dioxide provided the uniform dispersion of PANI nanostructures over the MWCNTs nanostructures. The electrochemical measurements for modified electrode showed quicker electro-reduction of chromium ions at relatively lower potential as compared to the bare electrode. The detection limit of 64.3 nmol L^{-1} was estimated for chromium ions using modified electrode. Hence, the developed sensor exhibited interesting

Table 4

Literature survey on the sensing performance of polymeric nanocomposites for copper (Cu^{+2}) and chromium (Cr^{+6}) ions.

Sensing material	Metal ion	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
PEI-BP-GCE	Cu^{+2}	0.02 μM	0.25–177 μM	River water	Outstanding performance with fast response time, and an excellent reproducibility	Amperometry	90.8–96.8%	Li et al. (2021)
PLA-EG	Cu^{+2}	0.22 ppm	–	–	–	Amperometry	–	Chakraborty et al. (2021)
P4VP-wrapped MWCNTs-PET	Cu^{+2}	0.5 ppm 7.8 μM	1.1–13.8 ppm 16.6–216 μM	Tap water Lake water Ocean water	Effective platform for continuous monitoring of metal ions	CV	94.0–103.2%	Fernando et al. (2021)
CDs-Ch-GCE	Cu^{+2}	5×10^{-10} M	$1 \times 10^{-9} - 1 \times 10^{-5}$ M	Tap water Well water	Good reproducibility, stability, and selectivity	EIS	96.0–104.0%	Echabaane et al. (2021)
QCDs-PVP-ZnO	Cr^{+6}	1.2 μM	0–4.9 μM 9.7–625 μM	River water	Cheap to manufacture	Fluorescence	–	Truskewycz et al. (2020)
Nd-PANI@LDH	Cr^{+6}	0.0015 μM	0.03–0.19 μM	Lake water	Excellent selectivity, sensitivity, and adsorption capacity	Fluorescence	57.0–97.0%	Wani et al. (2021)
PANI@ZrO_2–SO_4^{2-}@MWCNTs-GCE	Cr^{+6}	0.0643 μmol L^{-1}	0.55–39.5 μmol L^{-1}	Industrial waste water	High stability and good reproducibility	DPV	98.9–100.9%	Motaghedifard et al. (2021)
PANI-Ag (AMPSA)-GO QDs	Cr^{+6}	6 μg L^{-1}	0.01–0.06 mg L^{-1} 0.1–7.5 mg L^{-1}	Tap water Raw water	Faster response time, good selectivity, high reproducibility, stability and repeatability	Fluorescence	95.3–99.2%	Ebrahim et al. (2020)

features including wide linear concentration range, good reproducibility and high stability for detecting chromium ions both in buffer solution and in industrial waste water from barium chromate production.

In addition to the electrochemical sensors, polymeric nanocomposite sensor based on neodymium (Nd)-doped polyaniline (PANI) supported on Zn–Al layered double hydroxide (LDH) was synthesized by ex-situ polymerization method for fluorescence detection of hexavalent chromium ions (Wani et al., 2021). The fabricated sensor showed quite faster and selective adsorption and detection of chromium ions. A linear correlation was observed for the fluorescence intensity with concentrations ranging from 200 to 1000 ppb with a quantification limit of 96 nM and a detection limit of 1.5 nM for the nanocomposite sensor. The adsorption performance of nanocomposite sensor (PANI@Nd-LDH) for chromium ions in waste water displayed higher removal capacity (219 mg/g) as compared to the unmodified Nd-LDH (123 mg/g) or LDH (88 mg/g) sensor. The sensing mechanism was attributed to the (i) intercalation of chromium ions within the inter-gallery regime of LDH, (ii) inner filler effect of chromium ions, and (iii) synergistic affinity of heavy metal ions with the polymeric chains. The outstanding sensing results of nanocomposite sensor for chromium ions demonstrated the possible application of developed sensor as an excellent probe for environmental monitoring.

Truskewycz and colleagues reported the preparation and characterization of a novel composite hydrogel based on polyvinylpyrrolidone (PVP), zinc oxide (ZnO) and quantum carbon dots (QCDs) without the addition of cross-linkers (Truskewycz et al., 2020). The incorporation of QCDs into the hydrogel resulted in a specific interaction with chromium ions along with the increased photoluminescence behavior. This nanocomposite hydrogel was further used to fabricate a three-dimensional sensing platform for chromium ions offering several benefits such as inhibition of self-QCDs quenching, minimization of QCDs agglomeration, and provision for rapid diffusion of ionic species and water which eventually provides unconstrained interaction with fluorescent matrix. The composite hydrogel sensor (PVP–ZnO-QCDs) displayed a selective fluorescence quenching for chromium ions along with the deviating fluorescence profiles in the presence of different ionic species. The detection limit for developed sensor was 1.2 μM for environmental water samples, which was far below than the permissible limit of chromium ions in drinking water. The reported results were promising for the fabrication of hydrogel based novel sensing platforms for highly selective and sensitive detection of chromium ions in real water samples.

Ebrahim and colleagues fabricated a fluorescent nanocomposite based on polyaniline (PANI), graphene oxide quantum dots (GO QDs) and 2-acrylamido-2-methylpropanesulfonic acid capped Ag nanoparticles (Ag-AMPSA) through in-situ reaction for highly selective detection of chromium ions using luminescent quenching (Ebrahim et al., 2020). The fabricated probe displayed a lower detection limit of 6 μg/L, which is significantly lower than the permissible amount of chromium ions in drinking water. Moreover, the nanocomposite sensor offered several other benefits as well including faster response time, good selectivity, higher stability, repeatability and reproducibility. The sensing mechanism of nanocomposite sensor was linked to the synergistic effect of inner filler effect (IFE), ion binding/exchange and the formation of ground state compounds (see Fig. 7a). The spectral overlap between the absorption and emission spectra of nanocomposite sensor and the absorption peaks of chromium ions indicated the existence of inner filler effect (see Fig. 7b). The proposed fluorescent sensor exhibited promising results for the detection of chromium ions in real water samples. The sensing performance of different polymeric nanocomposites for chromium ions has been described in Table 4.

