

Electrochemical Sensors for Heavy Metal Ion Detection in Aqueous Medium: A Systematic Review

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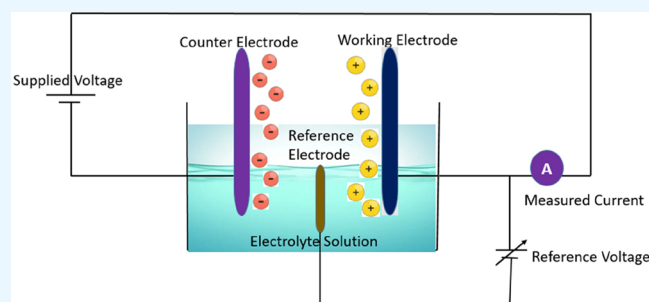
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ABSTRACT: Heavy metal ions (HMIs) are very harmful to the ecosystem when they are present in excess of the recommended limits. They are carcinogenic in nature and can cause serious health issues. So, it is important to detect the metal ions quickly and accurately. The metal ions arsenic (As^{3+}), cadmium (Cd^{2+}), chromium (Cr^{3+}), lead (Pb^{2+}), and mercury (Hg^{2+}) are considered to be very toxic among other metal ions. Standard analytical methods like atomic absorption spectroscopy, atomic fluorescence spectroscopy, and X-ray fluorescence spectroscopy are used to detect HMIs. But these methods necessitate highly technical equipment and lengthy procedures with skilled personnel. So, electrochemical sensing methods are considered to be more advantageous because of their quick analysis with precision and simplicity to operate. They can detect a wide range of heavy metals providing real-time monitoring and are cost-effective and enable multiparametric detection. Various sensing applications necessitate severe regulation regarding the modification of electrode surfaces. Numerous nanomaterials such as graphene, carbon nanotubes, and metal nanoparticles have been extensively explored as interface materials in electrode modifiers. These nanoparticles offer excellent electrical conductivity, distinctive catalytic properties, and high surface area resulting in enhanced electrochemical performance. This review examines different HMI detection methods in an aqueous medium by an electrochemical sensing approach and studies the recent developments in interface materials for altering the electrodes.



1. INTRODUCTION

Environmental monitoring is primarily concerned with identifying and measuring contaminants that are present in water, soil, and air as chemical, biological, microbiological, and radioactive containments. Due to the rising global demand for fresh, clean water, there is an increasing need to precisely monitor water quality. The quality of water could be significantly harmed by the emergence of new sources of pollution. One of the most important environmental issues that threaten global sustainability is heavy metal ion (HMI) pollution. HMIs are nonbiodegradable and highly toxic substances that can cause adverse effects on living organisms. They are among the most harmful water pollutants.

The majority of heavy metals found in the environment are caused by human activity, including air emissions from coal-burning plants, smelters, smokestacks, etc. Even at very low concentrations, heavy metals like cadmium, lead, arsenic, and mercury are highly toxic and carcinogenic.^{1,2} Since these metals are not biodegradable, they might persist in the environment for decades or even centuries. They may exist at measurable levels in food supplies and can accumulate in the food chain, contaminating the final consumer, humans, and

posing serious risks to the environment.^{3,4} Heavy metals may cause nausea, diarrhea, vomiting, or adverse reactions for low-level or short-duration exposure, once they have invaded the human body through ingestion (drinking or eating), inhalation, or skin contact.⁵

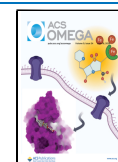
When an HMI enters the cell, it changes the biochemical lifecycle and becomes hazardous due to the metal's ability to form bonds with the thiol group of proteins. Several international organizations, including the World Health Organization (WHO),^{6–9} the Joint Food and Agricultural Organization (FAO), the Centers for Disease Control (CDC),¹⁰ and the International Agency for Research on Cancer (IARC) are investigating the harmful effects of HMI. Therefore, it is essential to develop fast and precise techniques for the analysis of low-concentration HMIs in samples from the

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environment, samples from food and medicine, and biological samples.

To examine heavy metals in food and environmental samples, standard analytical techniques have been developed. These include inductively coupled plasma methods,^{11–13} X-ray fluorescence spectrometry,¹⁴ and atomic absorption and emission spectroscopies^{15–17} that can operate in both optical and mass differentiation. These methods are well established and provide high accuracy of results when performed in highly equipped laboratories.^{18–20} However, they necessitate highly technical equipment, skilled personnel, challenging preconcentration steps before measurement, and lengthy procedures. For HMI detection, different methods such as electrochemical and optical analyses have acquired popularity due to their superior sensitivity, selectivity, speed, affordability, and user-friendliness compared to conventional analytical methods. When compared to the methods mentioned above, the electrochemical method is more advantageous because of its quick analysis with greater precision, economical, simple operation, and easy miniaturization. It is also suitable for in situ analysis, point-of-care analysis, and in vivo real-time analysis.²¹ The detection of HMIs in various samples has received significant attention in recent times, as shown in Figure 1. In the past decade, there

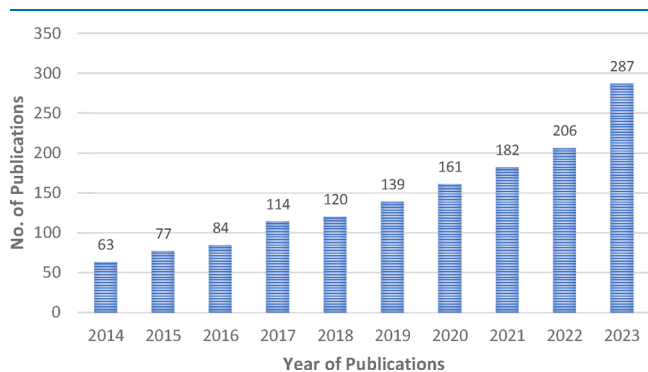


Figure 1. Number of publications in the field of electrochemical detection of heavy metal ions in the last 10 years (www.scopus.com; keywords: electrochemical detection of heavy metal ion).

has been a considerable increase in the number of scientific research studies dedicated to electrochemical sensing of HMIs according to the SCOPUS database. This increase may be attributable to the numerous benefits that electrochemical sensing offers in comparison to conventional approaches. Nanocomposite materials have recently emerged as an essential class of materials that represent the pioneering potential for a wide range of technological applications. They are excellent for detecting a wide variety of targets, including biomolecules, chemicals, and environmental pollutants, because their tunable characteristics permit customization of the sensor's response to stimuli.²² To enhance the sensitivity and selectivity of the HMI detection using electrochemical sensors, electrode modifiers made of nanocomposite materials are employed.²³ Many electrochemical devices make use of screen printed electrodes (SPEs) which have paved the way for the transition from conventional laboratory analytical methods to portable low-cost sensors.²⁴ However, they have their own limitations of lower sensitivity and detection limits compared with the traditional analytical methods. In a similar manner, nanomaterial-based ion-imprinted electrochemical sensors are

emerging as an excellent technology because of their good selectivity and fast detection speed.^{25,26}

This paper aims to examine different electrochemical sensing methods to detect HMIs in aqueous medium as well as to review recent developments in interface materials for altering the electrodes used in these methods. This Review covers the publications pertaining to the domain of electrochemical sensors utilized for HMI detection. Considerable attention was given toward the articles that detailed fundamental advancements in potentiometric, voltammetric, and amperometric techniques in addition to the reviews that addressed the relevant field. The papers that are significant to electrochemical sensors for HMI detection were identified through keyword searches in standard databases like SCOPUS, Web of Science, etc. Only original articles and reviews that were written in English were considered. Priority was given to the articles that reported new interfacing materials and sensing methodologies in the selection of references rather than applications. Nearly 200 articles were screened for this study.

