Magnetically recoverable hybrid materials for electrochemical monitoring of hazardous contaminants: a review

Aaliya Qureashi,[a] Arshid Bashir, [ID][ab] Irfan Nazir,[a] Firdous Ahmad Ganaie,[a] Kaniz Fatima,[a] Ziaul Haq,[a] Lateef Ahmad Malik,[a] Abdullah Yahya Abdullah Alzahrani[c] and Altaf Hussain Pandith [ID] *[a]

Environmental contamination due to toxic chemicals, heavy metals, and organic pollutants poses a significant threat to public health and ecosystems. Traditional methods for detecting and removing these contaminants often face limitations in sensitivity, selectivity, and efficiency. Among the different methods, electrochemical methods have taken the front seat due to various advantages over other methods. Magnetic sensors, particularly those based on magnetically recoverable nanocomposites, offer unique advantages such as high surface area, catalytic properties, and ease of separation. Integrating electrochemical techniques with these sensors allows for precise detection and efficient remediation processes. This review focuses on the advancement of magnetic sensors for the electrochemical detection and remediation of environmental contaminants. Herein, we explore recent developments in sensor design, focusing on functional materials such as magnetic nanoparticles, carbon-based materials, and conducting polymers. Various electrochemical detection methods, including amperometry, voltammetry, and impedance spectroscopy, are discussed in terms of their performance metrics, such as sensitivity, selectivity, and detection limits. Beyond detection, this review demonstrates the potential of magnetic sensors in contaminant remediation, specifically through adsorption, photocatalysis, and electrochemical degradation. Furthermore, we provide a critical assessment of the field's current challenges, including sensor stability, scalability for real-world deployment, and the development of cost-effective, sustainable solutions. Finally, this review outlines the promising prospects for this technology, underscoring the expanding role of electrochemical magnetic sensors as vital instruments in addressing environmental pollution.

Sustainability spotlight

Combating environmental contamination necessitates sensing technologies that are not only effective but also aligned with sustainability goals. This study presents a green advancement in the form of magnetically recoverable electrochemical sensors for the selective detection and remediation of contaminants. These sensors minimize secondary pollution, reduce energy and reagent consumption, and offer reusability by integrating environmentally friendly materials such as magnetic nanoparticles, carbon-based substrates, and conducting polymers. The unified system enhances both operational efficiency and environmental safety. This work directly supports the UN Sustainable Development Goals, particularly SDG 6 (Clean Water and Sanitation), SDG 12 (Responsible Consumption and Production), and SDG 13 (Climate Action), showcasing the promise of sustainable sensor technologies in real-world environmental monitoring and restoration.

1. Introduction

The quality of water has an impact on the overall health of all life on the planet. The increase in global population, associated with urbanisation, industries, and chemically modified agriculture, further harms the fragile water supplies.[1] Access to clean drinking water is becoming increasingly challenging for many people worldwide.[2] Therefore, it is urgently necessary to develop materials and technologies that are economically viable, easily accessible, ecologically sound, lightweight,

[a]*Laboratory of Nanoscience and Quantum Computations, Department of Chemistry, University of Kashmir, Hazratbal, Srinagar, Jammu and Kashmir, India. E-mail: altafpandit23@gmail.com*

[b]*Department of Chemistry, Govt. Degree College, Beerwah, Budgam, Jammu and Kashmir, India*

[c]*Department of Chemistry, Faculty of Science & Arts-Muhayil Asir, King Khalid University Saudi Arabia, Saudi Arabia*

thermally efficient and chemically robust to meet the growing demand for clean water throughout the world.[3,4] Numerous potentially harmful compounds are used, transferred, and handled daily in a range of contexts, from everyday activities to industrial procedures. Such activities often release pollutants as groundwater or surface water *via* explicit or implicit pathways.[5] Recent years have experienced an enormous increase in public interest in hazardous pollutants due to the severe environmental risks they pose and the adverse impact their presence has on human health (Fig. 1).[6] Some synthetic organic colors

Dr Aaliya Qureashi received her MSc degree in Chemistry from the University of Kashmir, India. She obtained her PhD in 2023 from the Department of Chemistry at the University of Kashmir under the joint mentorship of Dr Altaf Hussain Pandith and Dr Faheem Arjamend. Currently, she is working as a principal investigator, Women Scientist Scheme-A (WOS-A) [DST/WOS-A/CS-34/2021] sanctioned by the Department of Science and Technology (DST), New Delhi, Government of India. Her research interests involve the synthesis of magnetite-based nanocomposite materials for the electrochemical detection and abatement of environmental toxicants.

Aaliya Qureashi

Dr Arshid Bashir received his BSc and MSc degrees in Chemistry from the University of Kashmir, India. After obtaining a Junior Research Fellowship from the Council of Scientific & Industrial Research (CSIR), New Delhi, India, he joined the Department of Chemistry at University of Kashmir for his PhD He received his PhD degree in 2022 under the direction of Dr Altaf Hussain Pandith and G. N. Dar at Kashmir University. From 2017 to 2024, he served as a Lecturer in the School Education Department, UT of J&K. Currently, he is serving as an Assistant Professor, Chemistry in the Higher Education Department, UT of J&K. His research interests involve the synthesis of functionalized magnetic materials for heavy metal sensing and removal, and synthesis of conducting polymer-based heterojunction nanocomposites for photocatalysis and energy storage applications. He received the best graduate award from Mir Qasim Sir Syed Memorial Trust, Barzulla, Srinagar, India, in the year 2010. In 2016, he received a summer research fellowship from the Indian Academies of Sciences (IASc-INSA) to work with Prof. Mainak Roy at Bhabha Atomic Research Centre (BARC), Mumbai. He has authored 41 research articles, including three book chapters, in internationally reputed journals with 2330 citations. He has been recognized by Stanford University as one of the top 2% most influential scientists globally.
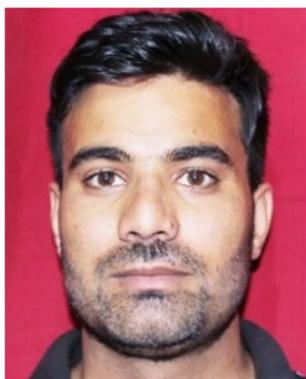
Arshid Bashir

Dr Irfan Nazir received his MPhil in Chemistry from Jiwaji University, Gwalior, India, in 2019 and completed his PhD at the University of Kashmir in 2025. His research focuses on the design and development of metal chalcogenide-based nanostructures and heterostructured catalysts for photocatalysis, electrocatalysis, and environmental remediation. He has authored more than 20 publications in reputed international journals and is currently working as a CSIR Research Associate at the National Institute of Technology Srinagar, India, where his work is centred on multifunctional nanomaterials for hydrogen evolution, pollutant detoxification, and electrochemical nitrogen reduction.

Irfan Nazir

Firdous Ahmad Ganaie is currently pursuing his PhD at the Department of Chemistry, the University of Kashmir, Srinagar, India. Firdous's research focuses on the design and synthesis of bio-based composite materials for photocatalysis, electrocatalysis, and decontamination of water contaminants. He has authored more than 15 publications in reputed international journals.

Firdous Ahmad Ganaie

and pigments are perceived by some as water contaminants. These colors are frequently used in a wide range of industries, such as textiles, tanneries, cosmetics, foods and in the treatment of humans and animals.[7] Natural artificial colorants have contaminated many areas of water and soil habitats due to their widespread use and production. Previous research has revealed the presence of dyes in ecological specimens such as fish species, soil, suspended fine particles, and water.[8] Therefore, in the words of Tkaczyk *et al.* (2021),[9] they are categorised as micro-pollutants that affect aquatic ecosystems. Most of the dyes belong to a dangerous family of water pollutants and have a large impact on the ecology. Specific dyes, such as methylene blue, rhodamine B, methyl violet, and congo red, fall into this category and are known to be toxic for life.

Recently, pharmaceuticals have been identified as environmental pollutants that pose an increasing threat to ground water and surface water in industrial and residential areas.[10] In general, drugs reach water sources primarily through discharge from pharmaceutical industries, municipal wastewater, and hospital effluents.[11] They are classified as stubborn bio-accumulative compounds and, because they contaminate aquatic and terrestrial environments, they are considered dangerous chemicals.[12] Unfortunately, many of these pharmaceutical substances are not completely removed by wastewater treatment plants (WWTPs), and as a result, they have been found in drinking water (ground and surface) and WWTP effluents all over the world.[13] Therefore, it is necessary to chemically or physically treat water that contains pharmaceuticals and their transformation products (TPs) to protect the environment and public health from potential toxicity and other negative effects.[14]

Similarly, when organisms directly or indirectly ingest nutritional metals in large quantities, they suffer acute or chronic poisoning that cannot be reversed.[15] For example, exposure to cadmium $(Cd)(II)$ significantly alters plant growth and leads to metabolic failure.[16] Consuming $Cd(II)$ contaminated water and food is known to cause cancer and possesses the ability to develop hazardous lesions in human bones, liver and kidneys.[17,18] Lead $(Pb)(II)$ is an additional toxic metal ion that can compete with calcium, iron, and zinc for binding sites in mammals, causing fatal adverse effects on healthy organisms.[19–21] The functioning of the heart and circulatory organs is adversely affected by $Pb(II)$, which causes prolonged

Ziaul Haq

Dr Ziaul Haq, born and raised in Kashmir, India, often described as the "Paradise on Earth," renowned for its landscapes, snow-capped mountains, serene lakes, and lush valleys, a region celebrated for its natural beauty, is a researcher specializing in advanced functional nano-materials. He received his Master's degree in Chemistry from Jiwaji University, Gwalior (MP), India, in 2016, followed by an MPhil in Chemistry from the same institute in 2018. In 2022, he qualified for the national GATE examination and is currently pursuing his PhD in Chemistry (Nanomaterial and Computational Chemistry Lab) at the University of Kashmir (joined in 2020). His doctoral research focuses on the synthesis, characterization, and environmental applications of two-dimensional (2D) layered-based composite materials for the abatement of water contaminants. Ziaul Haq has authored and co-authored more than 20 peer-reviewed publications in internationally reputed journals, including New Journal of Chemistry (RSC), Industrial & Engineering Chemistry Research (ACS), Langmuir (ACS), Materials Chemistry and Physics, and Journal of Alloys and Compounds. His contributions include the development of advanced nanocomposites and heterojunctions for electrochemical detection of heavy metals, pesticides, and pharmaceuticals, as well as the photocatalytic degradation of organic pollutants. His research interests extend to energy storage, electrocatalysis, photocatalysis, and interfacial tuning of 2D materials for multifunctional applications in environmental and energy-related fields.

Lateef Ahmad Malik

Dr Lateef Ahmad Malik received his MSc degree in Chemistry from the University of Kashmir, India. After obtaining a Junior Research Fellowship from the Council of Scientific & Industrial Research (CSIR), New Delhi, India, he joined the Laboratory of Nano-science and Quantum Computations headed by Prof. Altaf Hussain Pandith for his PhD at the Department of Chemistry, University of Kashmir. After obtaining his PhD degree, he served in the Higher Education Department of J&K, India. Currently, he is working as an Assistant Professor in the Higher Education Department, J&K, India. His areas of specialisation include the synthesis of novel nanocomposite materials for the electrochemical sensing and the sorption of potentially toxic wastes from contaminated and real water samples. He has been listed in the global top 2% scientist list, 2025, by Stanford University.

hypertension and myocardial dysfunction.[22] Although vegetable crops are a safe source of nourishment for humans, the presence of contamination with Cd and Pb in these crops exposes individuals to serious dangers.[23] In light of the discussion above, it is essential to create a reliable and precise method for analysing the presence of Cd(II) and Pb(II) in food materials and monitoring the extent to which these metal ions are ingested by the body. Inhalation of mercury vapor can cause fatal harm to the lungs, kidneys, mental health, digestive, and immune systems. Consumption of inorganic mercury salts can cause renal toxicity and damage to the skin, eyes, and digestive system.[24] This makes it essential that the contaminants present in wastewater are detected and removed urgently. Efficacy in the remediation of naturally occurring pollutants can be improved by employing a wide range of techniques.[25] The rapid development of highly specific and reliable analytical techniques in recent times that allow us to identify, monitor, and remove

Altaf Hussain Pandith received his PhD from the Aligarh Muslim University, India, in 2000, where he worked in the Applied Chemistry Group of Prof. K. G. Varshney. In September 2000, he joined the J&K State Pollution Control Board as a scientist and supervised the analytical laboratory for monitoring air and water pollution in and around the Kashmir Valley. In 2004, he joined the Department of Chemistry, University of Kashmir, and