4. Applications of polymeric nanocomposites for sensing pesticides

In order to meet the increasing demand of quality food, the pesticides are extensively used to avoid the undesirable losses of agricultural productions. However, careless handling, improper use and food or environmental (air, soil and water) contaminations lead towards a huge threat to human life (Loguercio et al., 2021). Variety of pesticides including carbaryl (Loguercio et al., 2021), parathion (Wang et al., 2021b), 2,4-Dichlorophenoxyacetic acid (Goswami and Mahanta, 2021), endosulfan (Masibi et al., 2021), niclosamide (Li et al., 2022), indoxacarb (Shirani et al., 2021), glyphosate (Sawetwong et al., 2021), Dichlorodiphenyltrichloroethane (DDT) (Miao et al., 2020), Chlorpyrifos (Joshi et al., 2020), Malathion (Migliorini et al., 2020), Carbofuran (Monireh et al., 2020), 2,4-dichlorophenol (Katowah et al., 2020b), Acetamiprid (Yi et al., 2020), etc. are known to control the amount of pests and weeds for various agricultural fields such as cereals, cotton, rice, vegetables, fruits, etc. These pesticides are well-known to affect the nervous system of pests and vertebrates, inhibit the growth of weeds, etc. (Goswami and Mahanta, 2021; Loguercio et al., 2021). However, due to their water solubility and non-biodegradability, these pesticides

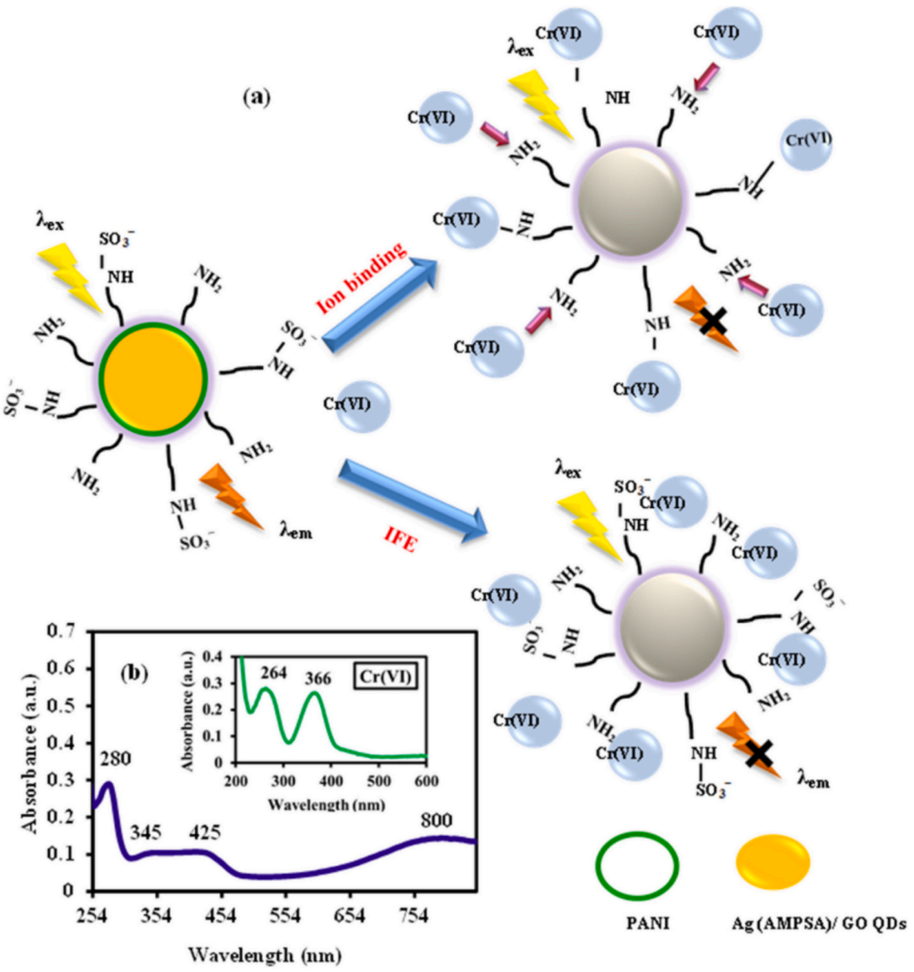

Fig. 7. (a) Schematic representation of the quenching processes of nanocomposite (PANI-Ag-AMPSA-GO QDs) by chromium ions, λ_{ex} and λ_{em} are the excitation and emission wavelengths, respectively; (b) UV–Vis spectra of nanocomposite (PANI-Ag-AMPSA-GO QDs), the inset shows the UV–Vis spectra of 5 mg L^{-1} chromium ions. This figure is opted from an open access article distributed under CC BY license (Ebrahim et al., 2020).

impose a serious negative impact on human health including nervous system damage, respiratory paralysis, DNA damage, muscle weakness, reduced concentration of sperm cells, convulsions, epilepsy, impaired memory, psychiatric disturbances, immunosuppression, etc. (Masibi et al., 2021; Wang et al., 2021b). In order to avoid these health problems, World Health Organization and Environmental Protection Agency have set the maximum permissible limits of these pesticides for drinking water. Hence, it is imperative to develop suitable, novel and portable sensing strategies for rapid, sensitive and selective detection of pesticides in real samples. The performance of different polymeric nanocomposites for sensing of different pesticides has been described in Table 5.

4.1. Sensing of carbaryl, parathion and fenitrothion

Carbaryl, parathion and fenitrothion are broad spectrum insecticides, which are typically used to kill various insects. Carbaryls are carbamate functionalized molecules, while parathion and fenitrothions are organo-phosphorus based molecules. The residues of these insecticides have been found in fresh water sources, which are responsible to pose toxic effects on plants, animals and human beings (Faria et al., 2022).

Loguerico and colleagues reported the production of an efficient enzymatic electrochemical biosensor based on dodecyl sulphate (DS) and indigo carmine (IC) doped polypyrrole, gold nanoparticles and acetylcholinesterase enzyme (AChE) from electric eel for the detection of carbaryl (Loguercio et al., 2021). The polymerization process offered the optimized surface conditions for the immobilization of the enzyme. The results showed a similar outcome, as already reported in literature for AChE from electric ray, with faster electron transfer. This lack of resistance resulted in a high binding interaction of carbaryl with the adsorption sites of enzyme. The fabricated biosensor exhibited a quantification limit of 0.11 ng cm^2 mL^{-1}, detection limit of 0.033 ng cm^2 mL^{-1}, sensitivity of 59.5×10^3 A cm^{-2} mL g^{-1} along with the linear concentration range of 0.05–0.25 ng mL^{-1} for carbaryl. Moreover, the biosensor displayed good inter-electrode reproducibility and intra-electrode repeatability, improved stability by storing at lower temperature (−15 °C) along with the RSD values of 3.7% towards carbaryl detection. Wu and colleagues developed a nanocomposite sensor based on zinc oxide-cerium oxide-polyacylic acid (ZrO_2–CeO_2-PAA) for the colorimetric detection of methyl parathion (MP) (Wu et al., 2021). The distribution of ZrO_2 in CeO_2 nanorods enhanced the phosphatase-like activity of CeO_2 nanorods while the coating of ZrO_2–CeO_2 nanorods with polyacrylic acid (PAA) resulted in improved stability, dispersion and robustness. Furthermore, the developed nanocomposites (ZrO_2–CeO_2-PAA) displayed excellent adaptability for a wide range of pH (4.0–12.0) and temperature (0–100 °C), i. e., high temperature and pH resistance. Additionally, the nanocomposites showed higher resistance towards the organic solution as compared to the natural alkaline phosphatase, as evident by almost 100% activity of nanocomposites in 60 vol% methanol solution. The results of colorimetric detection of pesticide (MP) using prepared

Table 5
Literature survey on the sensing performance of different polymeric nanocomposites for pesticides.