2. HMI DETECTION METHODS

Metals are necessary for carrying out biological processes, but their concentration range has a significant effect on human health. It is considered safe if the concentration range of the metals is below the hazardous limit. If it exceeds the allowable limits, then it has a number of cytological and physiological impacts. Various metals with their regulatory limit for drinking water and industrial effluents defined by the Central Pollution Control Board (CPCB), India, are shown in Table 1.

So, it is necessary to have proper detection methods to determine the presence of heavy metal ions and estimate their concentration quantitatively. To achieve this, time- and cost-efficient detection procedures should be developed. Additionally, the detection methods need to be accurate so that they can find even traces of metal ions. Many techniques are available for the detection of HMIs, but there is no specific method that is applicable to all of the ions.

2.1. Analytical Sensing Methods of HMIs. Analytical sensing methods include atomic absorption and emission spectroscopy, atomic fluorescence spectrometry, X-ray fluorescence spectrometry, etc. These methods are accurate but expensive and require pretreatment procedures in the lab. These methods can simultaneously determine the concentrations of HMIs for a wide variety of elements. Though these methods have a low detection limit, they are very expensive and demand skilled personnel to operate the complicated equipment. Some analytical methods include atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), X-ray fluorescence spectrometry (XFS), etc.

2.1.1. Atomic Absorption Spectrometry. In AAS, the isolated atoms are stimulated to an excited state from the ground state using a specific wavelength, and the energy absorbed during this process is quantified. The amount of energy absorbed is proportional to the concentration of metallic elements in a given sample. Figure 2 shows a block diagram of the general atomic absorption spectrometer. The basic parts of AAS are light source, atomizer, monochromator, detector, and electronic read out. Here, the light source is used for exciting ions of a specific element. To determine elements in the sample using AAS, it is necessary that individual atoms or ions in the sample are well isolated from one another. Here an atomizer is used to create the analytes from the sample. Flame emission can be used to identify the elements with low

Table 1. Regulatory Limits, Sources, and Health Effects of Various Heavy Metals

HMI	regulatory limits		sources	health effects
	drinking water	effluents		
arsenic (As)	0.01 ppm	0.2 ppm	it can be released through volcanic eruptions and forest fires; it can be released from pesticides and fertilizers; it can be released from industrial practices like coal burning mining, etc.	low-level exposure can result in symptoms including “pins and needles” in the hands and feet, nausea, vomiting, irregular heartbeats, decreased production of red and white blood cells, and darkening of the skin.
cadmium (Cd)	0.005 ppm	2 ppm	cadmium is present in all rocks and soils, including coal and mineral fertilizers; batteries; pigments, metal coatings, and plastics are a few of the products that use cadmium; it plays a significant role in electroplating.	severe damage to lungs, irritation in stomach, kidney related disease, and fragile bones due to long-term exposure
chromium (Cr)	0.05 ppm	0.1 ppm	its compounds are usually found in sediments in water; it is mostly found in electroplating of products, magnetic tapes as alloys, paint as pigment material, etc.	short-term exposure can cause breathing problems like wheezing, asthma, nose ulcers, skin ulcers, and skin allergies; long-term exposure causes kidney and liver damage
lead (Pb)	15 ppb	0.1 ppm	lead can be found in air, water, and soil due to human activities like manufacturing, burning, mining, etc; it is found in batteries, pipe solders, X-ray shielding devices, paints, gasoline, cosmetics, etc	long-term exposure leads to weakness in nervous system, increase in blood pressure and anemia and exposure to high levels lead to kidney and brain damage
mercury (Hg)	2 ppb	0.01 ppm	it can be found in thermometer, power plants, dental fillings, etc.	high-level exposure can damage kidneys, brain, and fetus development permanently; short-term exposure leads to changes in hearing or vision, skin irritations, nausea, increase in blood pressure, increase in heart rate, etc.
silver (Ag)	0.1 ppb	0.01 ppm	it can be found in electrical contacts, conductors, mirrors, photographic films, disinfectants, antibacterial agents etc.	high-level exposure cause argyria, a condition called skin to decolorization, breathing problems, throat irritation, etc.; low-level exposure can cause allergic reactions and inflammations
zinc (Zn)	5 ppm	5 ppm	it can be found in environment due to industrial activities like mining, steel processing, waste combustion etc.	short-term exposure can lead to loss of appetite, reduced sense of taste and smell, slow wound healing, etc; long-term exposure can cause damage to the pancreas, disturb the protein metabolism, and cause respiratory disorders
copper (Cu)	2 ppm	3 ppm	it is found in electrical equipment, industrial machineries like heat exchangers etc.	consuming copper in excess of what is advised on a daily basis, whether through food, drink, or supplements, can result in serious sickness including kidney and liver damage

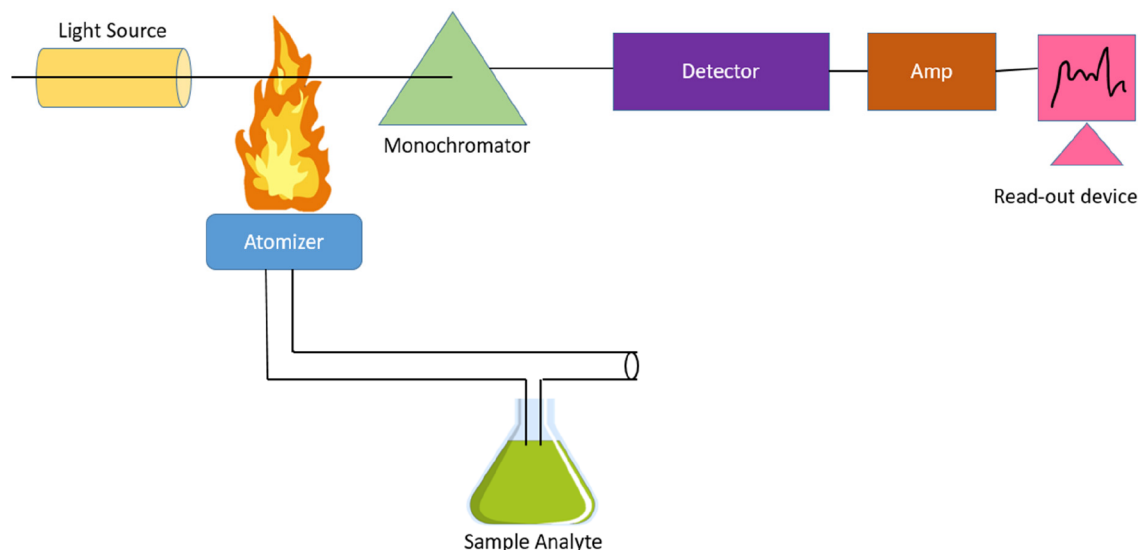


Figure 2. Block diagram of an atomic absorption spectrometer.

excitation energy and atomic absorption spectroscopy can be used to identify elements with high excitation energy. A monochromator is used to separate a specific wavelength before passing to the detector. The concentration of the analyte in solution can be determined by adopting any calibration technique in the readout device.