Altaf Hussain Pandith

is presently working as a Professor in the same department. In 2009 and 2011, he received an INSA Visiting Fellowship to work with Prof. Swapan K. Pati at the Theoretical Science Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore and another visiting fellowship by the Indian Academies of Sciences (IASc-INAS-INSA) to work with Prof. P. K. Chattraj, at the Indian Institute of Technology (IIT), Khargpur. Dr Pandith has received the Young Scientist Award of the Indian Chemical Society and an award by the Atomic Energy Commission of India. The research interest of his group encompasses broadly two main fields; computational chemistry and materials chemistry. In computational chemistry, he is interested in performing theoretical investigations over a broad spectrum of systems, ranging from molecules to materials, using a variety of quantum mechanical methods. The main focus of his research is on electronic structure and spectral properties of chiro-optic systems, energy storage and conversion systems, H_2 storage, structure–activity relationships of biological importance, and microscopic structure–property relationships for applications based on transport, optical, magnetic, and electrical behaviour of condensed systems. In materials chemistry, his interests are in developing new and novel materials with special functionalities, which are useful in catalysis, adsorption, and ion-exchange and have specific applications in hazardous waste cleanup from an industrial and environmental point of view.

pollutants within complex environmental matrices has enriched our understanding of the newly identified pollutants.[26] This review brings together the literature and discusses in detail the current status of the electrochemical detection based on magnetic materials. A vast variety of research articles were screened while preparing this review. We cited only those articles that are more relevant, provide in-depth investigations on sensing mechanisms, follow greenness principles, and have excellent reusability.[27]

2. Electrochemical sensors

Electrochemical sensors constitute an essential subgroup of chemical sensors. A chemical sensor is an apparatus that continuously reports information on the chemical composition of its surroundings.[28] The amount of a specific analyte is directly correlated with the selective response produced by a chemical sensor.[28] The sensor element is the core component of a sensor.[29] It directly interacts with the detector and is responsible for identifying and establishing a connection with the target species in a complex environment. The detector then transforms the chemical signals produced by the sensor element for the species of interest into an output signal that can be measured. The working electrode (sensing electrode) and the counter electrode of an electrochemical sensor are typically separated by an electrolyte layer.[28–30] Typically, electrochemical sensors function by redox reaction of the species on the electrode surface, which produces an electrical signal according to the concentration of analyte species.[30] To maintain a constant working electrode potential in a sensor, a reference electrode is utilised. Essentially, an excellent sensor should have the qualities listed below (Fig. 2):

(A) The signal output should be equivalent to the kind and number of target species.

(B) The sensor should have a high sensitivity to the species and be extremely particular.

(C) It should possess both high resolution and selectivity.

(D) It should be highly accurate and repeatable.

(E) It should have an immediate reaction time.

Electrochemical sensors have advanced to such an extent that they are now widely used, surpassing other categories of sensors, such as optical sensors. The prime example is of glucose meters using electrochemical sensors, which measure the blood glucose in an enzyme reaction.

Furthermore, the cost-effectiveness, economical approach, and user-friendly properties of electrochemical methods have attracted the attention of researchers to the detection of toxic contaminants over the last few years.[31] Cyclic voltammetry, linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and stripping voltammetry are some of the prominent electrochemical techniques for the detection of toxic contaminants in water bodies.[32] For the efficient detection of any contaminant, the conductive property and surface structure of the electrode material are the key factors that play a crucial role in their sensing ability. In this context, diverse materials, including graphene, carbon nanotubes (CNTs), conducting polymers, metal organic frameworks, metal oxides modified
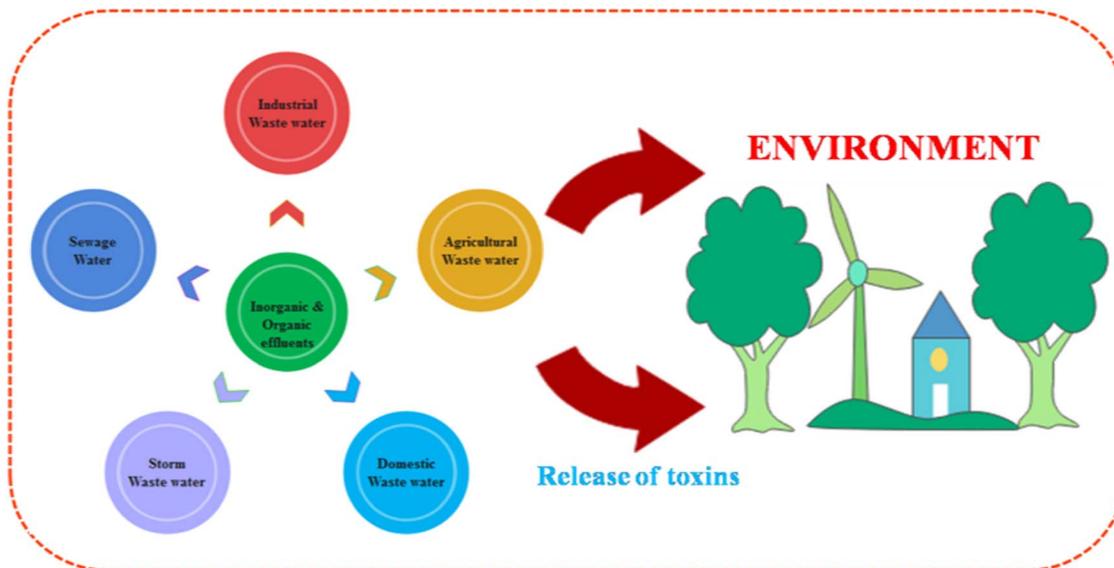
Fig. 1 Diagram illustrating various sources of environmental pollutants. Illustrations shown in the figure are partly created with Wondershare Edraw Max. All text and scientific analyses are the author's own work and undertaken without the use of any AI tools.
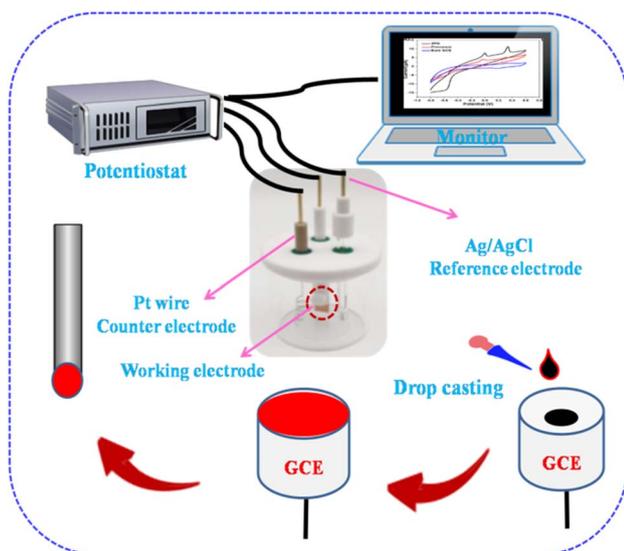

Fig. 2 Diagram illustrating the working principle of an electrochemical sensor.

particular attention to the use of magnetic metal oxides as sensors for detecting heavy metal ions, dyes, medicines, and pesticides from aqueous systems.

3. Magnetic materials

A huge number of novel materials have been fabricated for the detection and decontamination of potentially toxic wastes.[39] However, the majority of them face significant challenges mainly due to their poor recovery and reusability from the sorption medium. Recovery and renewal characteristics are essential properties of effective functional adsorbent

with polymers, *etc.*, have been designed and developed as electrochemical sensors for the detection of heavy metal ions and other contaminants.[15,33] Magnetic compounds such as zerovalent iron (nZVI), magnetite (Fe_3O_4), greigite (Fe_3S_4), and their composites are being used extensively due to their high surface area, excellent magnetic properties, ease of separation and therefore reduced post-treatment costs as illustrated in Fig. 3.[10,34–38] Moreover, the sensing performance of hybrid and magnetically recoverable nanomaterials outperforms pristine magnetic oxide nanoparticles and carbonaceous materials such as carbon nanotubes, graphene, biochar, metal organic framework and conducting polymers.[39] This overview will pay
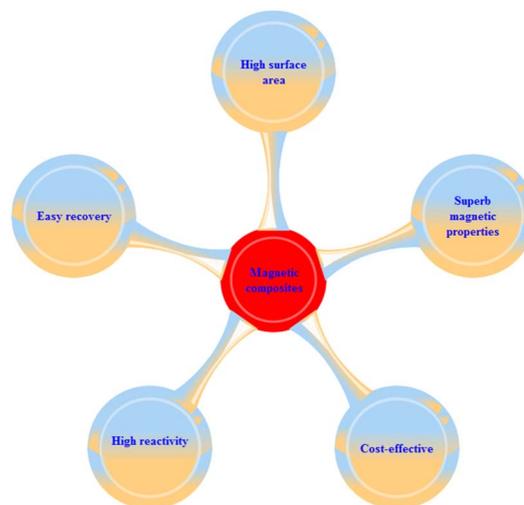

Fig. 3 Key properties of magnetic composites in a cyclic representation. Illustrations shown in the figure are partly created with Wondershare Edraw Max. All text and scientific analyses are the author's own work and undertaken without the use of any AI tools.
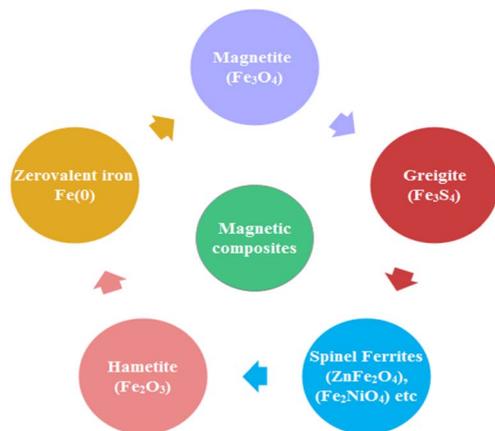
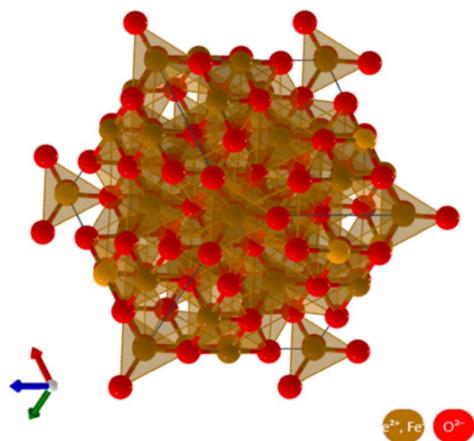Fig. 4 Types of magnetic composites and their key components.

Fig. 6 Mechanistic illustration of removal of positively charged heavy metal ions by which citrate-coated magnetite nanoparticles.

Fig. 5 A three-dimensional view of magnetite (Fe_3O_4).

Fig. 7 Role of zerovalent iron in the removal of inorganic and organic contaminants from aqueous systems. Source: reproduced with permission from Bao *et al.* (2022).[54] Copyright *J. Electroanal. Chem.*

materials.[40] Design and preparation of nanocomposite materials from suitable superparamagnetic substances, such as nano-zerovalent iron (nZVI), magnetite (Fe_3O_4), or greigite (Fe_3S_4), constitute one quick and efficient way to overcome this problem.[41–44]

Due to their superparamagnetic properties, biocompatibility, promising adsorption capacity, ease of recovery and reuse, magnetic nano-adsorbents have rapidly acquired popularity in the heavy metal contamination scenario.[45] The nanocomposite material consists of two or more materials where one material is of nanoscale range that provides properties unique to those of the other materials. The nanocomposite materials are viewed as the next-generation materials with the ability to detect and remove significant quantities of contaminants from wastewater. The following is a list of some magnetic substances that are used throughout the environmental detoxification process (Fig. 4).