Sensing material	Target pesticide	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Ref.
PDA@Fe_3O_4 MIP MNPs	DDT	6×10^{-12} mol L^{-1}	1×10^{-11} to 1×10^{-3} mol L^{-1}	Radish	Excellent selectivity, sensitivity, stability and reproducibility	EIS	Miao et al. (2020)
PPy–IC–DS-Au NPs	Carbaryl	0.033 ng cm^2 mL^{-1}	0.05–0.25 ng mL^{-1}	Stock solution of carbaryl	Good inter-electrode reproducibility and intra-electrode repeatability, higher stability	CV	Loguercio et al. (2021)
Ag NPs/PMMA	Parathion Fenitrothion	4.24×10^{-8} M 2.74×10^{-9} M	–	pesticide-contaminated tomato and lemon surface	High reproducibility, good uniformity, better mechanical stability, easy fabrication, straightforward detection on curved surfaces	SERS	Wang et al. (2021b)
Fe_3O_4-PANI-GCE	2,4-dichlorophenoxyacetic acid	0.21 μM	1.35–2.7 μM	Stock solution of 2,4-D	Simple, low-cost, and biocompatible	CV	Goswami and Mahanta (2021)
WC-doped PIN	Chlorpyrifos	5.94×10^{-8} mol L−1	25×10^{-7} to 225×10^{-7} mol L−1	Stock solution of CHL	Rapid electron shift, high electrical conductivity, enhanced stability and huge surface area	SWV	Joshi et al. (2020)
GCE-AO NPs-PANI-SWCNTs	Endosulfan	6.8 μM	32.3–77.6 μM	Stock solution of EDS River and tap water	Good anti-interference behavior and better selectivity	CV, SWV	Masibi et al. (2021)
FTO-PA6-PPy-RGO	Malathion	0.8 ng mL^{-1}	500–2×10^4 ng mL^{-1}	Stock solution of malathion River and tap water	High selectivity	CV	Migliorini et al. (2020)
PMAA-MWCNTs	Carbofuran	3×10^{-10} M	1×10^{-9} to 1×10^{-6} M	Human urine Tap water River water	Considerable sensitivity	SWV	Monireh et al. (2020)
c-PANI-CNMs	2,4-dichlorophenol	7.6 nmol L^{-1}	0.05–0.6 μmol L^{-1}	Fish farm water	Rapid response, short analytical time, excellent selectivity, high sensitivity and good reproducibility	DPV	Katowah et al. (2020b)
3DHPC@Ch-GCE	Niclosamide	6.7 nM	0.01–10 μM	Water Grass carp Brown rice	Good repeatability, reproducibility, stability, and selectivity	CV, DPV	Li et al. (2022)
ZrO_2–CeO_2-PAA	Methyl parathion	0.021 nM	7.60×10^{-11}-7.60×10^{-8} M	Corn	High specificity and stability, excellent adaptability	Colorimetric	Wu et al. (2021)
MIP@SiCQDs	Indoxacarb	1 nM	4–102 nM	Well water Apple Tomato	Excellent selectivity, low cost, facile preparation	Fluorescence	Shirani et al. (2021)
Mn–ZnS QDs-MIP	Glyphosate	0.002 μg mL^{-1}	0.01–30 μg mL^{-1}	Whole grain	High accuracy, good reproducibility, highly selective and sensitive	Colorimetric	Sawetwong et al. (2021)
3D-Ch-RGO-GCE	Acetamiprid	71.2 fM	0.1 pM to 0.1 μM	Tea	Good sensitivity	SWV	Yi et al. (2020)

nanocomposite displayed a detection limit of 0.021 nM and a linear concentration range of 7.60×10^{-11} – 7.60×10^{-8} M. Therefore, the fabricated nanocomposite can be used as a potential tool for detecting pesticide in real samples.

A group of researchers developed a lightweight, high performance and flexible surface-enhanced Raman scattering (SERS) substrate using a cost effective, green and facile fabrication method for detecting pesticides (Wang et al., 2021b). The photo-reduction technique was used to produce the plasmonic silver nanoparticles (Ag NPs) for the enhancement of Raman signal with the help of chemically patterned ferroelectric crystals. The PMMA films were then effectively transferred to these patterned Ag NPs using a drop and peel-off methodology, in order to produce a transparent Ag NPs/PMMA SERS substrate (see Fig. 8). In the practical application, the developed sensor showed an ultra-low detection limit and a high performance factor for the real time sensing of parathion and fenitrothion on the curved surfaces of lemon and tomato (see Fig. 8). Moreover, the fabricated sensor also detected the Raman peaks for beta-carotene on lemon/tomato peels without the requirement of tedious sample preparation. Furthermore, the proposed SERS based sensor displayed many interesting features such as high reproducibility, good uniformity, superior multiplex detection, and good stability. These enhanced sensing abilities of Ag NPs/PMMA SERS substrate can be associated to the creation of huge amount of hotspots by the closely

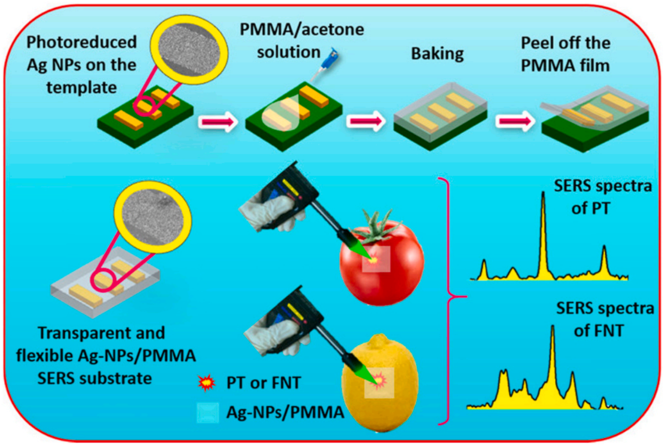

Fig. 8. Schematic representation of the fabrication method of the transparent and flexible SERS substrate and SERS sensing of pesticides on the curved surfaces of tomato and lemon along with the obtained SERS spectra. Reprinted with permission from (Wang et al., 2021b) copyrights @ American chemical society 2021.

packed Ag NPs extracted from the PMMA film. Hence, the suggested Ag NPs/PMMA flexible SERS based sensor has significant potential to be used for the real time, sensitive and selective detection of multiple pesticides (Table 5).