2.1.2. Atomic Fluorescence Spectrometry. This method makes use of the fluorescence spectra of each individual metal. In this method, the samples are pretreated to remove unwanted impurities. Then the elements of the sample are atomized by the same method adopted in AAS. The illumination of atoms by a radioactive light source causes atomic excitation, which results in emission of fluorescence signals. These signals are detected by the detector. The block diagram of AFS is shown in Figure 3. The construction and working principle of AFS are the same as those of AAS, but the main difference is AAS detects the light absorbed whereas AFS detects the emitted light.

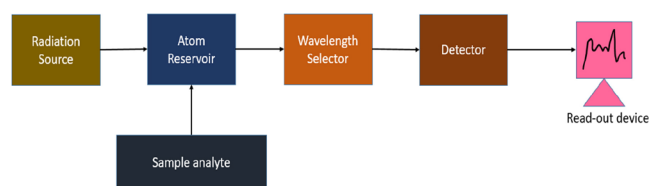


Figure 3. Block diagram of an atomic fluorescence spectrometer.

2.1.3. X-ray Fluorescence Spectrometry. By using XFS, the analytes of the sample are determined by measuring the emitted secondary X-rays from the sample when it is stimulated by the primary X-ray source. The secondary X-rays produced by the samples are unique for specific elements. So, XFS is considered an excellent technique for quantitative and qualitative analysis of analytes. Figure 4 shows the process carried out in the XFS analysis. Some of the HMI detections by analytical methods reported in literature are summarized in Table 2

2.2. Electrochemical Sensing Methods of HMIs. Electrochemical techniques are not only cost-effective but also user-friendly and reliable, and they incorporate basic

processes for monitoring contaminated samples. Another advantage afforded by electrochemical methods is the very small amount of time required for analysis in comparison to the time required by other spectroscopic techniques. In this technique, one electrode is chemically altered in order to vary its surface properties. Compared with the reference and counter electrodes, this chemically modified electrode operates as the working electrode. Based on the unique electrical signals produced by the presence of HMIs, electrochemical methods for detecting heavy metal ions in an aqueous solution are categorized. Several electrical properties, including current, voltage, electrochemical impedance, charge, and electro-luminescence, can be altered by the presence of HMIs.^{50–52} Based on different electrical signals, electrochemical techniques are categorized as potentiostatic techniques, galvanostatic techniques, impedance measurement techniques, and electrochemiluminescence techniques. In the majority of these methods, either the current or the potential is modified to measure the variation in the other parameter.

2.2.1. Potentiostatic Techniques. During potentiostatic procedures, a potentiostat is used to regulate the potential between its reference and counter electrodes, thus keeping the potential difference between the reference and working electrodes constant. The resulting current is monitored and recorded to predict the analyte concentration. The general experimental setup of potentiostatic technique is shown in Figure 5.

There are many subcategories available in potentiostatic techniques based on the voltage signal used and resulting current waveforms, which include amperometry, voltammetry (like linear sweep, normal pulse, staircase, reverse pulse, differential pulse, square wave, anodic stripping, cathodic stripping, cyclic voltammetry), and chronocoulometry. Amperometry uses a non-mercury working electrode to measure very small currents at a fixed voltage. This method uses a potential step signal between the reference and working electrodes in the electrochemical cell. In amperometric experiments, the current is measured and recorded as a function of time. The chronocoulometry method measures the amount of charge passed after applying a regulated potential that is computed from the integral of current versus time or voltage. Most of the

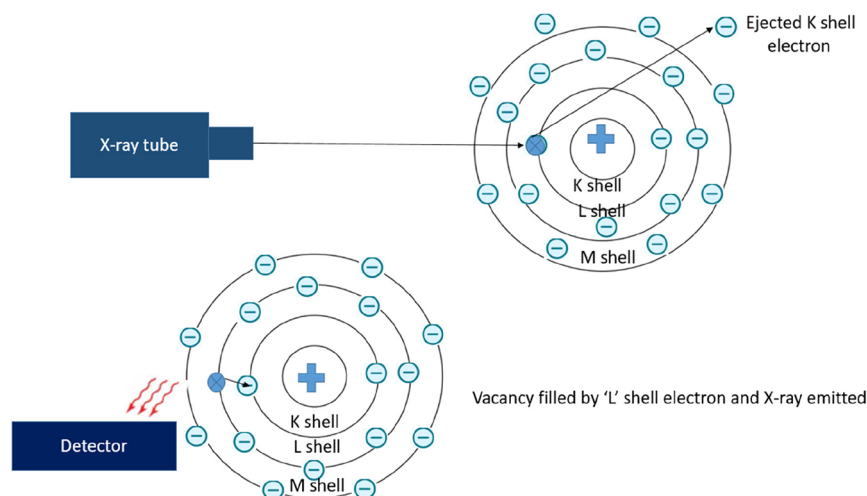


Figure 4. X-ray fluorescence spectroscopy.

Table 2. HMI Detection by Analytical Methods

sample taken	analytical technique	analytes	ref
tube wells of different depths	AAS	lead, antimony, aluminum, arsenic	27
Kulufo River	AAS	manganese, lead, chromium, cadmium	28
Chinese tea	AAS	lead, cadmium, chromium, copper, nickel	29
Chinese tablets	AAS	calcium, magnesium, iron, copper, zinc	30
rocks	AAS	platinum	31
wine	AAS	Cadmium	32
muscle samples of fish	AAS	mercury	33
natural and mineral waters	AAS	iron	34
brown rice	AFS	cadmium	35
water samples	AFS	lead	36
mining polluted soils	AFS	arsenic	37
acid mine drainage	AFS	arsenic(III), arsenic(V)	38
seafood	AFS	arsenic(III)	39
cow milk	AFS	selenium	40
sesame seeds	AFS	selenium	41
marine algae	AFS	antimony(III), antimony(V)	42
water	AFS	mercury	43
aqueous solution	XFS	copper, lead	44
coastal seawaters	XFS	iron, nickel, manganese, copper, zinc, lead	45
soil	XFS	arsenic, chromium, copper, nickel, lead, vanadium, zinc	46
soils	XFS	arsenic, cadmium, chromium, copper, nickel, zinc, lead	47
fish tissues	XFS	chromium, nickel, copper, zinc, mercury, lead	48
wastewater samples	XFS	mercury	49

time, these techniques are used to do exhaustive electrolysis for quantitative analysis, but they give very little information about the type of the analyte. In complicated environmental matrices, voltammetric methods are most commonly utilized to measure heavy metal ions. In contrast to the amperometric method, which uses a single potential point to measure current, these methods measure current at different potential points along a

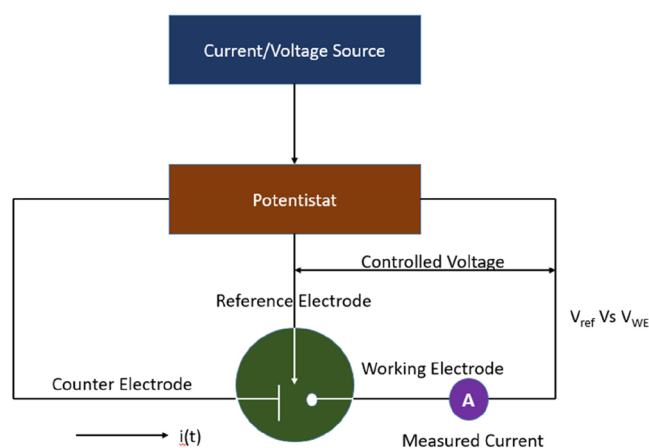


Figure 5. Experimental setup of potentiostatic techniques.

current–voltage curve. Voltammetry is often used to determine the type of trace metal, because it is accurate and sensitive.