3.1. Magnetite (Fe_3O_4)

Fe_3O_4 crystallises in the inverse spinel structure (Fig. 5). Fe_3O_4 has been extensively studied for its potential to immobilise
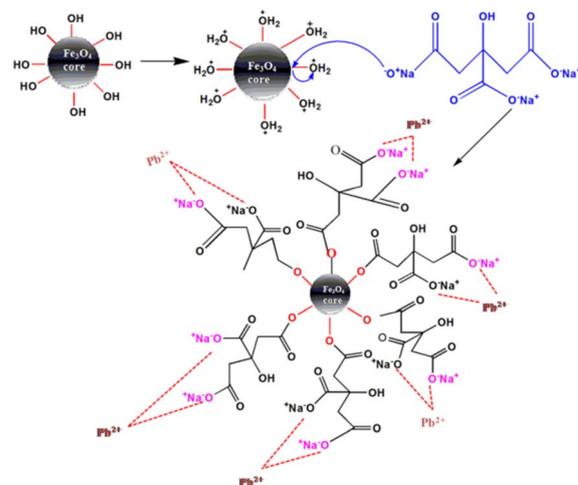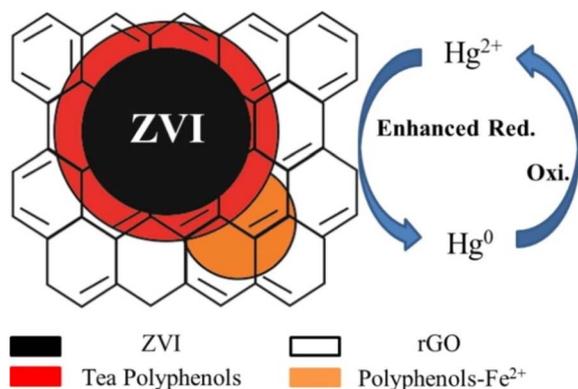
heavy metal atoms and other toxicants.[46] The pristine Fe_3O_4 nanoparticles could be applied for the detection and removal of toxic waste; however, their agglomeration, low selectivity and low surface area restrict their application in the native form.[47–49] Therefore, the chemical stability and sorption efficiency can be enhanced by either capping the pristine Fe_3O_4 and/or by forming composites of Fe_3O_4 nano-adsorbents with various functional materials.[47–49]

Our research group capped Fe_3O_4 nanoparticles with sodium citrate, and the findings show enhanced sorption ability (Fig. 6).[50] The existence of multiple functional groups of citrate on the surface of Fe_3O_4 nanoparticles improves the electrostatic attraction between positively charged metal ions and negatively charged citrate-coated magnetite. This electrostatic interaction enhances the electrochemical sensing of heavy metal ions. The glassy carbon modified with citrate-capped magnetite exhibited an outstanding electrochemical response to millimolar concentrations of Pb^{2+}, Cd^{2+}, and Zn^{2+} aqueous ions, with a response in the sequence of $Pb^{2+} > Cd^{2+} > Zn^{2+}$.
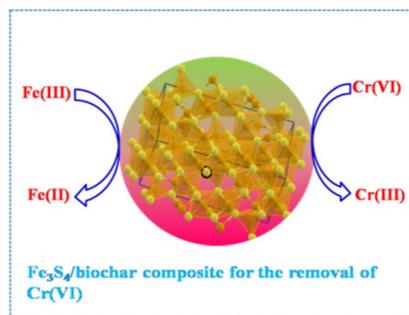
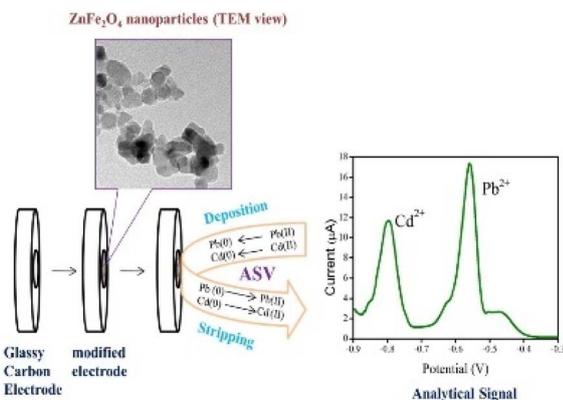**Fig. 8** Greigite-based composites for the removal of chromium ions.

Fig. 9 TEM micrograph of greigite (Fe$_3$S$_4$) and DPV analysis of Cd^{2+} and Pb^{2+} ions on ZnFe$_2$O$_4$ modified electrode ZnFe$_2$O$_4$. Source: reproduced with permission from Kumar *et al.* (2018)[59] *J. Environ. Chem. Eng.*

3.2. Zerovalent iron (nZVI)

Zero-valent iron nanoparticles have undergone extensive studies for environmental cleanup due to their various unique properties, such as strong reduction power, high surface area,

earthly abundance, economic viability, biocompatibility, *etc.* However, these spherical nZVI particles exhibit a core–shell type structure containing zero-valent iron and iron hydroxide.[51] The presence of the Fe(0) core and outer oxidised layer produces a unique reactive surface that allows the initial adsorption of contaminants and their subsequent modification on the surface *via* reduction or oxidation pathways.[52] Moreover, these nZVI particles are prone to agglomeration and oxidation, which consequently reduces their catalytic activity. Therefore, it becomes very important to modify these nanoparticles to inhibit their aggregation and increase their stability so that the catalytic activity of these nanoparticles is enhanced. One of the most efficient strategies is to immobilise such nanoparticles on a carbon-based solid support. Several carbonaceous substances, including biochar, graphene oxide, carbon nanotubes, metal–organic frameworks, activated carbon, and clay minerals, have shown a strong propensity to stabilise iron-based nanoparticles. In general, the FeO and iron hydroxides that make up the surface layer/shell and metallic core of the nZVI are negatively charged. The adsorption and quick reduction of metal ions are made possible by the role of the nZVI shell as an electron transport material.[53] In addition, the nZVI-based material is being used for heavy-metal ion sensing by a series of chemical reactions by the zero-valent iron core and subsequent adsorption of metal ions on the shell of the material. Bare nZVI corrodes and progressively loses its efficiency. Therefore, attempts were made to address this challenge. A common procedure is to decorate nZVI on the functional support material, such as a carbonaceous framework. Bao *et al.* developed a highly economical electrochemical sensor using tea polyphenols in combination with nZVI and reduced graphene oxide for the determination of Hg^{2+} in water (Fig. 7).[54]

The rGO-ZVI-P composite exhibits a distinctive attraction for aqueous Hg^{2+} as a result of a synergy between ZVI and rGO. Using square-wave anode stripping voltammetry (SWASV), the rGO-ZVI-P electrochemical sensor works exceptionally well for measuring Hg^{2+} in a pH 5.00 phosphate buffer over a 180 second
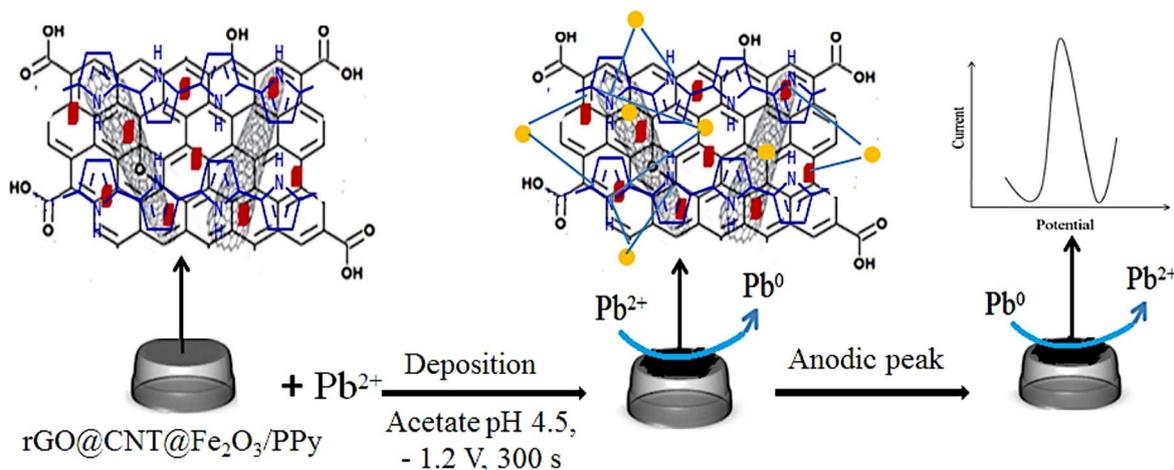

Fig. 10 Detection of Pb^{2+} ions on the surface of rGO@CNT@Fe$_2$O$_3$/PPy electrode. Source: reproduced with permission from Fall *et al.* (2021)[63] *Mater. Today Commun.*

accumulating period at 1.2 V accumulation potential. Under these conditions, the Hg^{2+} detection susceptibility and limit of Hg^{2+} detection are shown to be 41.42 A M^{-1} and 1.2 nM, respectively.

3.3. Greigite (Fe$_3$S$_4$)

Of the other iron–sulfur nanoparticles, Fe_3S_4 stands out as a top magnetic material, especially in gas detection and heavy metal decontamination. Fe_3S_4 has a saturation magnetism of 59 emu per g and is a semi-metallic, commercially sustainable magnetic material that is similar to magnetite. Although Fe_3S_4 is a preferred material for energy storage uses, there are not many reports that can explain how well Fe_3S_4 nanoparticles bind to surfaces. Its metastability and aggregation potential may be the cause of the low surface binding efficiency of Fe_3S_4 nanoparticles. The prevention of agglomeration requires the impregnation of Fe_3S_4 nanoparticles onto the surface of various functional materials such as biochar, graphene, and polymers. For example, scientists studied the ability of magnetic graphite/biochar composites (MGB) to remove Cr(VI) from wastewater,[55] which had been contaminated with heavy metals (Fig. 8).

Our research team achieved a successful integration of mechanically exfoliated g-C$_3$N$_4$ nanosheets with pure-phase Fe_3S_4 nanoparticles.[56] During the solvothermal synthesis, the Fe_3S_4 nanoparticles were wrapped in g-C$_3$N$_4$, giving them a spherical shape. The material exhibits and performs a wide range of electrochemical sensing and detoxification functions for pollutants in contaminated water. The soft sulfur centres in Fe_3S_4-g-C$_3$N$_4$ nanocomposite were identified as crucial for the interaction and capture of soft cationic contaminants such as Pb^{2+} and UO_2^{2+} ions. Charge transport at the electrode–electrolyte interface of the GCE-modified electrode, with KCl as the supporting electrolyte, was investigated by CV and DPV techniques. The electrochemical response of the modified glassy carbon electrode was highly responsive to micromolar concentrations of Pb^{2+} and uranyl ions with a limit of detection 0.71 and 0.22 μM for Pb^{2+} and UO_2^{2+}, respectively. The material is superior and sustainable in action because of its reusability and magnetic recovery without any appreciable loss in activity.[56]

3.4. Zincferrite (ZnFe$_2$O$_4$)

Zinc ferrite, typically $ZnFe_2O_4$, belongs to the family of spinel ferrites and finds applications in photocatalysis, sensing, and adsorption of contaminants. $ZnFe_2O_4$ depict a good

electrochemical sensing performance against various pollutants in addition to its ease of preparation and magnetic recovery.[57] For example, $ZnFe_2O_4$ exhibited 70% photocatalytic degradation of diclofenac.[58] Kumar drop-casted the glassy carbon electrode with a thin film of zinc ferrite.[59] The particle size and surface shape of the nanoparticles were determined using FT-IR, XRD, BET, FE-SEM, and TEM techniques. The typical TEM micrographs are shown in Fig. 9. The concentrations of Pb(II) and Cd(II) ions were detected simultaneously at trace levels using differential pulse anodic stripping voltammetry (DPASV) (Fig. 9). The sensor's detection limits for Pb(II) and Cd(II) metal ions were 1.12 and 2.52 ppb, respectively. These detection levels are well below the drinking water permissible limits set by WHO: 10 ppb for Pb(II) and 3.0 ppb for Cd(II) ions. The use of bare $ZnFe_2O_4$ is limited due to its agglomeration, low sensitivity and stability as an electrode material. This can be avoided by integrating the $ZnFe_2O_4$ with carbonaceous materials to develop a more sustainable material.[60] For example, the magnetic composite of ferrite/chitosan-curdlan (ZNF/CHT-CRD) was developed as a cost-effective adsorbent for the effective elimination of tetracycline from wastewater.[61]

3.5. Hematite

Alpha hematite (α-Fe$_2$O$_3$) is a low-cost and sustainable semi-conducting material with a wide range of applications in photocatalysis and electrochemical sensing.[62] α-Fe$_2$O$_3$, like other iron oxide nanomaterials, is more promising when integrated with other functional support materials. B. Fall et al. modified a glassy carbon electrode with a ternary composite of α-Fe$_2$O$_3$, viz, rGO@CNT@Fe$_2$O$_3$. The modified electrode serves a scaffold for the electrosynthesis of polypyrrole (PPy).[63] The thus formed quaternary magnetic composite depicts a strong electrochemical response to the trace detection of Pb(II) ions with a detection limit of 0.1 nM, well below the WHO set permissible levels. The amino groups on the PPy chains can chelate Pb^{2+}, creating a highly sensitive interface for Pb^{2+} detection. Additionally, rGO@CNT provides an enlarged surface area and promotes efficient electron transport, further improving the sensing performance. Therefore, the modified GCE rGO@CNT@Fe$_2$O$_3$/PPy was expected to provide greater performance and enhance the signal for trace detection of Pb^{2+} ions (Fig. 10).