4.2. Sensing of 2,4-Dichlorophenoxyacetic acid, endosulfan and niclosamide

Goswami and Mahanta modified the glassy carbon electrode with PANI-Fe_3O_4 nanocomposite by using drop casting technique for non-enzymatic, effective and sensitive recognition of 2,4-Dichlorophenoxyacetic acid (2,4-D) at neutral pH. A phosphate buffer solution of 0.1 M concentration was synthesized with the pH value of 7 (Goswami and Mahanta, 2021). The electrochemical measurements were performed for both bare and modified GCE electrode in the presence or absence of 2, 4-D with Ag/AgCl as a reference electrode. The characteristic peak was not observed for the electrochemical response of the bare electrode with or without the pesticide. On the other hand, modified GCE (PANI-Fe_3O_4-GCE) displayed redox peaks both in the absence and in the presence of 2,4-D. The fabricated sensor exhibited a sensitivity of 4.62×10^{-7} μA μM^{-1} cm^{-2}, detection limit of 0.2 μM, and a linear concentration range of 1.35–2.7 μM for 2,4-D, as evident from amperometric analysis. The sensing mechanism of the developed sensor is linked to the simple adsorption of pesticide molecules on the surface of PANI-Fe_3O_4 nanocomposite. The proposed sensor offers to be a cheap and simple non-enzymatic sensor for the detection of 2,4-D.

Likewise, Masibi et al. reported a unique sensor based on polyaniline (PANI), acid functionalized single walled carbon nanotubes (fSWCNTs) and antimony oxide nanoparticles (AONPs) for the detection of endosulfan (EDS) in minute quantity (Masibi et al., 2021). The experimental outcome displayed that the current response for composite sensor (PANI-AONPs-fSWCNTs-GCE) was higher with relatively low potential as compared to the other electrodes, which eventually confirmed the superiority of modified GCE. Moreover, the electrochemical analysis for composite sensor showed good electro-catalytic activities along with the sensitivity of 0.0623 μA μM^{-1}, quantification limit of 20.6 μM and detection limit of 6.8 μM. In addition, the results showed a reduction in current response for EDS of about 2.0% in the presence of interfering substances along with the 97% average recovery of EDS in real samples.

Li et al. fabricated the chitosan decorated three dimensional hierarchical porous carbon (3DHPC-Ch) composite using an ultrasonic assisted, low cost, simple and green methodology (Li et al., 2022). The prepared composite (3DHPC-Ch) was then effectively used to modify the GCE surface to produce a 3DHPC-Ch-GCE sensor for the electrochemical detection of niclosamide. Due to the presence of both chitosan and 3D hierarchical porous carbon, the prepared sensor showed a linear concentration range of 0.01–10 μM along with the detection limit of 6.7 nM for niclosamide. Furthermore, the developed sensor displayed good reproducibility, repeatability, selectivity and stability along with the good practicability for the sensing of niclosamide in various food samples with satisfactory recoveries and lower RSD values. Hence, this study offers a very interesting system for the sensitive detection of niclosamide in food samples. However, further research is needed to analyze the influence of interfering substances on the sensing efficiency (Table 5).

4.3. Sensing of glyphosate

Glyphosate is an organo-phosphorus based molecule used for the protection of crops and plants against herbs and pets. Glyphosate inhibits the shikimate mechanism in plants, while this mechanism is very important that allows the biosynthesis of aromatic amino acids. This has also been proved carcinogenic and it is detected in blood and urine of exposed workers. Glyphosate is also found responsible to cause cytotoxicity, genotoxicity and oxidative stress (Peillex and Pelletier, 2020). Hence, there is a continuous need to monitor glyphosate in various mediums to prevent its harmful effects. A colorimetric technique for detecting glyphosate in whole grain samples using a novel 3D microfluidic paper-based analytical device (3D-μPAD) was reported by (Sawetwong et al., 2021). The microfluidic device was prepared from Mn–ZnS quantum dot embedded molecularly imprinted polymer (Mn–ZnS QD-MIP). The binding or non-binding ability of glyphosate molecules on the recognition sites of Mn–ZnS QD-MIP determines the catalytic activity. The selective binding of glyphosate on the surface cavities of Mn–ZnS QD inhibited or turned off the oxidation of 2, 2′-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid (ABTS) and the color change to light green, which is actually dependent on the concentration of glyphosate (Fig. 9). The foldable microfluidic device was prepared in the form of three layers: (i) detection layer (top), (ii) immobilized Mn–ZnS QD-MIP disc (center), and (iii) sample loading (bottom) (Fig. 9). The results showed that the device can be operated within the range of 0.005–50 μg mL^{-1} along with a detection limit of 0.002 μg mL^{-1}. Moreover, the fabricated device exhibited a high accuracy of 0.7% (inter-day) and 0.4% (intra-day) relative difference from the value of certified reference material along with the good reproducibility (i.e., 1.7% RSD value for ten devices) (Table 5). Hence, the developed microfluidic platform offers an alternative highly sensitive and selective colorimetric detection method for environmental monitoring and food quality control applications without the need of sophisticated equipment.

5. Applications of polymeric nanocomposites for sensing antibiotics

Antibiotics are commonly known as anti-bacterial agents and widely used for treating humans and animals as well as for improving animal growth because of their ability to increase the effectiveness of feed (Amiri et al., 2021). Generally, there are seven classes of antibiotics known as streptogramins, β-lactam antibiotics, peptide antibiotics, lincosamides, macrolide antibiotics, aminoglycosides, and tetracyclines (Alsaiari et al., 2021). The most commonly used antibiotics include Ciprofloxacin (Surya et al., 2020; Mahmoudpour et al., 2021), Ceftazidime (Bunkoed et al., 2020b; Amiri et al., 2021), Norfloxacin (Bunkoed et al., 2020a; J. Louw et al., 2020), Chloramphenicol (Mani et al., 2020; Karuppiah et al., 2021), Tetracycline (Sun et al., 2020; Sereshti et al., 2021), etc. However, antibiotics can have a negative effect on human health, even in trace amounts, due to their capability to accumulate in food chains and to originate many diseases such as hearing loss, organ toxicity, nausea, diarrhea, spermatogenesis, etc. (Behravan et al., 2021; Bilal et al., 2021; Güney et al., 2021). Additionally, the excessive exposure of antibiotics can result in a decrease in treatment efficiency because of the increase in associated resistance genes as well as the growth of antibiotic-resistant bacteria (Sereshti et al., 2021). Therefore, it is imperative to detect antibiotics using cheaper and faster analytical methods with good practicability for food samples, human fluids and pharmaceutical formulations. The performance of different polymeric nanocomposites for sensing of different antibiotics has been described in Table 6.