2.2.2. Galvanostatic Techniques. In galvanostatic techniques, a current source is used to regulate the electric current between the working electrode and the counter electrode, and the resulting potential is then measured between the working and reference electrodes, as shown in Figure 6. In contrast to potentiostatic techniques, galvanostatic techniques require less complex instrumentation due to the absence of feedback from the reference electrode. However, these methods have significant drawbacks due to the huge double-layer charging effects that occur during the experiment.

2.2.3. Impedance Measurement Techniques. Electrochemical impedance spectroscopy (EIS) and AC voltammetry are two of the most popular impedance measurement techniques for estimating the concentration of analytes in aqueous solution. Between these two methods, EIS is more commonly used for metal ion speciation from a wide variety of biological and other environmental samples. The EIS method is frequently used to investigate the interfacial characteristics of changed electrodes, in particular, for multilayer films. It was also demonstrated to be an effective technique for identifying relevant interface characteristics that can be used in biosensing.⁵³ EIS uses electrically equivalent circuits to describe the products of an electrochemical process in an

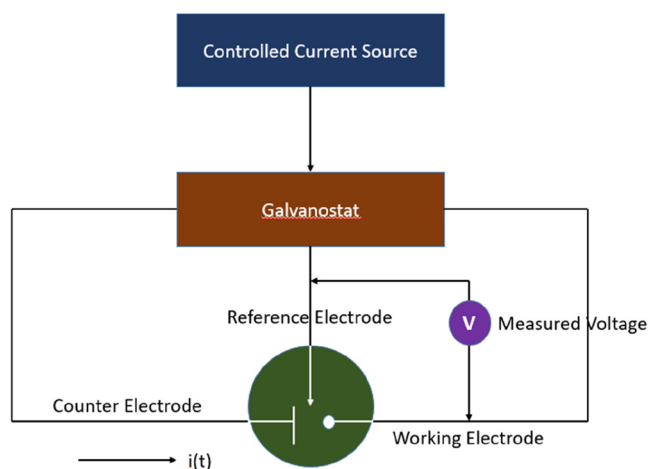


Figure 6. Experimental setup of galvanostatic techniques.

electrolytic cell. As charge moves through an electrified interface as a result of an electrochemical reaction, both Faradaic and non-Faradaic components are produced. The metal ion concentration in an electrolytic solution can be predicted by determining this impedance parameter of the electric equivalent circuits. The block diagram representation of EIS is shown in Figure 7.

2.2.4. Electrochemiluminescence Techniques. The phenomenon of chemiluminescence is produced by certain homogeneous electron transfer mechanisms in radical-ion-containing chemical solutions. These techniques are often used to find specific metal ions in a solution. They are based on fluorescence detection, which is simple, cheap, and very sensitive (parts per billion or trillion).

3. STUDIES ON HMI DETECTION USING ELECTROCHEMICAL SENSING

Electrochemical sensing evaluates the analyte concentration by chemical reactions. The electrochemical sensors transform chemical reaction data into measurable current, conductivity, and voltage or potential. These sensors use a chemically selective layer to recognize electrocatalyzed chemical reactions and an electrochemical transducer to translate chemical changes into electrical signals as shown in Figure 8.

Electrochemical sensing methods have been shown to be a good replacement for traditional methods of both qualitative and quantitative analysis. The advantages of electrochemical sensing systems are simple instrumentation, fast response, selectivity, ease of use, compact size, minimal sample pretreatment, short analysis time, and portability. A significant number of studies have been carried out in making portable electrochemical sensors for HMI detection. Among several heavy metals, arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) are the most likely candidates for the majority of heavy-metal-related diseases.

3.1. Research on Electrochemical Sensing of Arsenic.

Arsenic is usually considered one of the most hazardous elements found in nature. Arsenic is predominantly found in inorganic forms, called arsenite and arsenate. As per the studies done, arsenite is more highly toxic than arsenate.⁵⁴ The recommended level of arsenic in drinking water is below 10 ppb.^{55–57} Nanomaterials are increasingly being employed for the modification of electrodes to enhance performance by electrochemical sensing methods.^{58–62} By utilizing different nanoparticles like carbon nanoparticles, noble metal nanoparticle, bimetallic nanoparticle, and metal oxide nanoparticle modified electrodes, there is excellent performance in detecting arsenic in terms of sensitivity, the limit of detection, and anti-interference.

Carbon nanoparticle modified electrodes in electrochemical sensors provide a rapid response with minimum detection limits. It has been observed that Au electrodes modified with thiolated multiwalled carbon nanotubes are effective for the measurement of Arsenic. Kato et al.⁶³ described the synthesis of uniformly dispersed Au nanoparticles on a carbon film electrode using unbalanced magnetron cosputtering. The resulting particles had an average size of 5 nm. The mechanical stability of the Au nanoparticles size was enhanced, and the high catalytic activity was preserved. The effect of Au nanoparticles with various crystal facets on arsenic(III) was studied, and the obtained results show that the highest electrochemical performance was obtained with the Au(III) facet.⁶⁴

The adsorption capability of an electrode surface is significant in electrochemical behavior. Ferrite nanoparticles have received a lot of attention due to their excellent adsorption capacity and supermagnetism. This property is utilized to detect arsenic in water using monodispersed ferrite

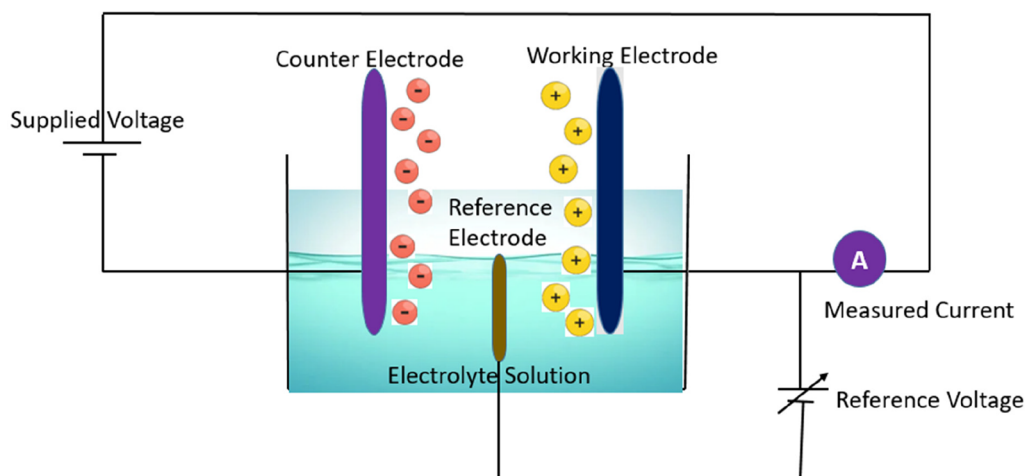


Figure 7. Diagrammatic representation of electrochemical impedance spectroscopy.