Table 1 Maximum concentration level of potentially toxic metal ions in drinking water

S. no	Metal ion	MCL (WHO) mg L^{-1}	MCL (WHO) μM
1	Pb(II)	0.01	0.048
2	Cd(II)	0.05	0.445
3	Hg(II)	0.001	0.005
4	Zn(II)	3.0	45.88
5	Cr	0.003	0.057
6	As	0.01	0.133
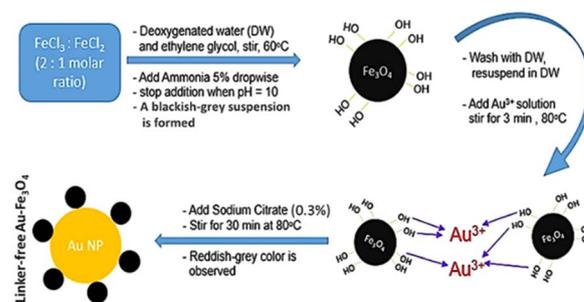
Fig. 11 Diagram illustrating the synthesis and proposed formation mechanism of Fe$_3$O$_4$–Au nanoparticles. Source: reproduced with permission from Sedki et al. (2021)[67] Sensors.

4. Electrochemical detection of contaminants by magnetic sensors

4.1 Electrochemical sensing of heavy metal ions by magnetic metal oxides

Potentially toxic metal ions such as Pb(II), Hg(II), Cd(II), Cr(VI/III), As(III/V), and Zn(II) pose a threat to humanity. They are persistent and accumulate in the biosystem. Table 1 lists the WHO-recommended permissible levels of such metal cations in drinking water. The electrochemical detection technique is an ideal choice to detect the trace levels of potentially toxic metal cations well below their permissible levels.

Fe_3O_4 is the most common form of magnetic oxide used to detect toxic metals.[64] Furthermore, Fe_3O_4 has been reported to act as a good adsorbent for heavy metal ions. However, they have certain shortcomings, e.g., they are susceptible to aerial oxidation and agglomeration that decrease their conductive behaviour and limit their use as sensors.[65] Therefore, the capping of these iron oxide nanoparticles with some functional moieties is essential for the rapid detection of heavy metal ions. Our research group reported the synthesis of citrate-coated magnetite for the sensing of Zn(II), Pb(II), and Cd(II) by differential pulse voltammetry. The best electrochemical response was observed for Pb(II) with a detection limit equal to 0.3 μM, followed by Cd(II) and Zn(II).[50] Though the material offers good sensitivity and stability, the detection levels for all three metal cations are above their maximum permissible limits. This marks the limitation of such materials. W. Wu et al. synthesised low-cost Fe_3O_4 nanoparticles crowned on fluorinated multi-walled carbon nanotubes for the sensitive detection of Cd(II), Pb(II), Hg(II), Zn(II) and Cu(II) ions.[66] Square wave stripping voltammetry was used for the simultaneous detection of Cd(II), Pb(II), Hg(II), Zn(II) and Cu(II) ions, with a detection limit equal to 0.014, 0.0084, 0.0039, 0.012, and 0.0053 μM, respectively. The limit of detection is well below the maximum permissible levels for all the tested metal cations. In another such study M. Sedki et al. demonstrated an environmentally friendly approach to synthesise linker-free Fe_3O_4–Au nanoparticles (Fig. 11).[67] Au nanoparticles with a 70 nm diameter were decorated with small Fe_3O_4 nanoparticles of 10 nm diameter that provide a large surface area for Fe_3O_4–Au nanoparticles. The prepared Fe_3O_4–Au modified glassy carbon electrode was used for the detection of arsenic(III). The detection limit was found to be 0.22 μg L^{-1}
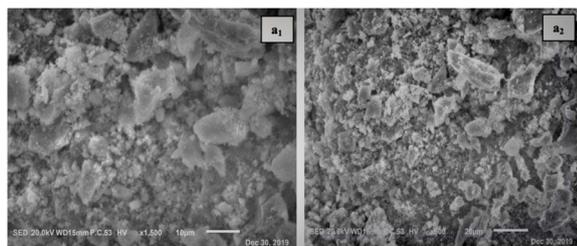

Fig. 13 Typical SWASV responses of (a) $CoFe_2O_4$, (b) $CoFe_2O_4$/rGO, (c) EDA/$CoFe_2O_4$/rGO, and (d) PEI/$CoFe_2O_4$/rGO. Source: reproduced with permission from Xiong et al. (2016).[69] Copyright *Electrochim. Acta*.

Fig. 14 CV curves (a) and DPASV curves (b) of 2.0 μM Pb(II), 2.0 μM Cu(II), and 1.0 μM Hg(II) for different electrodes in 0.1 M HAc–NaAc buffer solution (pH = 5.0). Source: reproduced with permission from Fan et al. (2021).[70] Copyright *ACS Appl. Nano Mater.*

Fig. 12 SEM images (a$_1$ and a$_2$) of the Fe_2O_3@Ni/Al-LDH sample. Source: reproduced with permission from Dib et al. (2021).[68] Copyright *Inorg. Chem. Commun.*
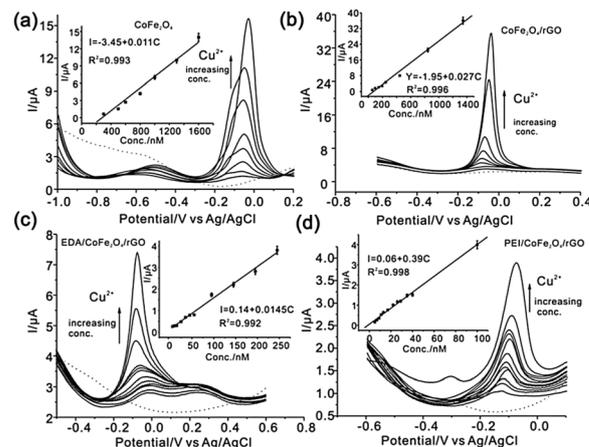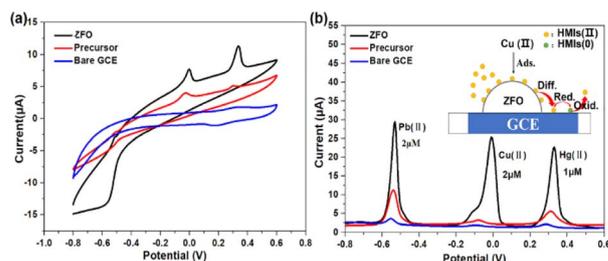
(0.0029 μM) by using square-wave anodic stripping voltammetry. The detection level is again well below the permissible level.

To detect even smaller concentrations of potentially toxic metal ions down to the nanomolar range, various studies were carried out. For example, M. Dib et al. modified the glassy carbon electrode using a Fe_2O_3@Ni/Al-LDH magnetic nanocomposite for the electrochemical detection of Hg(II).[68] The prepared electrode acts as an excellent sensor for Hg(II) ions due to its mesoporous nature (SEM images, Fig. 12(a$_1$ and a$_2$)), which enhances the catalysis and adsorption of Hg(II) ions. The obtained voltammograms depict the reversible process in line with the Hg(II)/Hg couple. The detection limit was found to be 0.00046 μM (0.46 nM).

Another work was carried out on some iron-based spinel magnetic oxides ($CoFe_2O_4$) by Shiquan.[69] In this work, a $CoFe_2O_4$-reduced graphene oxide composite was fabricated and tested for the nanomolar detection of Cu(II) ions. The addition of polyethyleneimine (PEI) or ethylenediamine (EDA) resulted in the size reduction of $CoFe_2O_4$ nanoparticles vis-à-vis enhanced adsorption/electrochemical detection of Cu(II) ions through its amine coordination. The modified electrodes were used for the electrochemical detection of Cu(II) ions by cyclic
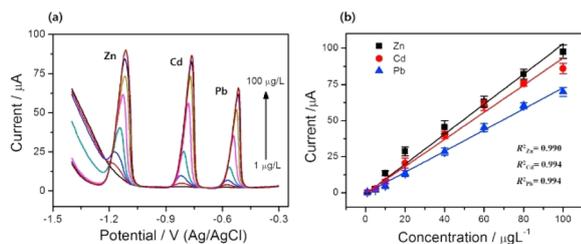
Fig. 15 (a) Stripping voltammograms for varied Zn^{2+}, Cd^{2+}, and Pb^{2+} ion concentrations on the Fe_2O_3/G/Bi composite film electrode. (b) Calibration plot for the detection of Zn^{2+}, Cd^{2+}, and Pb^{2+}. Source: reported with permission from Lee *et al.* (2016), *Talanta*.[71]
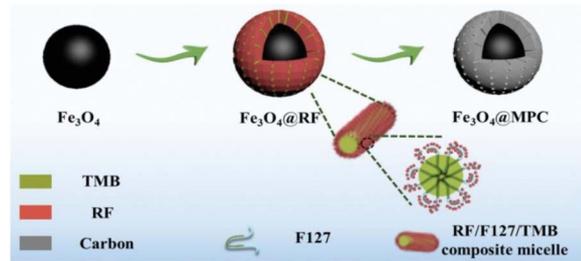

Fig. 16 Mechanism of preparation of magnetic Fe_3O_4@MPC core–shell nanospheres. Source: reproduced with permission from Liu *et al.* (2022).[72] Copyright *Adv. Mater. Interfaces*.

Fig. 17 SEM images of (a) Fe_3O_4, (b and c) Fe_3O_4@MPC-1, (d and e) Fe_3O_4@MPC-2, (f and g) Fe_3O_4@MPC-3, and (h) Fe_3O_4@MPC-4. Source: reproduced with permission from Liu *et al.* (2022).[72] Copyright *Adv. Mater. Interfaces*.

Fig. 18 Cyclic voltammograms of various modified electrodes in (a and b) 5 mm Fe $(CN)_6^{3-/4-}$ redox probe containing 0.1 m KCl. (c) Nyquist plots of PCM/GCE, Fe_3O_4@MPC-2/GCE and Fe_3O_4. Source: reproduced with permission from Liu *et al.* (2022).[72] Copyright *Adv. Mater. Interfaces*.

and square wave anodic stripping voltametric analysis with a detection limit down to picomolar level, *ca.* 0.02 nM (20 pM). From cyclic voltammograms, the reduction peak around −0.19 V increases with the increase in scan rate, which is typical of an irreversible reaction (Fig. 13). Moreover, the polyethyleneimine (PEI)-modified electrode showed the best stripping response, indicating a higher sensitivity for Cu(ɪɪ).