5.1. Sensing of doxorubicin, chloramphenicol and ciprofloxacin

Behravan and colleagues reported the modification of GCE electrode by nanocomposite based on gold nanoparticles, reduced graphene oxide (RGO) and polypyrrole prepared via in-situ polymerization of pyrrole on the surface of Au-RGO modified electrode for detection of doxorubicin (Behravan et al., 2021). The results showed that the optimum amount of gold nanoparticles and pyrrole monomer was 2 v/v% and 3 v/v%, respectively. The modification of GCE enhanced the BET surface area, surface roughness and conductivity because of the higher conductivity and surface area of RGO and gold nanoparticles as well as due to the increased spacing among RGO layer. The highest current for the modified electrode was obtained at a pH of 5.5 during electrochemical measurements. Moreover, the fabricated electrode displayed a lower

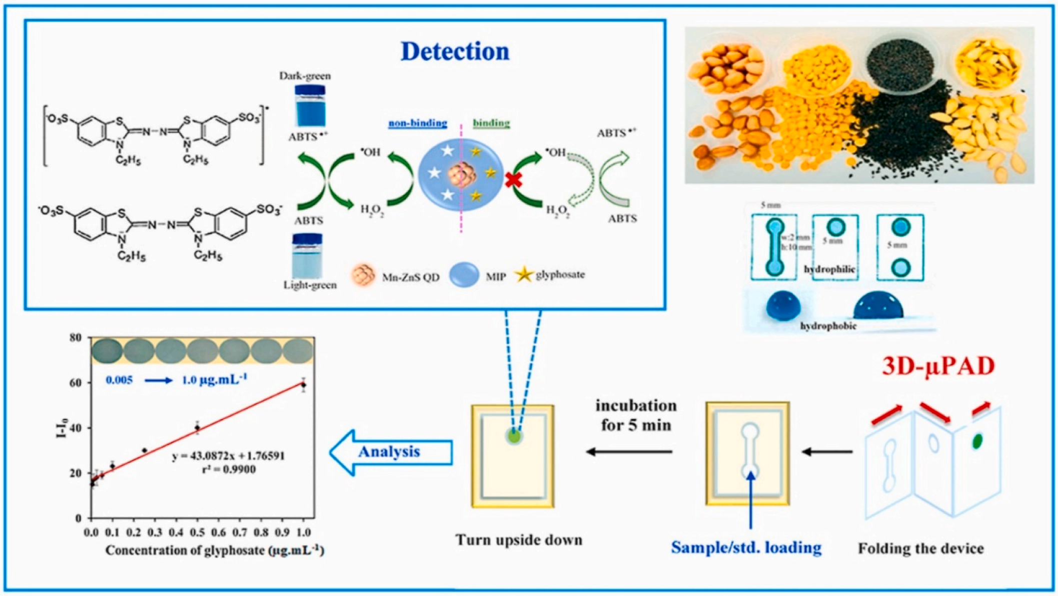

Fig. 9. Schematic illustration of the design of foldable microfluidic device (3D-μPAD) and the procedure for glyphosate detection along with the sensing mechanism of glyphosate colorimetric detection and the resultant calibration curve. Reprinted with permission from (Sawetwong et al., 2021), Licence number: 5282370942896

detection limit of 0.02 μM, a higher sensitivity of 185 μA mM^{-1} and a wider linear concentration range of 0.02 μM–25 mM. Hence, the developed sensor provides a stable and reproducible way of detecting antibiotics (doxorubicin) in real samples.

Karuppiah et al. performed the surface functionalization of vapor grown carbon fiber (VGCF) using polydopamine (PDA) through the self-polymerization technique and modified the GCE electrode by using the resultant material (PDA-VGCF) for sensing chloramphenicol (Karuppiah et al., 2021). The electrochemical analysis displayed a higher sensitivity (0.68 $\mu A \mu M^{-1}$ cm^{-2}) for modified electrode as compared to the pristine VGCF and bare electrode. Furthermore, the developed modified sensor showed higher selectivity, lower detection limit (3 nM), reproducibility, good linear concentration range (0.01–142 μM), repeatability and stability (30 days) for sensing chloramphenicol. The modified sensing behavior of modified electrode was linked to the improved dispersibility of VGCF by surface functionalization with PDA, which eventually modified the uniform layer in electrode preparation and increased the electron transfer for VGCF. Therefore, the proposed methodology can provide an effective dispersion of carbon nanomaterials, which can be utilized to prepare modified electrodes for antibiotics sensing, fuel cells, super-capacitors, and battery applications.

On the other hand, a label-free, facile and novel electrochemical aptasensor for selective and sensitive detection of ciprofloxacin (CFX) using a modified electrode was reported (Mahmoudpour et al., 2021). First of all, the GCE electrode surface was modified with RGO through electro-reduction of GO in the presence of buffer solution. Then, poly (amidoamine) (PAMAM) encapsulated gold nanoparticles based dendrimer (3D-Au-PAMAM) was prepared via chemical reduction and attached to the already modified GCE surface (RGO-GCE). Finally, the specific aptamer was immobilized onto the modified electrode surface through Amino-gold affinity binding (see Fig. 10). The fabricated nano-probe (3D-Au-PAMAM-RGO-Apt-GCE) showed a higher sensitivity, better selectivity, linear concentration range of 1 mM–1 nM along with the lower quantification limit of 1 nM for CFX in milk samples. The presence of RGO with active functional groups provided higher surface area and good electrical conductivity. On the other hand, 3D-Au-PAMAM dendrimers offered enhanced sensitivity, accelerated electron transfer, and satisfactory amount of loading sites for aptamer to detect CFX. The proposed sensor is also competitive with other sensors developed so far for detecting CFX, particularly in terms of test time, sensitivity and simplicity. However, further research is still required in order to utilize this nano-probe for simultaneous detection of target drugs in real samples (Table 6).

5.2. *Sensing of ceftizoxime, 5-aminosalicylic acid and ofloxacin*

Ali and colleagues fabricated an electrochemical sensor based on molecular imprinted polymer (MIP) for highly selective and sensitive detection of ceftizoxime (Ali et al., 2021). The GCE electrode was first modified with MWCNTs, in order to enhance the sensitivity, followed by the electro-polymerization of poly-cysteine (*P*-Cys) on modified electrode (MWCNTs-GCE). During the polymerization, a target drug was utilized as a template molecule. The optimum experimental parameters were used for the synthesis process including pH, polymerization conditions, and molar ration between monomer and template molecules. The proposed sensor showed a detection limit of 1×10^{-10} $molL^{-1}$ and linear concentration range of $1 \times 10^{-9} - 1 \times 10^{-4}$ $molL^{-1}$ for ceftizoxime under optimal conditions, along with the good recoveries when tested for real samples.