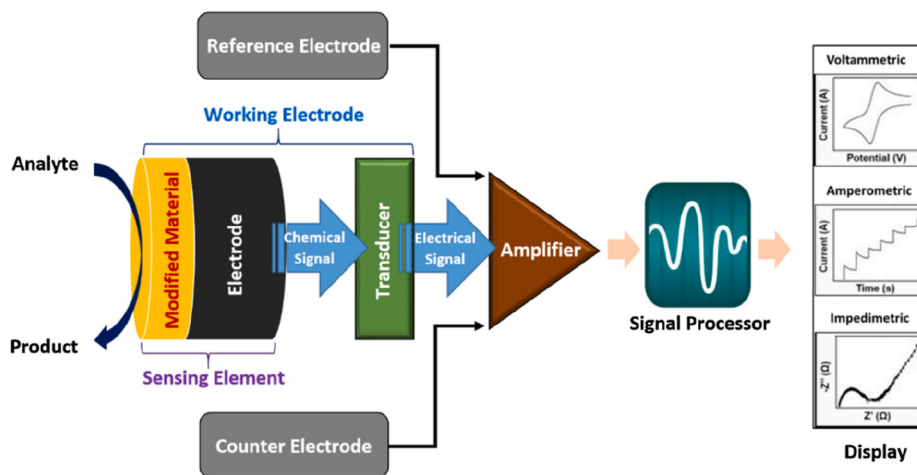


Figure 8. Schematic diagram of electrochemical sensor. Reprinted with permission from ref 51. Copyright 2021 Elsevier.

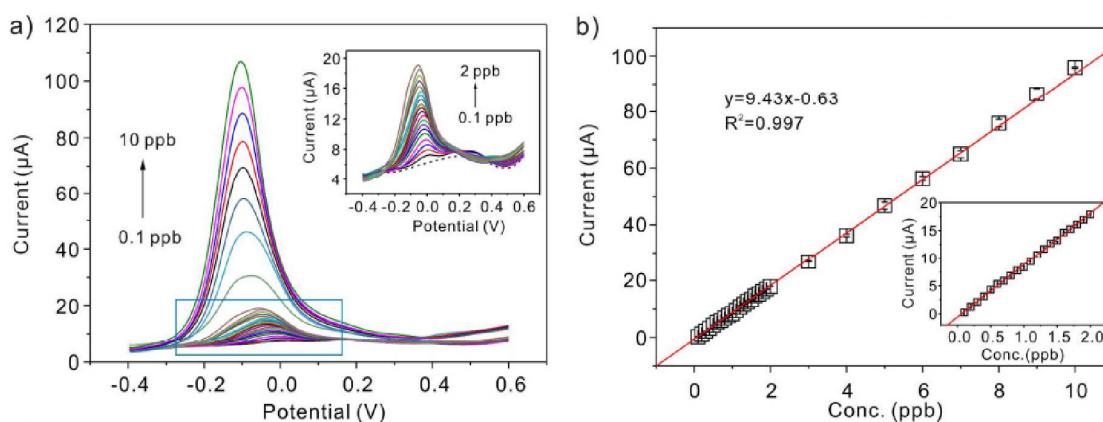


Figure 9. (a) Typical SWASV response of arsenic(III) at a Au/Fe₃O₄ screen-printed electrode across different concentrations. (b) Corresponding linear calibration plot of peak current against arsenic concentrations from 0.1 to 10 ppb. Insets in (a) and (b) are the enlarged views that correspond to a range of 0.1–2 ppb. Reprinted with permission from ref 70. Copyright 2018 American Chemical Society.

nanoparticles.⁶⁵ A manganese oxide (MnO_x)/Au nanoparticle modified glassy carbon electrode (GCE) for the detection of arsenic in alkaline media was studied, and this procedure is free from interference produced by other metal ions present in the water.⁶⁶ A nanocomposite electrochemical sensor based on Au nanoparticles/MnO₂ was reported by Dong et al.⁶⁷ for the detection of arsenic(III). A GCE was modified to resemble nanorods during fabrication of the sensor and was utilized to measure As(III) in extremely alkaline solutions. The developed sensor was reported to be effective and interference-free, and its alkaline medium detection capability was similar to that of a realistic water environment.

Because of improved properties like higher conductivity and catalytic activity compared to their monometallic counterparts, bimetallic nanoparticles have recently been the subject of substantial research for sensing applications. An efficient hydrothermal technique was proposed by Yang et al.⁶⁸ for preparing bimetallic nanoparticles of varying Au and copper (Cu) composition. The electrochemical performance was investigated by square wave anodic stripping voltammetry (SWASV) for the detection of arsenic, and it was found that the bimetallic nanoparticles show better performance than Au nanoparticles and conventional Au electrodes and parts per billion level while retaining the low detection limits. Assessing the sensing capabilities of electrodes with bimetallic gold

nanostructures was aided by computational studies using Au–Cu and Au–Pd clusters for the adsorption of trivalent arsenic.

Recently, noble metal nanoparticles have attracted extensive interest for heavy metal detection due to their excellent electrical conductivity, high surface area, and catalytic activities. Electrodeposition of noble metal nanoparticles can be easily done, and it has been demonstrated as a potential technique for heavy metal detection. Silver (Ag) nanoparticles have been used to create an integrated chitosan-modified GCE for sensing arsenic by differential pulse anodic stripping voltammetry (DPASV).⁶⁹ This method exhibits high sensitivity with a limit of detection of 1.2 ppb, which is found to be much lower than the recommended level of WHO. The specified electrode tolerated copper and significant concentrations of surfactants and chemical substances. This approach can also be used to determine arsenic(V) concentration after chemical treatments.

Dumbbell-like Au/Fe₃O₄ nanoparticles modified with a screen-printed carbon electrode (SPCE) can be used as an effective sensing method for arsenic.⁷⁰ It has been reported that the developed electrochemical sensor shows a 9.43 µA/ppb sensitivity and a detection limit of 0.0215 ppb. Figure 9 shows typical SWASV responses and linear calibration plots of peak current against arsenic concentrations at an Au/Fe₃O₄ SPCE in various concentration ranges from 0.1 to 10 ppb.

Table 3 presents a quick overview of reports of electrochemical sensing of arsenic that have been published in recent years.