Similarly, the one-step hydrothermal method was adopted to prepare zinc ferrite, $ZnFe_2O_4$ (ZFO) nanoparticles with a relatively large surface area of 54.1 m^2 g^{-1}.[70] The electrochemical properties of $ZnFe_2O_4$ were examined using CV and DPSAV techniques for Hg(ɪɪ), Pb(ɪɪ), and Cd(ɪɪ). From CV, three oxidation peaks were observed at 0.3 V, −0.52 V, and −0.03 V for the above three metal ions (Fig. 14). Finally, the $ZnFe_2O_4$-modified electrode was initially used for the concurrent detection of Hg(ɪɪ), Pb(ɪɪ), and Cu(ɪɪ) with a limit of detection (LOD) down to the nanomolar range *viz*, 1.61, 7.38, and 12.03 nM, respectively. The mechanism of sensing is believed to proceed in two distinctive steps: (a) fast adsorption of metal ions at the surface of the modified electrode material, driven by the fast diffusion coefficient. Thereafter, the metal cations are transferred to the surface of the glassy carbon electrode for the stripping process. We expect the surface area of the modified electrode to largely influence the preconcentration of metal ions, and the same was observed as well. (b) During the stripping process, the metal ions are stripped off the electrode, wherein the electrochemical signal could be observed by the DPASV technique. The signal is very sensitive to the concentration of the metal ions. Both events are shown as an inset to Fig. 14b.
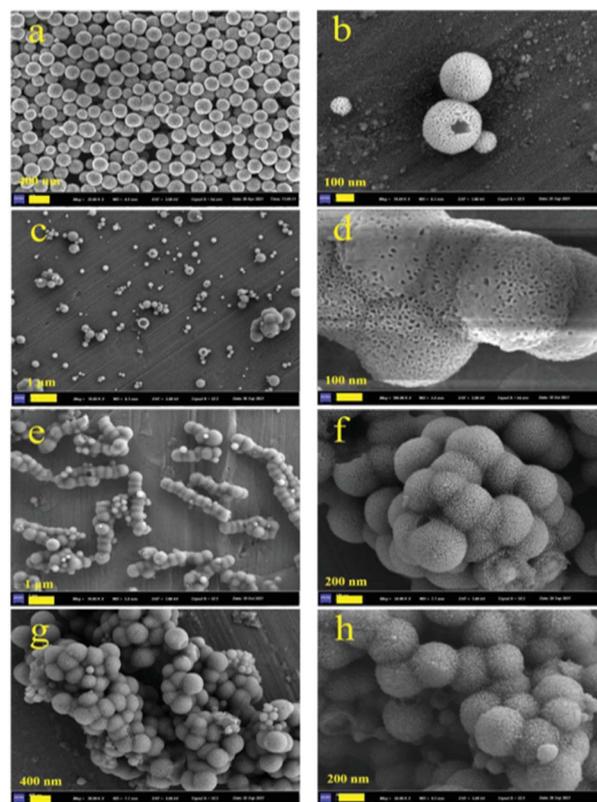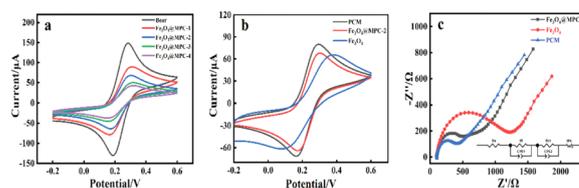
Undoubtedly, the inorganic metal oxide nanoparticles demonstrated an excellent electrochemical performance with ultra-low detection limits well below their WHO-set permissible levels. The use of pristine inorganic electrode material is limited by its agglomeration and disintegration under working conditions. Such limitations can be avoided by the fabrication of composite materials.[71,72] Lee *et al.* provide a quantitative analysis of a novel and highly efficient electrochemical sensor designed for the detection of trace levels of Zn^{2+}, Cd^{2+}, and Pb^{2+} ions. A strongly electroactive, ternary electrode material, (Fe_2O_3)/graphene/Bi nanocomposite, was fabricated by a solventless thermal decomposition technique.[71] Differential pulse

Table 2 The limits of detection of various modified electrochemical magnetic sensors for the detection of heavy metal ions

Modified electrode	Method adopted	Target metal ions	Limit of detection	References
Fe_2O_3/Bi graphene oxide electrode	DPV	Zn^{2+}, Cd^{2+}, Pb^{2+}	0.11 μg L^{-1}, 0.08 μg L^{-1}, 0.07 μg L^{-1}	72
GO-Fe_3O_4-PAMPAM	SWASV	Pb^{2+}, Cd^{2+}	130 ng L^{-1}, 70 ng L^{-1}	73
$MnFe_2O_4$/GO	SWASV	Pb^{2+}	0.0883 μM	74
Co_3O_4–CeO_2–ZnO	SWASV	Pb^{2+}, Hg^{2+}	0.054 nM, 0.097 nM	75
Amino-functionalized $MgFe_2O_4$/reduced graphene oxide (rGO)	SWASV	Cu^{2+}	0.2 nM	76
Fe_3O_4/SiO_2/CS/Nafion/GCE	DPASV	Cu^{2+}	5 nmol L^{-1}	77
$NiWO_4$ nanoparticles	CV, DPV	Hg^{2+}	2.25 nM	78
Fe_3O_4@citrate/GCE	CV/DPASV	Pb^{2+}	0.0061 μg L^{-1}	77
GSH@Fe_3O_4/MGCE	SWASV	Pb^{2+}	0.182 μg L^{-1}	77
		Cd^{2+}	0.172 μg L^{-1}	
Fe_3O_4@SiO_2–NH_2	DPV	Pb^{2+} and Hg^{2+}	6.06 and 9.09 nmol L^{-1}	79

voltammetry was employed to analyse Zn^{2+}, Cd^{2+} and Pb^{2+} ions. The sensor successfully achieved the simultaneous detection of metal ions at concentrations ranging from 1 to 100 g L^{-1}, with detection limits down to the nanomolar range *ca.* 0.11 μg L^{-1} (1.68 nM) for Zn^{2+}, 0.08 μg L^{-1} (0.71 nM) for Cd^{2+}, and 0.07 μg L^{-1} for Pb^{2+} (0.33 nM) (Fig. 15). Furthermore, the Fe_2O_3/graphene composite was applied to detect these heavy metal ions in real samples, producing results consistent with those obtained using ICP-MS.

The formation of Fe_3O_4@MPC, or mesoporous carbon nano chains of the core–shell Fe_3O_4 nanospheres (MPC), as an electrode-active composite for the detection of heavy metal ions, In this arena, mesoporous carbon is another greener alternative to address the disintegration of metal oxide nanoparticles *vis-à-vis* its ability to capture a range of metal cations owing to its peculiar properties, such as high surface area and ease of synthesis. Y. Liu *et al.* synthesised a core–shell nanocomposite composed of magnetite core and mesoporous carbon shell, hereafter Fe_3O_4@MPC, with resorcinol–formaldehyde resin as a source of mesoporous carbon shell (MPC). The core–shell composite was prepared using a simple emulsion-induced interface assembly technique (Fig. 16).[72]

Four different samples of Fe_3O_4@MPC were prepared (numbered as 1–4) by just using different volumes of NH_3–H_2O. Among them, Fe_3O_4@MPC-2 depict the excellent performance where 1.0 mL has been used during the synthesis. In the sample, 280 nm size Fe_3O_4 nanospheres were present, together with an MPC shell that was approximately 150 nm thick and mesopores of approximately 40 nm (Fig. 17a–h).

Fe_3O_4@MPC demonstrated an efficient electrocatalytic response for the detection of Hg(II) and Pb(II) with LOD down to the nanomolar range, *ca.* 7.8 and 12.1 nM, respectively (Fig. 18a–c). Moreover, the material demonstrated a good magnetic recovery with excellent reusability without an appreciable loss in activity. The Fe_3O_4@MPC-modified electrode demonstrated superior electrochemical sensing performance compared to pure Fe_3O_4, which was brought about by the cooperative action of numerous functional components in the core–shell-nanochain structure. While Fe_3O_4 nanospheres speed up the ion enrichment step, the conductivity of the mesoporous carbon layer encouraged electron transport during the electrochemical analysis phase. The method for creating mesoporous carbon-coated magnetic nano chains is new and is presented in this paper. This core–shell arrangement improves both the durability of the nano chains and the effectiveness of the electrochemical detection of metal ions.

Many such other studies are available in the literature. For better understanding, we have tabulated the results of metal oxide-based electrode materials for the detection of metal cations in Table 2.

Fig. 19 (a) SEM of La^{3+}-doped Co_3O_4. (b) Cyclic voltammograms of (a) pristine, (b) La^{3+}-modified Co_3O_4 nanocubes/SPE without Sudan I, and (c) bare SPE, (d) La^{3+}-modified Co_3O_4 nanocubes/SPE. (c) LSV plots of La^{3+} doped Co_3O_4 nanocubes/SPE in 150.0 μM Sudan. (d) DPV of La^{3+} doped Co_3O_4 nanocubes in different concentrations of Sudan. Source: reproduced with permission from Moghaddam *et al.* (2019).[81] Copyright *Food Chem.*

4.2. Electrochemical sensing of dyes by magnetic metal oxides

Not only the sensing of nanomolar concentration of metal ions, magnetic oxide nanomaterial can effectively be used to detect
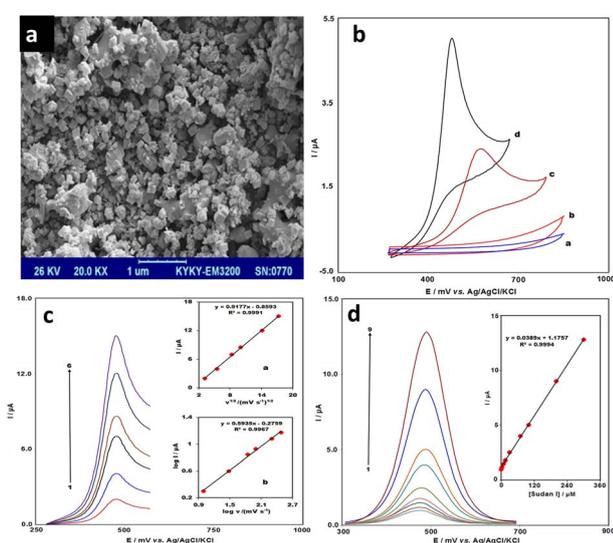
other classes of contaminants such as dyes, pharmaceuticals, and pesticides. Magnetic oxides due to their remarkable properties in terms of easy preparation, large surface area, and excellent catalytic, conductive, and electronic properties have been recently explored for the electrochemical detection of dyes/food colorants that are extremely toxic to mankind.[80] For example, Sudan I is an orange-red coloured organic azo dye typically used as a colouring agent in hydrocarbon solvents and chilli powder. It is a potential carcinogen and has been banned for use in many countries. Moghaddam *et al.* fabricated an electrode material using the nano cubical La^{3+} doped Co_3O_4 for the trace analysis of Sudan I.[81] The nanotube-like morphology of La^{3+} doped Co_3O_4 was determined from SEM (Fig. 19a). The electrochemical behaviour of this prepared screen-printed electrode (SPE) was found to be suitable for Sudan I (Fig. 19b). As can be seen from the cyclic voltammogram, no significant oxidation peak was found in the absence of the La^{3+} doped Co_3O_4 electrode, but in the presence of the La^{3+} doped Co_3O_4, the maximum current increases considerably, which supports the detection of Sudan I. Furthermore, the LSV and DPV studies showed a linear change in current with a detection limit equal to 0.05 μM (Fig. 19(c and d)).

The use of screen-printed electrodes is appreciated for the on-site detection owing to the low cost; however, their non-homogeneous surface and relatively less reproducibility demand the use of a glassy carbon electrode for the detection of potentially toxic dyes. H. Yin *et al.* modified the glassy carbon electrode by superparamagnetic Fe_3O_4 nanoparticles for the nanomolar detection of Sudan I in food samples.[82] A prominent oxidation peak was seen on the surface of the bare electrode with a potential value of around 0.67 V when Sudan I was introduced to Phosphate-Buffered Saline (PBS). Under the aforementioned experimental circumstances, the electrochemical oxidation of Sudan I was completely irreversible on the bare electrode since there was no such decline peak for the reverse scan from 1.0 to 0 V. For Fe_3O_4/GCE, the oxidation peak potential (0.643 V) decreased while the oxidation peak current increased dramatically. This behaviour should be attributed to immobilised Fe_3O_4 nanoparticles, which can enhance the oxidative current and facilitate the catalysis of Sudan I, thus reducing the oxidation potential by adsorbing more Sudan I
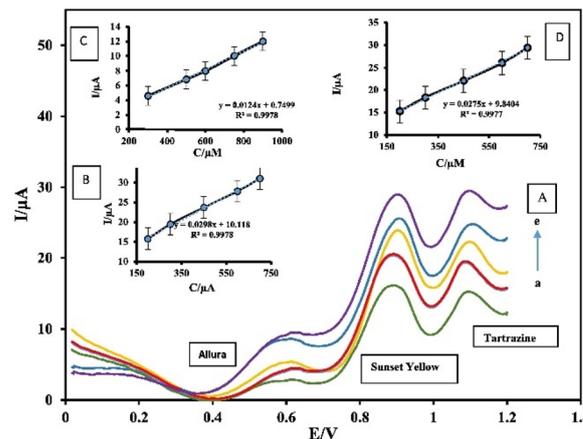