Hosu and colleagues developed an electrochemical sensor based on GCE electrode modified by poly (methylene blue)-carbon nanotubes (PMB-CNTs) film for highly selective and sensitive determination of 5-aminosalicylic acid (5-ASA) (Hosu et al., 2021). PMB film was electrochemically prepared in deep eutectic solvents (DES). The presence of PMB film provided the electro-catalytic properties and higher surface area which were greatly enhanced by the incorporation of carbon nanotubes. The experimental conditions such as applied potential and pH of the supporting electrolyte were studied and optimized along with the different architectures of CNTs and PMB for detecting 5-ASA. The fabricated modified sensor was used to simultaneously detect acetaminophen and 5-ASA. The results showed that the sensitivity towards 5-ASA reduced to about 5.7% in the presence of acetaminophen. Moreover, the robustness and applicability of the proposed methodology was tested by detecting 5-ASA in a drug tablet, without any tedious sample pre-concentration or pre-treatment, which showed the recovery values within the range of 97.8%–105.2%. Hence, the developed sensor shows promising potential for detecting target drug in real samples.

Zhang and coworkers fabricated COOH functionalized TiO_2 derived from MIL-125(Ti) and grafted with molecular imprinted polymers (MIPs) for the selective and sensitive photo-electrochemical (PEC)

Table 6

Literature survey on the sensing performance of different polymeric nanocomposites for antibiotics.

Sensing material	Target compound	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
RGO-Au-PPy-GCE	Doxorubicin	0.02 μM	0.02 μM–25 mM	Ampoule	Excellent reproducibility and stability	CV	–	Behravan et al. (2021)
PDA-VGCF-GCE	Chloramphenicol	0.003 μM	0.01–142 μM	Honey Apple juice Milk	Long-time stability of 30 days, admirable selectivity and practical feasibility	DPV	97.8–99.4%	Karuppiah et al. (2021)
HA-GQDs-MIP	Norfloxacin	0.35 μg L^{-1}	1.0–100 μg L^{-1}	Chicken meat Milk	Easy preparation, rapid detection, excellent selectivity and sensitivity	Fluorescence	93.8–99.3%	Bunkoed et al. (2020a)
Au-PAMAM-RGO-GCE	Ciprofloxacin	1 nM	1 μM-1 nM	Pasteurized milk Raw milk	Cheap, suitable, user-friendly and reliable	DPV, SWV	–	Mahmoudpour et al. (2021)
GCE-oxMWCNTs-UPPy$_{MIP}$	Sulfamethoxazole	413 nM	1.99–10.88 μM	Milk	Good reproducibility, good replicability, easy to prepare	DPV	97.2–103.3%	Turco et al. (2021)
GQDs@Fe_3O_4-MIP	Ceftazidime	0.05 μg L^{-1}	0.1–10 μg L^{-1}	Milk	Better sensitivity, faster and easier to operate	Fluorescence	90.7–99.2%	Bunkoed et al. (2020b)
PMG-Fe_2O_3-GCE	Dapsone	0.33 μM	0.5–20 μM	River water	Efficient for practical applications with excellent reliability	DPV	97.9–103.6%	da Silva et al. (2020)
PPy-AMN-SPCE	Furazolidone	0.003 μM	0.1–10, 18–906 μM	–	Outstanding sensitivity and prominent selectivity	DPV	–	Abinaya and Muthuraj (2020)
CDs-SMIP	Ceftazidime	0.06 μg L^{-1}	0.18–1.27 μg L^{-1}	Urine	Simple, low cost, rapid, reliable, and eco-friendly	Fluorescence	97.5–107.5%	Amiri et al. (2021)
$NiMoO_4$-Ch-GCE	Amlodipine	4.62 nM	0.025–373.6 μM	Urine Pharmaceutical formulation	High sensitivity and reproducibility	DPV	93.6–96.8%	Lou et al. (2020)
HA NPs-MWCNTs-Ch-GCE	Nitrofurantoin	1.3 nM	0.005–982.1 μM	Tap water Pond water Pharmaceutical formulation	Good sensitivity and excellent repeatability and reproducibility	CV	92.0–97.9%	Velmurugan et al. (2020)
APT-Fc-β-CD–SH–Au@Fe_3O_4-GCE	Kanamycin	1.87 nM	10–500 nM	Tap water Artesian water Ground water Milk	Good selectivity, stability and reproducibility	DPV	96.5–101.5%	Bi et al. (2020)
α-Fe_2O_3-en-Ch-g-PANI	Paracetamol	5.7 μM	5–100 μM	Hospital sample	Stabile for 40 days, cost-effective	CV	98.4–101.6%	Kushwaha and Shukla (2020)
MWCNTs-*P*-Cys@MIP- GCE	Ceftizoxime	0.1 nmol L^{-1}	0.2–100 mol L^{-1}	Blood serum Urine	Great sensitivity	DPV	97.8–98.2%	Ali et al. (2021)
Ch-Au MIP-GCE	Ciprofloxacin	0.21 μmol L^{-1}	1–100 μmol L^{-1}	Tap water Mineral water Milk Pharmaceutical formulation	Easiness of electrode preparation, low-cost	DPV	93.9–108.4%	Surya et al. (2020)
MIP-GO-GCE	Amoxicillin	2.9×10^{-10} M	5.0×10^{-9} – 9.1×10^{-7} M	Pharmaceutical formulation	Selective and highly precise analysis, great sensitivity	CV, DPV	98.0–102.1%	Güney et al. (2021)
SPCE-PAA-Co NPs	Norfloxacin	0.979 mM, 0.228 mM	1–5×10^{-4} M	–	Robust and easily synthesized in lab making them a promising low cost alternative	SWV	–	(J. Louw et al., 2020)
CNTs-PDA-Au NPs-GCE	Chloramphenicol	36 nM	0.1–534 μM	Milk Powdered milk Honey	Highly efficient	CV	95.0–98.4%	Mani et al. (2020)
Ag NPs-CuMOF-PPy-RGO-CPE	Metronidazole	24 nM	0.08–160 μM	Urine Pharmaceutical formulation	Excellent sensitivity, selectivity, repeatability, and reproducibility	CV, SWV	96.0–103.4%	Saedi et al. (2021)
PANI-GO	Tetracycline	2.4–7.6 μg L^{-1}	8–750 μg L^{-1}	Pasteurized milk Raw milk	Facile, rapid, cost-effective, sensitive and efficient	Potentiometric	71.0–104.0%	Sereshti et al. (2021)
Ti_3C_2-MWCNTs-Ch-GCE	Ifosfamide Acetaminophen Domperidone Sumatriptan	0.00031 μM 0.00028 μM 0.00034 μM 0.00042 μM	0.0011–1.0 μM 0.0042–7.1 μM 0.0046–7.3 μM 0.0033–61 μM	Blood serum Urine	High sensitivity, stability, reproducibility, and selectivity	CV, DPV	95.2–98.3% 95.4–97.7% 95.7–98.3% 95.5–98.0%	Kalambate et al. (2020)
PMB-CNTs-GCE		7.7 nM	0.5–100 μM		Simple, sensitive, easy to apply, and economical	CV, DPV	97.8–105.2%	Hosu et al. (2021)