Table 3. Electrochemical Sensing of Arsenic

technique	electrochemical platform	limit of detection (ppb)	detection range (ppb)	ref
linear sweep anodic stripping voltammetry (LSASV)	Au-reduced graphene oxide modified GCE	0.1	0.3–20	71
SWASV	Reduced graphene oxide-MnO ₂ /GCE	0.05	1–10	72
SWASV	exfoliated graphite-gold nanoparticles	0.58	1–50	73
SWASV	reduced graphene oxide-Fe ₃ O ₄ /GCE	0.12	0.1–20	74
LSASV	CB-AuNPs-SPE	0.4	2–30	75
LSASV	Au-PtNPs/GCE	0.28	0.375–225	76
SWASV	FePt Nanoparticles	0.8	1–15	77
SWASV	Au-IrM	0.038	0.75–3.75	78
DPASV	nanogold-SCPE	8.14	4–1498	79
SWASV	AuNP-carbon film electrode	0.55	1–100	80
SWASV	NP-Au/GCE	0.137	0.5–15	81
SWASV	Fe ₃ O ₄ /SPCE	0.00185	2–14	82
DPASV	ThO ₂ NPs/CPE	0.1	0–180	83
CV	F-doped cadmium oxide film	0.00455	56.25–450	84
CV	ZrO ₂ -Nafion/Au electrode	5	5–60	85
SWASV	SnO ₂ nanosheet gold electrode	5	5–300	86
LSASV	MnOx-AuNPs/GCE	0.057	0.5–80	87
SWASV	Au@Fe ₃ O ₄ -RTIL/SPCE	0.0022	0.1–1	88
SWASV	MnFe ₂ O ₄ -AuNPs/GCE	3.37	10–110	89
SWASV	gold nanoparticles/ α -MnO ₂ /GCE	0.828	1–10	90
ASV	chitosan-Fe(OH) ₃ /GCE	0.072	2–100	91
ASV	thiacrown 1,4,7-trithiacyclononane-AuNP-graphene-PE	0.0006	0.0019–2.55	92

3.2. Research on Electrochemical Sensing of Cadmium. The use of cadmium (Cd) in industrial applications, such as nickel cadmium rechargeable batteries, resistance to corrosion in electroplating, photoconductive surfaces in television picture tubes, solar modules, fluorescent probes in fluorescence microscopy, etc., is increasing significantly, despite cadmium's hazardous effects to the environment. It has been reported that excessive Cd exposure causes kidney problems, lung cancer, demineralization of the bones, breast cancer, etc. In addition, prolonged Cd inhalation can cause fever, hypertension, and even death. The recommended level of cadmium in drinking water is below 3 ppb. Thus, simple and effective approaches for the detection and monitoring of harmful metal ions in water are crucial. It has been observed that the development of electrochemical cadmium ion sensors relies heavily on nanocomposite materials.

The cadmium ion can be detected using a GCE with high adsorption capabilities modified with Fe₃O₄/Bi₂O₃/C₃N₄.⁹³ The linear response sensor displayed remarkable levels of sensitivity of 0.01–3 μ mol/L with a less than 3×10^{-9} mol/L detection limit. By utilizing ethyl green and multiwalled carbon nanotubes, a DNA-based electrochemical sensor for detecting cadmium ion was developed and this approach showed that ion detection has a linear detection range with a sensitivity of approximately 5 nA/nM and a minimum detection level of 2 nM.⁹⁴ Qin et al.⁹⁵ proposed an electrochemical sensor for detecting cadmium by utilizing β -cyclodextrin functionalized with Au nanoparticles. Because of the strong cadmium adsorption properties of β -cyclodextrin and the presence of Au nanoparticles, the nanocomposites described in this work have excellent electrical properties. Under optimal stripping circumstances, the peak currents for cadmium in the interface are linearly proportional to these elements' concentrations over the range of 40–1200 g/L.

Cadmium ions can be detected by anodic stripping voltammetry using nanostructured magnesium–aluminum layered double hydroxides that are highly selective and sensitive.⁹⁶ This double hydroxide has the benefit of requiring minimal modification, and its surface has specific hydroxyl functional groups that can react with metal ions via chemical binding to produce inner-sphere complexes. Figure 10a demonstrates the SWASV responses of nanostructured magnesium–aluminum layered double hydroxide/Nafion to

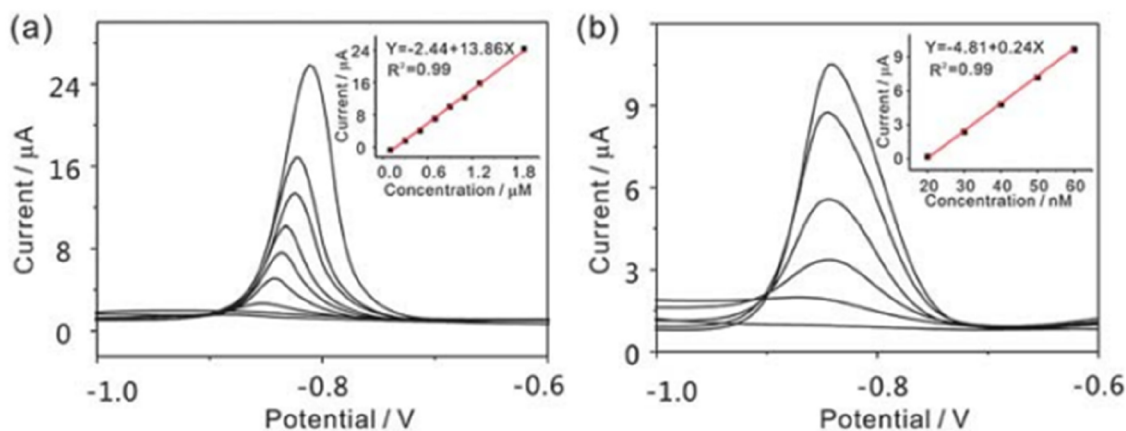


Figure 10. SWASV response and corresponding calibration plot (inset) of magnesium–aluminum double layered hydroxide/Nafion glass carbon electrode toward cadmium over the concentration range of (a) 0.1–1.9 μ M by depositing for 120 s and (b) 20–60 nm by depositing for 30 min. Reprinted with permission from ref 96. Copyright 2018 Royal Society of Chemistry.

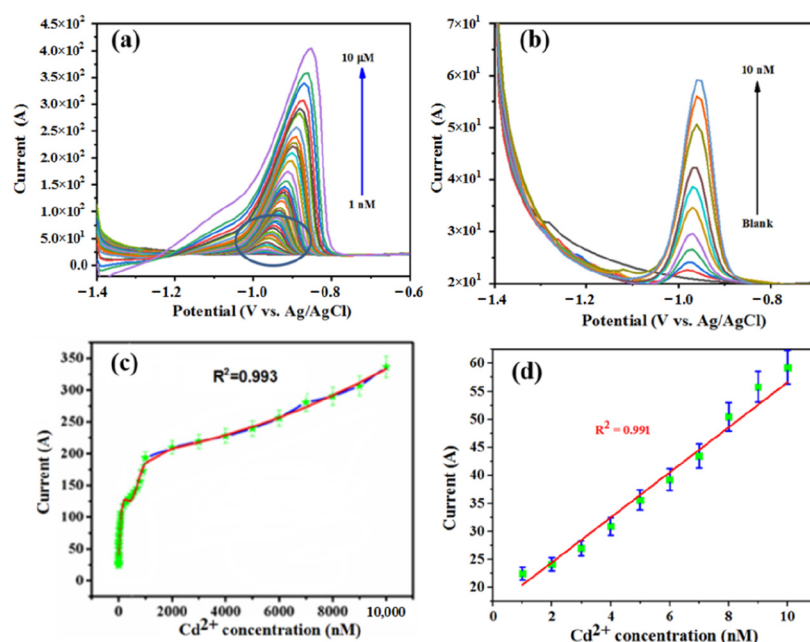


Figure 11. (a) DPV curves of cadmium with various concentration levels (from 1 nM to 10 μM) on a PB-PEDOT/LSG/glassy carbon electrode. (b) Magnified DPV curves of cadmium with low concentration (from 1 to 10 nM). (c,d) corresponding current versus cadmium concentration calibration curves. Reproduced from open access article ref 97 distributed under the terms and conditions of the Creative Commons Attribution license <http://creativecommons.org/licenses/by/4.0/>.