Fig. 21 DPV of $IL/NiFe_2O_4/rGO/CPE$ in pH 3 with varying concentrations of Allura Red, Sunset Yellow, and Tartrazine DPVs; insets: linear ranges for Allura Red (B), Sunset Yellow (C), and Tartrazine (D). Source: reproduced with permission from Darabi *et al.* (2021).[85] Copyright *Food Chem.*

molecules on the electrode surface. Similar to the bare GCE, the oxidation peak observed at Fe_3O_4/GCE electrode surface is irreversible, indicating the irreversible oxidation of Sudan I under current experimental conditions. Furthermore, the modified electrode of Fe_3O_4 was devised to identify Sudan I by DPV. The manufactured electrode had a greater linear range between 0.01 and 20 μM. The detection limit for Sudan I was 0.001 μM. The interference effect due to the co-presence of chemical entities other than the target analyte is very common in the electrochemical detection, especially in real water samples. Such effects should be minimised for better results. One common method is to fabricate a highly target analyte-selective electrode material. For instance, a 500-fold concentration of Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, and Cl^-, did not influence Sudan I determination, speaking of the superior selectivity of Fe_3O_4 nanoparticles for the Sudan I.[82]

Artificial food and pharmaceutical colouring agents such as Tartrazine (a synthetic lemon-yellow azo dye) and sunset yellow (orange-red azo food dye) are potentially toxic due to their persistence. Therefore, their early detection is essential to avoid
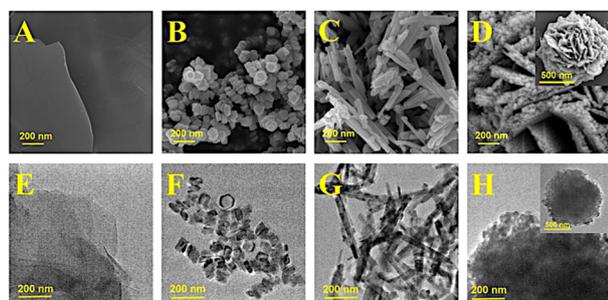
Fig. 20 SEM (A–D) and TEM (E–H) images of EG (A and E), p-Fe_2O_3 (B and F), r-Fe_2O_3 (C and G) and f-Fe_2O_3 (D and H). The insets in (D) and (H) show the low-magnification SEM and TEM images, respectively. Source: reproduced with permission from Chen *et al.* (2019).[84]
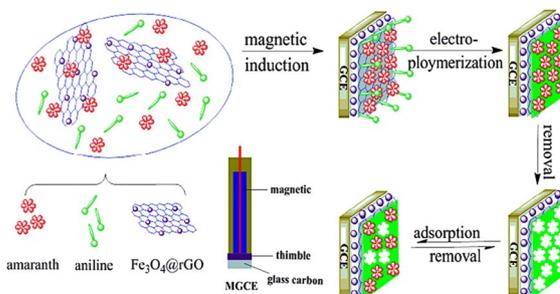
Fig. 22 Figure illustrating the process of creating a $Fe_3O_4@rGO$ doped molecularly imprinted polymer membrane that uses a magnetic field to detect amaranth. Source: reproduced with permission from Han *et al.* (2014).[86] Copyright *Talanta.*

their accumulation found in various products like candies, drinks, and cosmetics. M. Arvand *et al.* fabricated a carbon paste electrode functionalized with a core–shell $Fe_3O_4@SiO_2$/MWCNT nanocomposite, used for the simultaneous detection of sunset yellow and tartrazine.[83] Square wave voltammetry was performed, which showed a linear response for both sunset yellow and tartrazine, having a very low detection limit *ca.* 0.05 and 0.04 μmol L^{-1}, respectively.

There is always a search for a more robust electrode material that can analyse the nanomolar concentration of tartrazine. One such material is hydrothermally grown Fe_2O_3 nanoparticles by Chen and his co-workers with three distinct morphologies: nanoplates (p-Fe_2O_3), nanorods (r-Fe_2O_3), and a three-dimensional flower (f-Fe_2O_3).[84] The research group developed the composite electrode material using expanded graphite (EG) and Fe_2O_3 nanoparticles. The typical micrographs are shown in Fig. 20. The composite material composed of flower-shaped Fe_2O_3 (f-Fe_2O_3) exhibited superior electrochemical detection of sunset yellow and tartrazine dye with a limit of detection down to the nanomolar range, *ca.* 0.89 nM and 2.17 nM, respectively. This research is crucial because it reveals the relationship between the morphology of nanomaterial and the electrocatalytic activity of Fe_2O_3 nanoparticles (and other similar nanomaterials), allowing the creation of novel electrochemical uses for these materials and their composites.[84]

In another study, R. Darabi *et al.* reported the development of an electrode modified with 1-ethyl-3-methylimidazolium chloride as an ionic liquid (IL) and a $NiFe_2O_4$-rGO nanocomposite (IL/$NiFe_2O_4$/rGO/CPE). This modification resulted in a promising electrochemical sensor for monitoring sunset yellow.[85] The electrochemical properties were analysed by CV and DPV techniques. Higher catalytic activity and increased surface area of the prepared electrode promote better electron transfer, resulting in efficient sensitivity. DPV studies were analysed to determine the LOD value for sunset yellow, and it was found to be 0.03 μM. Compared to $Fe_3O_4@SiO_2$/MWCNT, the IL/$NiFe_2O_4$/rGO offers more selective detection of sunset yellow dye in addition to a lower detection limit. In the interference study, the sunset yellow analysis was carried out in a ternary mixture containing Allura red and Tartrazine. The DPV showed distinct anodic peaks for the three dyes and the sunset yellow, and a higher sensitivity was observed for the sunset yellow (Fig. 21).

Now we will introduce how a novel molecularly imprinted electrochemical sensor (MIES) was created using magnetic field-directed self-assembly (MDSA). A magnetite-reduced oxide composite ($Fe_3O_4@rGO$) was synthesised for the detection of amaranth anionic azo dye (Fig. 22). The pre-assembly solution that included amaranth, aniline and $Fe_3O_4@rGO$ was electro-polymerized with the help of MDSA to create the imprinted membrane. By changing the ratio of Fe_3O_4 and rGO in $Fe_3O_4@rGO$ composites, one can easily alter the thickness and shapes of the doped molecularly imprinted electrochemical electrodes.[86] The doped patterned membrane and $Fe_3O_4@rGO$ composites were characterised using spectral and electrochemical methods. Additionally, the manufactured MIES

demonstrated high sensitivity and outstanding selectivity when used to detect amaranth in fruit beverages.

We have highlighted in this section the use of magnetic metal oxide nanomaterials in the electrochemical detection of trace amounts of food colouring dyes. The results significantly support the use of a nanocomposite material for the best electrochemical results. This paves the way for future investigations to delve more into such materials to develop a realistic and sustainable material.

4.3. Electrochemical detection of pesticides/pharmaceuticals by magnetic metal oxides

Modernisation has introduced new challenges in food analysis due to the influx of various pollutants, including residual pharmaceuticals and pesticides, which are increasingly entering our ecosystem. In response, the detection of pesticides has become crucial, necessitating continuous advancements in detection methodologies.[87,88] Researchers have developed an enzyme-based biosensor for the rapid electrochemical detection of organophosphorus pesticides, specifically dimethoate.[89] This biosensor involves the immobilisation of acetylcholine esterase (AChE) on a Fe_3O_4/Au magnetic nanoparticle (MNP) electrode surface (Fe_3O_4/Au-AChE). The Fe_3O_4/Au-AChE absorption is facilitated by a composite membrane of CNT/nano-ZrO_2/Prussian blue (PB)/Nafion (NF) on a screen-printed carbon electrode (SPCE) under an external magnetic field. The detection limit for dimethoate was determined to be 5.6×10^{-3} ng mL^{-1}, with a linear relationship between the degree of enzyme inhibition and pesticide concentration ranging from 1.0×10^{-3} to 10 ng mL^{-1}. Another group of researchers has synthesised $Fe_3O_4@ZrO_2$ carbon-based magnetic core–shell nanoparticles, employing them as an electrochemical biosensor for methyl parathion (MP) detection.[90] These $Fe_3O_4@ZrO_2$ nanoparticles were deposited on a glassy carbon electrode to construct a magnetic electrochemical sensor. The cyclic voltammetry analysis of MP on the modified electrode revealed that ZrO_2 exhibited a significant affinity for sensing phosphoric moieties of organophosphate compounds. Under optimal conditions, the simple square wave voltammetry technique was used to quantify methyl parathion, with the cathodic peak current exhibiting a linear increase with MP concentrations ranging from 7.60×10^{-8} M to 9.12×10^{-5} M, and a detection limit of 1.52×10^{-8} M. Additionally, for the ultrasensitive detection of methamidophos or omethoate in vegetable samples, a biomimetic electrochemical sensor (BECS) has been developed. This sensor incorporates a Fe_3O_4/reduced graphene oxide nanocomposite (Fe_3O_4/rGO) integrated with a metal organic framework MIL-101(Cr) coated molecularly imprinted polymers film as a recognition element. The BECS sensor recorded strong responses for ultra-low concentrations of methamidophos or omethoate and the limit of detection of the BECS method was 2.67×10^{-13} mol L^{-1} for methamidophos and 2.05×10^{-14} mol L^{-1} for omethoate, respectively.[91] Qinghua designed an innovative biomimetic electrochemical sensor for the rapid detection of acephate, using a Fe_3O_4@carboxyl-functionalized multiwalled carbon nanotube/chitosan nanocomposite.[92] The
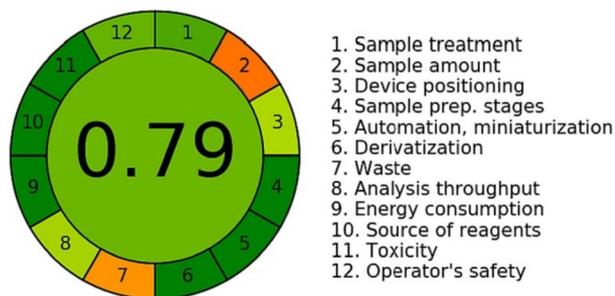
Fig. 23 Greenness assessment of the developed voltammetric method with a sustainable sensor strip employing AGREE metric assessment tool. Source: reproduced with permission from Raymundo-Pereira *et al.* (2023) *Biomater. Adv.*[96]
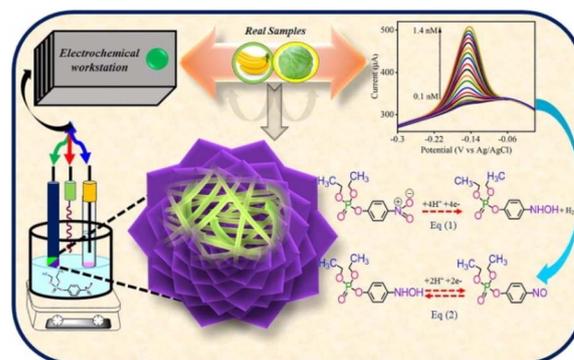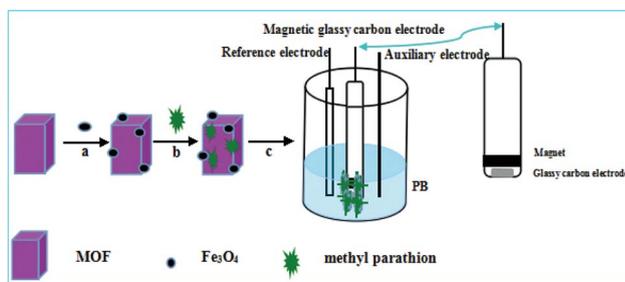

Fig. 24 Schematic representation of Fe_3O_4/MOF synthesis. Source: reproduced with permission from Hu *et al.* (2014) *Anal. Sci.*[97]

electrochemical performance of the fabricated electrode was evaluated using cyclic voltammetry and differential pulse voltammetry. The electrode exhibited linear current responses for acephate and trichlorfon concentrations ranging from 1.0×10^{-4} M to 1.0×10^{-10} M and 1.0×10^{-5} M to 1.0×10^{-11} M, respectively. The sensor was again found to have ultra-low detection limits of 6.81×10^{-11} M and 8.94×10^{-12} M for acephate, and trichlorfon, respectively. Aptamers are tailor-made functional oligonucleic acids with a great affinity for the target analyte. In the arena of pesticide detection, aptamers were found very promising. For example, Yancui *et al.* developed a simple and highly sensitive sensor for the electrochemical detection of chlorpyrifos using a novel composite film with carbon black (CB) and GO@Fe_3O_4 with the chitosan chlorpyrifos aptamer (Apt) as one of the bio-recognition elements.[93] The developed aptasensor, Apt/GO@Fe_3O_4/CB/GCE provided a linear range of 0.1 to 10^5 ng mL^{-1} with a lower LOD *ca.* 0.033 ng mL^{-1}. The other properties that make this aptasensor useful are its good selectivity, stability, and reproducibility. Furthermore, a practical use of this aptasensor is to monitor the presence of chlorpyrifos residues in actual samples of vegetables such as cabbage, lettuce, leeks, and pakchoi.