(*continued on next page*)

Table 6 (*continued*)

Sensing material	Target compound	Limit of detection (LOD)	Linear range	Sample analyzed	Adv. or disadv.	Detection method	Recovery	Ref.
	5-Aminosalicylic Acid			Pharmaceutical formulation				
Au-POAP-co-POPD-TiO_2	Ampicillin	0.28 nM	0.25–14 nM	Blood Liver	Long term stability, high conductivity, excellent activity and sensitivity	CV	–	Shahidi et al. (2020)
G-DNAzyme-TC-Apt-IL-Ch@MGO	Tetracycline	21 fM	0.16 pM–2 nM	Local milk School lake water	Selective, reproducible and stable	CI	97.0–102.2%	Sun et al. (2020)
MIL-53(Fe)@MIP	Metronidazole	53.4 nM	1–200 μM	Milk Human serum Pharmaceutical formulation	High selectivity	Fluorescence	93.2–102.0%	Zhang et al. (2021b)
CDs@mMIP	Penicillin-G	0.34 nM	1–32 nM	Pasteurized milk Raw milk	Excellent specificity, rapid, portable, user-friendly and eco-friendly	Fluorescence	98.2–103.3%	Jalili et al. (2020)
MIP-Zr-LMOF	Chloramphenicol	0.013 μg L^{-1}	0.16–161.6 μg L^{-1}	Honey Milk	Good reusability and stability	Fluorescence	96.0–105.0%	Amiripour et al. (2021)
MIP@TiO_2–C-ITO	Ofloxacin	2.91 ng mL^{-1}	0.01–3000 ng mL^{-1}	Tap water	Excellent stability, interference resistance and practicability, cost effective	PEC	96.6–105.8%	Zhang et al. (2021a)

detection of ofloxacin (OFL) (Zhang et al., 2021a). The precursor MIL-125(Ti) was synthesized by hydrothermal technique followed by the calcination to obtain cake-like TiO_2–C. The resultant cake-like TiO_2–C having functional groups was then utilized as a matrix for grafting MIPs. The presence of TiO_2–C provided higher surface area, which eventually allowed more drug molecules (OFL) to be imprinted on MIPs and to form more banding sites after photo-desorption. During electrochemical measurements, the modified sensor specifically identified and combined with OFL molecules to create a decrease in photo-current, which was associated to the replenishing of the imprinting cavity and the resultant hindrance to the separation of photo-generated hole-electron pairs. The developed sensor exhibited a wide linear concentration range (0.01–3000 ng mL^{-1}), lower detection limit (2.91 ng mL^{-1}), excellent stability and selectivity, good applicability and higher interference resistance. Therefore, the combination of molecular imprinting technology and photo-electrochemistry provided an interesting and cheaper alternative for detecting antibiotics and other chemicals in the environment (Table 6).

5.3. *Sensing of other antibiotics*

Sereshti and colleagues employed the electrochemically controlled solid phase micro-extraction (EC-SPME) technique for sensing tetracycline, oxytetracycline and doxycycline from milk samples by using copper electrode modified with polyaniline-graphene oxide nanocomposite (PANI-GO) (Sereshti et al., 2021). In-situ chemical oxidative polymerization technique was used to prepare PANI-GO nanocomposite, which was then attached to the electrode surface by using high purity conductive double-sided adhesive carbon glue (see Fig. 11). The experimental parameters influencing the performance of micro-extraction such as pH, electro-extraction voltage, adsorption time, desorption solvent and time were optimized through a detailed analysis. The modified electrode exhibited a detection limit within the range of 0.32–1.01 μg L^{-1} and 2.42–7.59 μg L^{-1} in water and milk samples, respectively under the optimum conditions. The linear concentration range was found to be 8.05–750 μg L^{-1} for milk samples and 1.06–750 μg L^{-1} for water samples along with the inter-day and intra-day precisions of 3.29–4.25 and 2.32–3.80, respectively. The target drug was detected by using the proposed methodology in water and milk samples having different fat contents and the recoveries were observed within the range of 71–104%. Hence, the suggested EC-SPME method offers a rapid, sensitive, facile, cheaper and efficient procedure for the extraction and detection of target drugs in complex fluids (Table 6).

6. Conclusions

Unique features of polymeric nanocomposites such as excellent conductance, mechanical and chemical stability, light weight, presence of various active sites and their strong adherence to electrode surface made them valuable materials for the development of sensors. In this review, the recent advancement in polymeric nanocomposites for sensing heavy metals, pesticides and antibiotics have been summarized. Moreover, this review mainly focuses to open new windows for practical applications of polymeric nanocomposites towards the development of unique sensing platform with enhanced characteristics. Advantages, disadvantages and operating conditions of various polymeric nanocomposites for sensing various environmental pollutants have also been discussed. Various polymeric materials such as PMMA, PANI, polypyrrole (PPY) and polymethylene green (PMG) hybridized with various inorganic components have been explored for their potential to detect antibiotics, pesticides and heavy metals in aqueous systems. Hybridized materials showed enhanced conductivity, many active sites, great sensitivity and selectivity towards targeted pollutants. Hence, polymeric nanocomposite based platform proved as an appropriate candidate for the detection of different pollutants in sensing limit from ppb to ppm