Table 4. Electrochemical Sensing of Cadmium

technique	electrochemical platform	limit of detection	detection range	ref
SWASV	antimony film CPE	0.8 and 0.2 $\mu\text{g L}^{-1}$	4.0–150.0 $\mu\text{g L}^{-1}$	98
SWASV	Bi–C nanocomposite	0.65 and 0.81 $\mu\text{g L}^{-1}$	1–100 ppb	99
SWASV	Au nanoparticles-carbon nanofibers	0.1 μM	0.1–1.0 μM	100
SWASV	silicon nanowires-SH/GCE	0.04 mA/nM and 0.074 $\mu\text{A/nM}$	5–250 nM	101
SWASV	Chemically modified CPE	0.3 m L^{-1}	1.5–1000 ng m L^{-1}	102
SWASV	Nafion/ionic liquid/graphene/SPCE	0.06 ng m L^{-1}	0.1–100.0 ng L^{-1}	103
ASV	GCE	3.2 $\mu\text{g L}^{-1}$	50–250 $\mu\text{g L}^{-1}$	104
SWASV	NH_3 -pn-MWCNTs	0.0272 nM	0.0025–0.0225 M	105
SWASV	MgSiO ₃ modified GCEs	0.186 nM	0.1–1.0 M	106
SSCP	mercury Film SPE	2.2 nM		107
SWASV	mercury Film SPE	1.78 nM	0.2–20 $\mu\text{g L}^{-1}$	108
SWASV	B-doped diamond-like carbon film	4.83 nM	2–25 $\mu\text{g L}^{-1}$	109
DPASV	boron-doped diamond films	3.29 nM	up to 35 nM	110
SWASV	complexing polymer films	500 nM	10 ⁻⁷ –10 ⁻⁵	111
conductometry	alkaline phosphatase	10–20 M		112
SWASV	multiwalled carbon nanotube tower based GCE	25 nM	2–8 μM	113
SWASV	graphene NS	10 ⁻⁷ M		114
SWASV	cucumber like hydroxyapatite	0.027 nM	0.01–10 nM	115
ASV	RGO/bismuth nanocomposite	2.8 $\mu\text{g L}^{-1}$	20–120 mg L^{-1}	116
SWASV	porous manganese oxide nanoflowers	81 pM	40–140 nM	117
SWASV	SnO ₂ /reduced graphene oxide nanocomposite	0.1 nM	0–1.3 μM	118
EIS	polyethylene terephthalate-SPE	1 nM	0–50 μM	119
galvanostatic stripping chronopotentiometry (GSCP)	latent mercury film type D-LMF (Istran) based carbon electrode	0.02 $\mu\text{g L}^{-1}$	0.07 $\mu\text{g L}^{-1}$	120
SIA-ASV	screen-printed carbon nanotube electrodes	0.8 $\mu\text{g L}^{-1}$	2–100 $\mu\text{g L}^{-1}$	121
SWASV	bismuth nanoparticles	5 $\mu\text{g L}^{-1}$		122
SWASV	bismuth nanopowder	2.54 $\mu\text{g L}^{-1}$		123

cadmium in the concentration range of 0.1–1.9 mM in 0.1 M PBS. As demonstrated in the calibration curve of cadmium (inset in Figure 10a), peak currents increased linearly in relation to cadmium concentrations, with a sensitivity of 13.86 $\mu\text{A}/\mu\text{M}$. SWASV responses were also tested in the low

concentration range of 20–60 nM by increasing the deposition duration to 30 min (Figure 10b). The experiment yielded a sensitivity of 240 $\mu\text{A}/\mu\text{M}$ and a lowest detectable concentration of 20 nM.

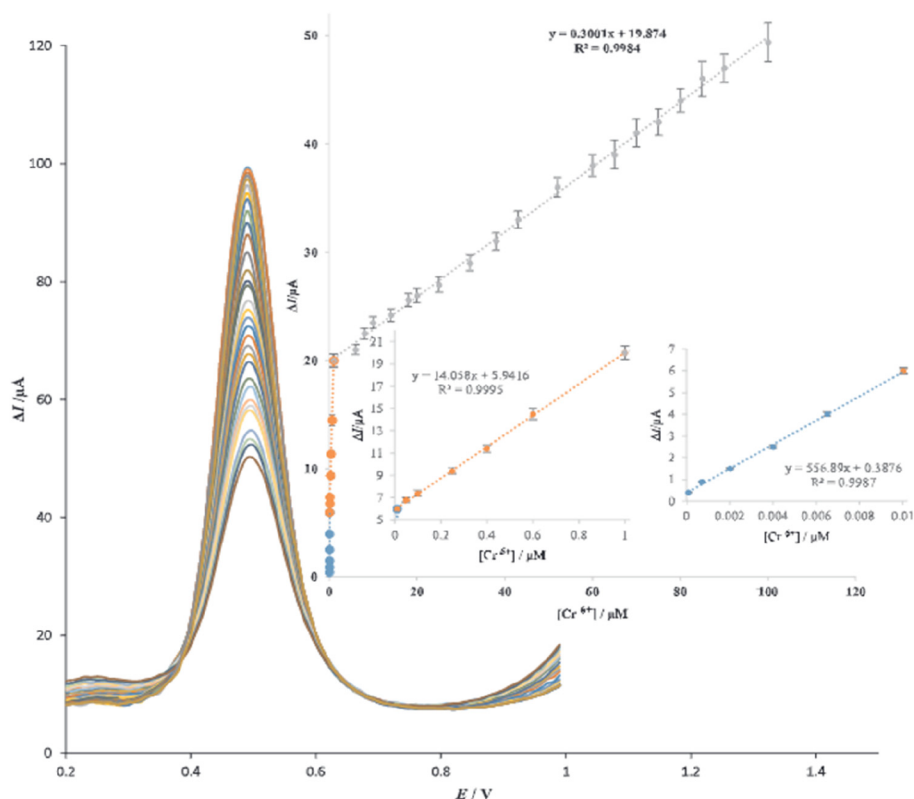


Figure 12. DPV of graphite paste electrode/silver nanoparticles biphenol biphenanthroquinone nanoribbons in 0.1 M PBS containing various concentrations of chromium. Insets represent the plots of anodic peak current Vs concentrations of chromium. The error bars represents the standard deviation of three parallel test Reprinted with permission from ref 131. Copyright 2018 Elsevier.

In order to detect cadmium in drinking water and sewage samples, a simple and effective synthesis process has been developed which combines a conductive polymer, poly(3,4-ethylenedioxythiophene) polystyrene sulfate (PEDOT), with Prussian blue (PB) and laser-scribed graphene (LSG) and the electrocatalytic performance was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).⁹⁷ Under optimal conditions, cadmium was directly and easily detected over a wide linear range (1 nM–10 M) with low detection limits (0.85 nM) as depicted in Figure 11.

Table 4 presents a quick overview of the reports on the electrochemical sensing of cadmium that have been published in recent years.