Non-enzymatic detection of pesticides using electrode materials such as metal oxides, graphene oxide, and metal–organic frameworks (MOFs) is emerging because of its increased stability, simplicity, and cost-effectiveness. Georgette *et al.* have employed a facile one-pot co-precipitation method to

Fig. 25 Synthesis of $NiCo_2O_4$-SWCNT composites for the detection of paraoxon ethyl. Reproduced with permission from Kulkarni *et al.* (2023) *J. Electroanal. Chem.*[98]

develop a non-enzymatic electrochemical sensor, $CuFe_2O_4$ and reduced graphene oxide nanocomposites for the detection of Malathion.[94] It has been observed that the highest inhibition was observed at optimised conditions corresponding to 15% rGO loading, with a linear detection range of 0.5–8 ppm. Tadele *et al.* devised a Fe_3O_4 NP-modified graphite pencil electrode (GPE) sensor to detect chlorpyrifos pesticide with a detection limit of 2.8×10^{-6} mol L^{-1}.[95] Raymundo-Pereira *et al.* demonstrated the flexible, selective and stable on-site detection of carbendazim and paraquat using sustainable sensors printed on cellulose acetate (CA) substrates.[96] The sensor is classified as a wearable sensor, which is its ability to non-invasively detect analytes in real time by integrating sensor material with everyday items. The sensor exhibited a very low detection limit, *ca.* 54.9 and 19.8 nM for carbendazim and paraquat, respectively. More importantly, the eco-friendliness of the developed sensor film was evaluated using the Analytical Greenness Metric Approach (AGREE).[96] Briefly, AGREE is based on 12 green analytical chemistry principles in the form of a colour pictogram wherein the values range from 0 to 1, with 1 as most environmentally friendly. In the present case, the sustainability index using AGREE is 0.79, signifying eco-friendly detection of carbendazim and paraquat (Fig. 23).
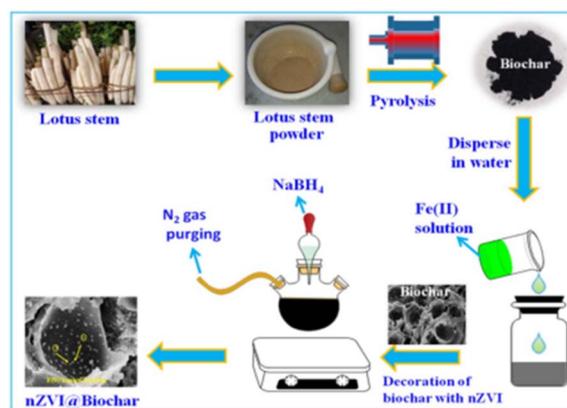

Fig. 26 Synthesis of nZVI@Biochar. Source: reproduced with permission from Qureashi *et al.* (2023).[99] Copyright *Nanoscale Adv.*
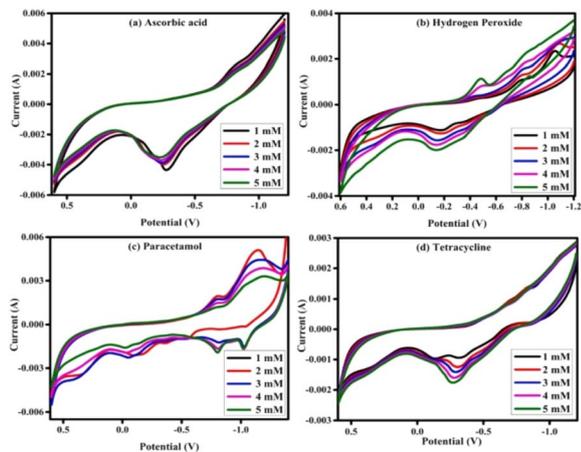
Fig. 27 Cyclic voltammograms of Fe_3O_4–MoS_2 for the detection of (a) AA (b) HP (c) PCM and (d) TC. N Source: reproduced with permission from Halligudra et al. (2022).[100] Copyright Ceram. Int.

In another study, a magnetic metal–organic framework (MOF) was synthesised by impregnating magnetite nanoparticles into the MOF matrix. The as-synthesised nanocomposite offers an enormous surface area for the electrochemical detection of methyl parathion (Fig. 24). Electrochemical analysis revealed that the multifunctional molecular organic framework (MOF) composite served as a superb matrix for the simultaneous adsorption of methyl parathion. The structured arrangement, expansive surface area, excellent compatibility and magnetic characteristics of the material facilitated efficient accumulation, separation, and direct detection of methyl parathion in the solution with remarkable sensitivity and a low detection limit of 3.02×10^{-6} g L^{-1}.[97]

Kulkarni describes a quick and easy process to create a highly associated nickel cobaltite ($NiCo_2O_4$) single-walled carbon nanotube (SWCNT) hybrid for the electrochemical detection of pesticide paradoxes ethyl (PEL), which is very commonly found.[98] Raman spectroscopy and X-ray photoelectron spectroscopy studies revealed a significant electronic interaction between the two components (Fig. 25). The $NiCo_2O_4$-SWCNT-modified glassy carbon electrode demonstrated an exceptional detection limit of 2.03 pM, which is two orders of

magnitude lower than that of bare $NiCo_2O_4$ (33.7 nM) and significantly outperforms other metal oxide-based composites reported in the literature. This remarkable performance in photoelectrochemical (PEL) detection is attributed to the strong coordination between the two components. Furthermore, the sensor exhibited excellent repeatability and stability with the potential to simultaneously detect paraoxon ethyl and dopamine.

Similarly, the phosphonate herbicide glyphosate [N-(phosphonomethyl)glycine] is frequently used for a variety of agricultural uses. It is one of the most toxic and hazardous chemicals found in drinking water, because of its wide distribution, probable toxicity, and widespread bioaccumulation. This requires accurate detection and removal of glyphosate from contaminated water. In this work, Altaf et al. describe how nano zero-valent iron (nZVI) nanoparticles were used to decorate new, highly porous biochar to create a useful electrochemical sensor for glyphosate trace detection. Modern instrumental techniques were used to fully define the composite as it was produced.[97] Electron micrographs revealed the presence of a cavity-like structure and a substantial loading of nanoscale zero-valent iron (nZVI) particles in the composite materials (Fig. 26). The existence of Fe(0) and oxygen-rich functionalities in the composite nanostructure was confirmed by FTIR and XPS studies. An electrochemical investigation suggested a detection limit as low as 0.13 ppm using CV, LSV, and DPV methodologies. The chronopotentiometry response additionally indicated good and stable long-term usage of this material.

Pharmaceuticals are another important class of compounds that need immediate quantification in the drinking water samples owing to their biological threat. Halligudra successfully developed a durable, highly efficient, magnetically recoverable, and reusable Fe_3O_4–MoS_2 heterogeneous catalyst using a cost-effective and environmentally friendly hydrothermal method.[100] This catalyst was used for the reduction of p-nitrophenol and organic dyes using $NaBH_4$ as a hydrogen source in an ethanol medium at room temperature. The presence of MoS_2 and Fe_3O_4 co-catalyst enabled the Fe_3O_4–MoS_2 catalyst to achieve efficient catalytic removal of organic pollutants, including p-nitrophenol (p-NP), methylene blue (MB) and methyl orange (MO). After the reaction, the catalyst was easily and effectively recovered using a magnetic field and reused in subsequent reactions. Up to nine rounds of reuse and recycling were demonstrated by the catalyst, with nearly unaltered efficacy. Additionally, paracetamol (PCM), ascorbic acid (AA), hydrogen peroxide (HP), and tetracycline (TC) could be detected using the synthesised material, as demonstrated by the specified cyclic voltammetry and impedance approaches (Fig. 27a–d).

In another classic example, Raymundo-Pereira et al. hydrothermally synthesise nitrogen-doped carbon spherical shells (N-CSSs) for the effective and sensitive quantification of diclofenac in saliva, urine, water, and tablets with a low limit of detection ca. 0.36 μM.[101] The material offers a huge specific surface area for the interaction of trace levels of diclofenac in addition to its superior AGREE greenness index of 0.75.[101] The results are highlighted in Fig. 28. Furthermore, the material offers

Fig. 28 Electrochemical quantification of diclofenac using N-CSSs. Source: reproduced with permission from Raymundo-Pereira et al. (2024).[101] Copyright ACS Appl. Nano Mater.

promising sensitivity and selectivity for diclofenac in the presence of various competing organic and inorganic ions, including biologically relevant molecules.

Such studies pave the way for the design and fabrication of effective electrode materials for the quick detection of pharmaceuticals.

5. Mechanism of interaction of contaminants with magnetic sensors

5.1 Mechanism of interaction of toxicants with magnetic composites

Hydrophobic, electrostatic, hydrogen bonds, 140 – interactions, and covalent bonding can all be used to categorize how contaminants adhere to the surface of carbon nanomaterials (CNMs). Sorption of both organic and inorganic substances is a component of the hydrophobic interaction/sorption mechanism. Instead of their total surface area, the surface functional group density of CNMs is what primarily determines the inorganic sorption capability of these materials. The primary reason for electrostatic interaction, a key factor in the removal of metal ions and dyes, is the contact between contaminants and oxygen-containing particles of carbon nanotubes (CNT) that possess a negative residual charge. It has been proposed that the adsorption of organic contaminants onto the surfaces of carbon nanomaterials is attributed to hydrogen bonding, hydrophobic, electrostatic, and π-interactions. For instance, contaminants with functional groups (e.g., amine, hydroxyl, and carboxyl groups) can be absorbed through hydrogen bonding interactions, wherein the oxygen-rich groups of CNPs interact with the hydroxyl groups of the contaminants.

The presence of environmental pollutants including heavy metal ions, dyes, and pharmaceutical ingredients significantly contributes to environmental contamination, which directly affects the water bodies.[101] The recent developments in the contamination mitigation approaches, processes and materials lead the scientific community to directly address the problems through the mechanistic approach. The mechanism of adsorption varies from system to system. The driving forces responsible for the adsorption of toxins are those processes that include hydrogen bonding, charge transfer nature, van der Waals, electrostatic interaction, complexation, etc. Based on the systems used for environmental mitigation purposes, the mechanistic details fall under various categories, which are discussed briefly in the subsequent sections. Magnetic materials, consisting of multi-walled carbon nanotubes combined with magnetite, emerge as promising candidates for the adsorption of heavy metal ions from wastewater. The removal of heavy metal ions such as Pb(II), Cu(II) and Cd(II) from wastewater using the 6O-MWCNTs@Fe$_3$O$_4$ involves the interaction between empty d orbitals of metal ions and lone pair of electrons on oxygen atoms, which are present on the surface of multi-walled carbon nanotubes in the form of carboxyl and hydroxyl groups thus forming a complex.[102] In addition, the presence of hydroxyl and carboxyl groups leads to deprotonation at certain pH values, rendering the surface more negative, which interacts
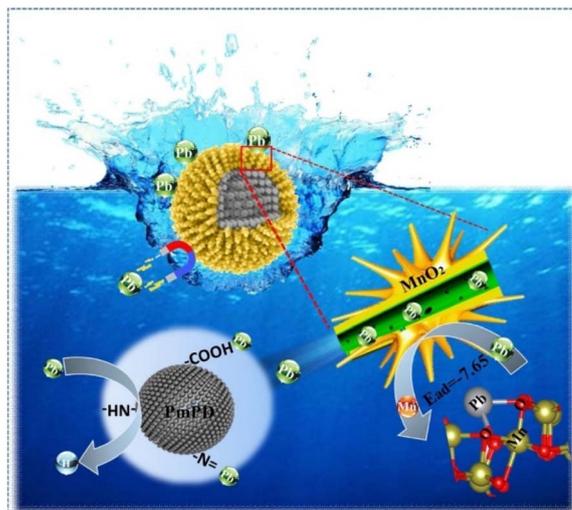

Fig. 29 Mechanism of interaction of magnetic composites with environmental contaminants. Source: reproduced with permission from Xiong et al. (2020).[104] Copyright Ecotoxicol. Environ. Saf.