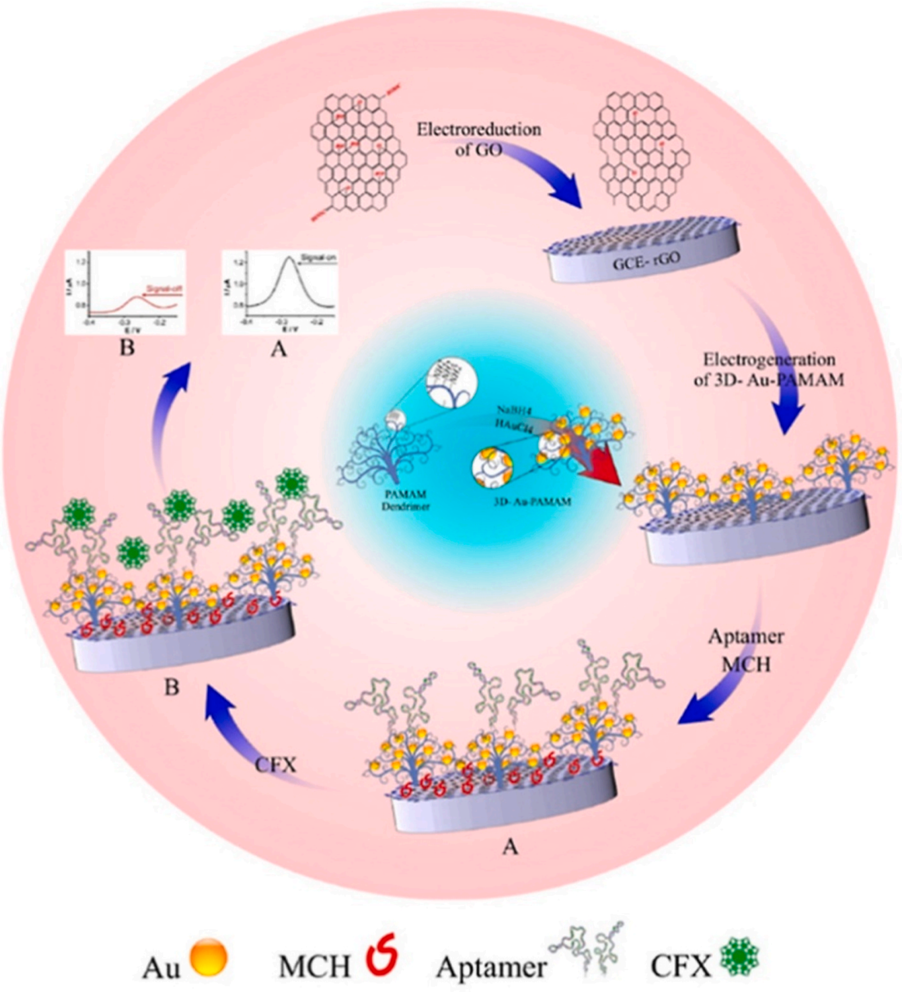

Fig. 10. Schematic diagram of the synthesis process of aptasensor for ciprofloxacin (CFX) sensing. Reprinted with permission from (Mahmoudpour et al., 2021), License number: 5282370194289

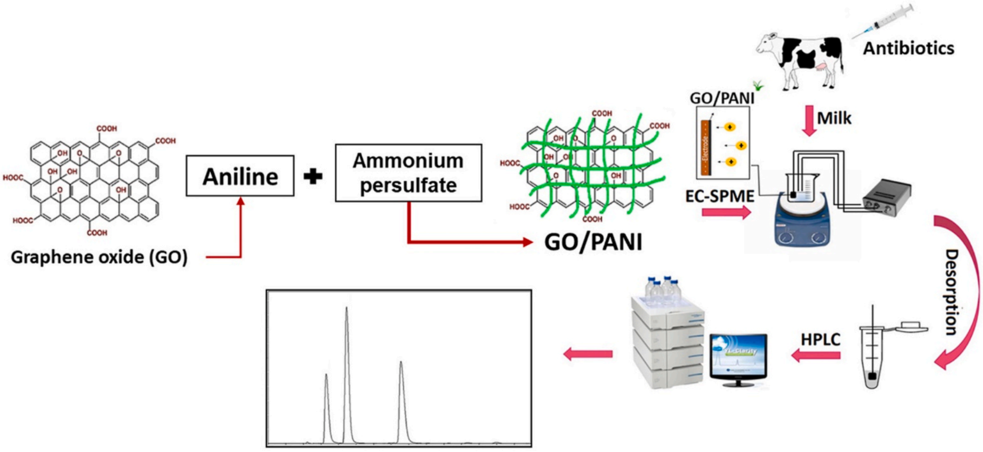

Fig. 11. Schematic illustration of the synthesis of modified sensor and the procedure for detecting selected antibiotics in milk samples. Reprinted with permission from (Sereshti et al., 2021). License number: 5282370710787

with efficient response and less recovery time, as described in Tables 1–6 with reported literature. These tables also provide a comparison among sensing efficacy of various polymeric nanocomposites for the detection of pollutants.

7. Challenges and future perspectives

Polymeric nanocomposites showed great performance as a sensing tool for the detection of pollutants. Sensors based on nanocomposites showed great response even at low concentrations of analyte. Presently, the sensing methodology is still practiced on a lab scale and there is a dire need to push this nanotechnology to be launched in market as a low cost tool to sense water pollutants at initial stages, in order to timely and efficiently control the pollution. Extensive collaboration among sciences and engineering disciplines may facilitate to design and synthesize facile sensors for monitoring environmental pollution. Different sensing approaches have been developed and all of them are focused on sensitivity, selectivity and accuracy. Keeping in view the sensitivity, improvement and strengthening of response signal is the principal way. The novel nanomaterials like carbon based materials, porous materials and polymeric materials shall continue to play important role for sensing approaches in future. Carbon based materials with excellent features and abundant resources are highly recommended. Adoption of proper reaction system and incorporation of specific approaches in order to reduce the possibility of false results are favorable factors to obtain accuracy.

Electrochemical sensors are more advantageous in terms of sensitivity and they easily meet the needs of detection and safety warning of low concentration pollutants in aqueous system. There is an urgent need to use more particular chemical reaction system and more specific materials to increase the target specific recognition in complex environmental systems. The production of polymeric nanocomposites at a large scale is still a problem due to the involvement of complex synthesis steps. Therefore, scientists must focus to introduce novel and facile protocols for the fabrication of nanocomposites at suitable operating conditions. Current sensing approaches are not up to the standards of practical applications in terms of regeneration. Sensing is mainly focused upon contact response and capturing effect. The sensor regeneration, based on contact catalysis, is fulfilled through normal cleaning and separation. Hence, regeneration is difficult and complex for sensors based upon capturing effect because of various unknown and known mechanistic actions involve during capturing. It is important to understand clear mechanisms for efficient regeneration, which still needs further research. Therefore, it is urgent to solve this problem for efficient practical use of sensing approaches in monitoring of environment. Presently, the designing of disposable sensors is a suitable substitute to ease out this issue. Furthermore, the integration of nanomaterials in present technologies may be helpful to design the potent chemical sensors.

Author contributions statement

Ahmad Shakeel: Conceptualization, Visualization, Writing – original draft. **Komal Rizwan**: Conceptualization, Project administration, Writing – original draft. **Ujala Farooq**: Investigation, Formal analysis, Writing – review & editing. **Shahid Iqbal**: Supervision, Writing – review & editing. **Tanveer Iqbal**: Formal analysis, Writing – review & editing. **Nasser S. Awwad**: Supervision, Writing – review & editing. **Hala A. Ibrahiu**m: Writing – review & editing

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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