with positively charged metal ions through electrostatic interactions as well. In addition to this, the magnetic material composed of graphene oxide varies in its adsorption capacity of heavy metal ions as well drugs, specifically tetracycline, depending upon the type of variant used which may include magnetic graphene oxide (MGO), magnetic chemically-reduced-graphene (MCRG) and magnetic annealing-reduced-graphene (MARG). The adsorption capability is dependent on the change in the pH value in the vicinity of the chemical environment. The three variants eliminated toxins that include tetracycline and arsenate [As(V)]. The predominant interaction driving the adsorption varies based on the surface functionalities of each variant. In the case of magnetic graphene oxide, the enhanced adsorption is ascribed to its high dispersibility, the presence of thin nano-sheets, and the existence of oxygen-containing functional groups on its surface. These functional groups coordinate more effectively with tetracycline through hydrogen bonding as well as π–π interactions. Furthermore, in the case of chemically reduced magnetic graphene (MCRG) and magnetic annealing-reduced magnetic graphene (MARG), the predominant functionality is attributed to oxygen-containing groups, with the primary π–π interaction between tetracycline and these variants.[103]

In another work, poly-(m-phenylenediamine) in combination with MnO$_2$@Fe$_3$O$_4$ serves as a potential adsorbent to capture heavy metal ions as explained by Xiong.[104] Incorporation of the magnetic composite enhances the surface area and alters surface electronegativity. The greatest capacities for magnetic materials to remove heavy metals were 438.6 mg g^{-1} for Pb(II) and 121.5 mg g^{-1} for Cd(II), respectively. Heavy metals and MnO$_2$@Fe$_3$O$_4$/PmPD exhibit mainly attraction through electrostatic forces, ion exchanges, and coordinated contact. Due to its rich amine and imine functional groups, poly-(m-phenylenediamine) (PmPD) possesses outstanding redox capabilities, chelation abilities, and large-scale pollutant adsorption sites (Fig. 29).
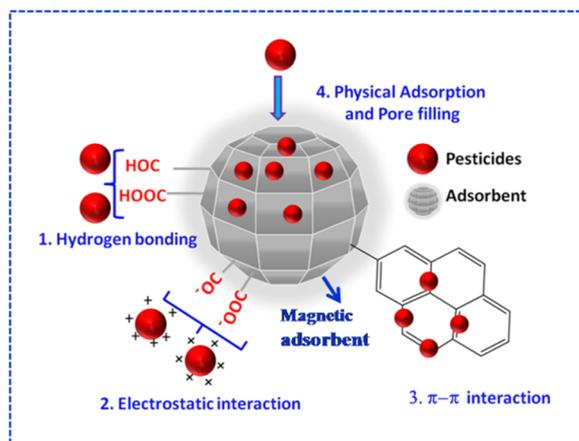
Fig. 30 Mechanism of interaction of magnetic composites with environmental toxicants. Illustrations shown in the figure are partly created with Wondershare Edraw Max. All text and scientific analyses are the author's own work and undertaken without the use of any AI tools.

Scheme 1 The outcome of this review article highlights the role of iron oxide nanoparticles when integrated with carbonaceous functional support for fabricating a nanocomposite electrode material.

Similarly, the development of pesticides is effective in controlling the pests that harm crop plants.[105] However, their widespread use leads to contamination in the food chain and subsequently in water bodies leading to their pollution. The accumulation of pesticides in water bodies in quantities more than the permissible limits poses a serious problem that needs to be addressed before its accumulation. The development of various materials, mostly magnetic composites, is fruitful in combating this problem. Many magnetic materials incorporate carbon-based magnetic composites, such as metal–organic frameworks (MOFs), and covalent organic frameworks (COFs), and their various combinations. These materials also include pristine carbon nanotubes (CNTs) or CNTs enhanced with other substances, as well as graphene and functionalized graphene. These advanced materials have been utilized to help mitigate pesticide pollution. Specific magnetic compounds were developed from iron oxide and carbon nanotubes (Fe_3O_4-MWCNTsOH@poly-ZIF67) for the detection of aromatic acids.[106] Basic mechanistic details related to the adsorption behaviour involve the π–π interaction between the adsorbent and the hydroxyl groups enhanced by carbon nanotubes.[107] Similarly, one of the main advantages of magnetic separation of dangerous contaminants, which is emerging as a method for wastewater purification, is the removal of colors more effectively than conventional treatment methods. In addition to having negative impacts, dye compounds have an unsightly appearance in water. Dyes used in the textile industry encompass a wide range of structural types, including metal complex dyes, as well as acidic, reactive, basic, disperse, azo, and diazo dyes. Limin explored the use of ethylenediamine-modified magnetic chitosan nanoparticles for adsorbing Acid Orange 7 and Acid Orange 10 from aqueous solutions. The adsorption process is attributed to ionic interactions between dye ions and amino groups of the ethylenediamine-modified magnetic chitosan nanoparticles.[108] The adsorbed dyes were desorbed using an NH_4OH/NH_4Cl solution at pH 10.
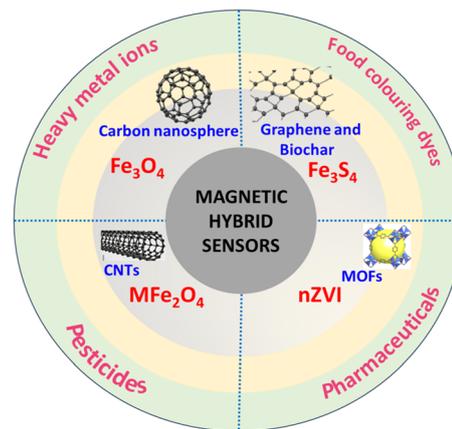
Zheng Yong synthesized magnetic Fe_3O_4/C core–shell nanoparticles using a straightforward method and demonstrated their application as adsorbents to remove organic dyes from aqueous solutions.[109] The functional groups (such as –OH and CO) present on the surface of the composite, combined with the negative potential of the magnetic nanocomposites, promote a mild electrostatic attraction between the cationic dyes and the nanoparticles, leading to an increased adsorption capacity, particularly for methylene blue (MB). Drugs, essential for both humans and animals, play a crucial role in the combating of various diseases. The consumption of drugs leaves residues that pose a threat to the environment through the dumping of garbage and waste products into the water bodies, and also have a strong tendency to enter the food chain through meat, milk, eggs, etc., into humans.[110] The challenge for the scientific community is to adopt and design certain materials that take care of their recovery.[111] Magnetic composites have been designed from time to time, which leads to an improvement in their recovery and hence leads to a decrease in their level of contamination. The porphyrin-functionalized Fe_3O_4-graphene oxide composite (TCPP/Fe_3O_4-GO) has a strong adsorption capacity for certain drugs.[112] Pi–pi stacking interactions and the electrostatic attraction between the positive charge of sulfonamides and the negative charge of porphyrins are the mechanistic insights that cause drug molecules to interact with magnetic composites. The probable mode of interaction of magnetic composites with environmental toxicants is shown in the following Fig. 30. The illustrations shown in Fig. 30 are partly created with Wondershare Edraw Max. We have used Edraw Max only for the template drawing, without the use of any AI functionality. All the text and scientific analyses are the author's own work and undertaken without the use of any AI tools.

6. Conclusions and future perspectives

Rapid industrialisation, urbanisation, and population explosion result in the discharge of potentially toxic pollutants such as heavy metal ions, hazardous synthetic dyes, pharmaceuticals,

pesticides and pesticide residues in the water bodies. This has a potential impact on human and aquatic lives and is thus a serious global environmental concern. WHO has set the maximum permissible limits for all the categories of contaminants in the drinking water; the majority of them fall within the micromolar concentration range. Therefore, electrochemical sensing emerges as a superior approach to selectively detect the contaminants up to the picomolar range. The most important component in the electrochemical sensing is the electroactive electrode material that could sense trace levels of the analyte. An ideal electrode material exhibits high electrical conductivity, possesses a large active surface area, excellent stability, sensitivity and reusability, minimum interference due to co-existing ions, and low toxicity. In this arena, magnetically recoverable iron oxide and iron oxide-based nanocomposite materials have received considerable attention. There is still a need for comprehensive review articles that provide an in-depth overview of the uses of iron oxide-based nanomaterials for the picomolar/nanomolar detection of heavy metal ions, hazardous food colouring agents, pharmaceuticals and pesticides. In this review, we have highlighted the role played by Fe_3O_4, Fe_3S_4, Fe_2O_3, nano-zerovalent iron, and $ZnFe_2O_4$ nanoparticles in the electrochemical analysis of a range of contaminants. The results demonstrate excellent sensitivity, selectivity, and reusability of the electrode material when the iron oxide nanoparticles were integrated with strongly conducting non-metallic functional support, especially with carbonaceous materials. We have schematically shown the magnetic hybrid sensors in Scheme 1. Among various carbonaceous materials reported in this review, graphene oxide, biochar, metal organic frameworks, and mesoporous non-metal doped carbon depict superior performance in terms of selectivity, sustainability, very low limit of detection and reusability. We also highlight the greenness index of some of the electrode materials according to the Analytical Greenness Metric Approach (AGREE). Additionally, we have provided an in-depth mechanistic detail of sensing and uptake of the toxicants on such oxide-based nanocomposite fabricated electrodes. Thereafter, we investigated and highlighted optimum parameters for the effective analysis of contaminants not only in the water samples but also in the real food samples. The integration of nanotechnology, functionalized magnetic materials, and advanced sensing mechanisms has significantly enhanced their performance in environmental applications. However, challenges such as sensor stability, interference from complex matrices, and large-scale deployment need to be addressed to ensure their widespread adoption.

6.1 Perspectives

We highlight in this review some examples of electrode fabrication using a collaborative effect of carbon nanomaterials with magnetically recoverable iron oxide nanoparticles. However, there is always scope for advancement in terms of specificity, cost of electrode fabrication, sustainability and on-site detection. In this context, we will provide a future perspective as follows.

6.1.1 **Real-time, *in situ* detection.** Most of the reported studies rely on the electrochemical detection of contaminants on a laboratory scale. Though the results were intriguing, the scenario in the real water samples is quite different. For example, the electrode may face interference due to the presence of co-existing species, fouling of the sensor surface by organic matter, and the limited stability for long-term monitoring. Such limitations demand fabrication of nanostructured, miniaturised and screen-printed electrodes with antifouling properties (use of antifouling biopolymers-integrated oxide nanomaterials) and extended stability for more robust electrodes.

6.1.2 **Selective and targeted pollutant identification.** The selectivity of the sensor material is very crucial for the on-site and practical application for the detection of a particular toxin. More research is needed with much emphasis on design and fabrication of non-enzymatic electrode materials, molecularly imprinted polymers, low-cost and environmentally relevant nanocomposite materials based on carbonaceous materials and metal organic frameworks containing specific metal/analyte trap centres. This will certainly help us in achieving targeted and selective detection of target analyte in nano/femto scale concentration range.

6.1.3 **Scalability and practical implementation.** Most of the electrode fabrication relies on the bench-level application. A range of contaminants and the level of pollution demand pilot-scale monitoring and removal of the contaminants. In this arena of research, 2D and 3D printing strategies facilitate the precise and scalable fabrication of miniaturised and portable electrode arrays. This will improve the reproducibility of the field-deployable sensor.

6.1.4 **Sustainable material design.** In this review, we highlight the iron oxide-based sensor materials for the detection of nanomolar concentrations of contaminants. However, the classical synthesis of iron oxide nanoparticles requires a huge chemical input. Such electrode fabrication would undoubtedly increase the cost of the electrode for market use. Moreover, the majority of the studies used a modified glassy carbon electrode, which again adds to the cost of sensor setup. Scalable green synthesis of oxide nanomaterials using biomaterials is an alternative for the synthesis of low-cost, reproducible and sustainable oxide materials. Moreover, the limitations of using glassy carbon modified electrodes will be controlled by fabricating molecularly imprinted miniaturised electrodes and integrating the electrode material with portable detection devices.

With continued innovation, magnetic nanomaterials have the potential to revolutionise environmental monitoring and remediation strategies, contributing to a cleaner and more sustainable future.

Author contributions

Aaliya Qureashi: writing, editing and original draft, and reviewing. Arshid Bashir: review and editing. Irfan Nazir and Firdous Ahmad Ganaie: writing. Kaniz Fatima, Zia-ul-Haq, and Lateef Ahmad Malik: editing. Abdullah Yahya Abdullah

Alzahrani: investigation, methodology. Altaf Hussain Pandith: conceptualization, supervision, review, and editing.

Conflicts of interest

The authors declare no conflict of interest for this work.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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