3.3. Research on Electrochemical Sensing of Chromium. Although it is one of the most frequent environmental contaminants, chromium is highly toxic when concentrations exceed safe levels, causing severe harm to humans and aquatic life. The recommended level of chromium in drinking water is below 0.05 ppb. Due to its widespread use in electroplating, leather tanning, wood polishing and preservation, and artificial gem and jewel fabrication, chromium in the environment is associated with the increasing industrialization of towns and metropolitan regions. The wastewater from these metal plating industries adds to the rise in chromium levels in biosystems. Due to the potential health risks of ingestion and different exposure limits imposed by different countries, monitoring chromium concentrations in natural waters is crucial.¹²⁴

Chromium is often detected electrochemically through a reduction at the electrode's surface. Nanomaterial-modified electrodes show a lot of benefits, such as a higher ratio of surface area to volume, low cost, high porosity, and easy

modification. Carbon nanotubes were used to print on different electrodes, such as fluorine-doped tin oxide glass, a flexible paper electrode, and a screen-printed electrode for the fabrication of an amperometric sensor for chromium ion measurement.¹²⁵ With the help of carbon nanotubes, the current response can be made stronger, which makes it possible to measure the heavy metal ion even at trace levels at concentrations as low as 5 $\mu\text{g}/\text{L}$. The same method was used by Rosolina et al.¹²⁶ to investigate the effect of carboxylated, single-walled carbon nanotubes on glassy carbon electrodes, as well as pyridinium-functionalized sol–gel thin films on the detection of chromium ions by square wave voltammetry.

In addition to carbon nanotubes, graphene nanomaterial can also be used to detect chromium ions in aqueous medium. The glassy carbon electrode was successfully modified with graphene for chromium detection by the method of electrostatic interaction in an acidic solution.¹²⁷ Graphene enhances the electron transmission and reduces the transfer resistance by 9 times when compared to the glassy carbon electrode, thereby detecting chromium at 7.8 $\mu\text{g}/\text{L}$. Chen et al.¹²⁸ developed an electrochemiluminescence sensor by quenching the cathodic signal of chromium ion on peroxodisulfate and graphene quantum dots. Graphene quantum dot concentration has been shown to decrease the relative standard deviation of the intensity of electrochemiluminescence as the signal-to-noise ratio increases. The sensor was useful for accurately detecting chromium ion concentrations as low as 1.04 $\mu\text{g}/\text{L}$.

For chromium detection, different metallic nanoparticles have been reported in the literature. An electrochemical sensor for chromium detection at a concentration of 0.05 $\mu\text{g}/\text{L}$ using a bismuth film on a mesoporous carbon electrode was

Table 5. Electrochemical Sensing of Chromium

technique	electrochemical platform	limit of detection	detection range	ref
ion-selective electrodes (ISEa)	platinum electrode material modified with iodine	2 μM	0.006–2 mM	132
CV	platinum electrode modified with Poly (4-vinylpyridine)	10 nM	0.01–1 μM	133
DPASV	mercury drop electrode modified with diethylenetriamine pentaacetate complex	20 ng/L	20–2000 ng/L	134
polarography	mercury drop electrode modified with NaClO_4	200 nM	0.2–60 μM	135
polarography	platinum	0.02 ppm	0.05–17.2 ppm	136
polarography	mercury film electrodes	0.3 ppm	1–10 ppb	137
linear sweep voltammetry (LSV)	platinum electrode modified with poly-3-methylthiophene	100 ppb	NA	138
polarography	mercury drop electrode modified with sodium pentamethylene dithiocarbamates	0.01 ppm	NA	139
LSV	mercury drop electrode modified with 5-Br-diethylamino phenol complex	0.9 nM	3–90 nM	140
anodic stripping voltammetry (ASV)	mercury drop electrode modified with diphenylcarbazine complex	0.02 $\mu\text{g/L}$	0–10 nM	141
LSV	diphenylcarbazine	13 nM	0.013–100 μM	142
CSV	mercury drop electrode modified with bipyridine complex	20 pM	0.02–50 nM	143
ASV	mercury drop electrode modified with pyrocatechol violet complex	3 nM	15–100 nM	144
CSV	diethylenetriamine pentaacetate complex	0.28 nM	9.62–170 nM	145
DPASV	diethylenetriamine pentaacetate complex	30 pM	0.1–10 nM	146
DPASV	ethylenediamine triacetic acid, pyrocatechol violet complexes	30 nM	4.85–105 nM	147
SWASV	mercury film	32.3 nM	0.01–0.6 μM	148
DPV	natural or synthetic diamond	10^{-12}	10^{-10} – 10^{-8}	149
Amp	blank phosphate buffers/glucose oxidase electrodes	0.49 $\mu\text{g/L}$	0.49–95.73 $\mu\text{g/L}$	150
Amp	polypyrrole/tyrosinase	0.5 μM	0.5–100 μM	151
DPV	bentonite/diphenyl carbazine	17 $\mu\text{g/L}$	0.03–0.5 mg/L	152
Amp	gold nanoparticles	0.1 μM	0.5–50 μM	153
Amp	silicate/nanoAuNPs	0.1 ppb	0.2–3 ppb	154
SWASV	bismuth film	5.27 ppb	10–70 ppb	155
Amp	Prussian blue	0.15 ppb	0.5–200 ppb	156
CSV	trioctylamine	3.4 nM	500 nM to 1 mM	157
Amp	L-dihydroxyphenylalanine	6.01 $\mu\text{g/L}$	10–125 $\mu\text{g/L}$	158
DPV	polycarbonate/ IrO_2 nanotubes	0.2 μM	1–10 μM	159
Amp	silver nanoparticles	0.65 ppb	2–370 ppb	160

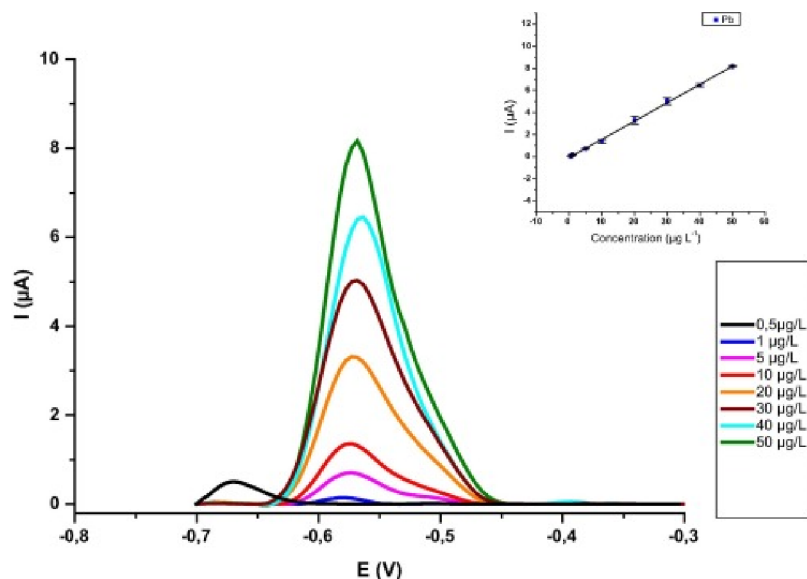


Figure 13. SWASV for different concentrations of lead ions from a carbon paste electrode modified with polydiaminonaphthalene and bismuth film. (inset) Calibration curve of lead ions. Reproduced from open access article ref 162 distributed under the terms and conditions of the Creative Commons Attribution license <http://creativecommons.org/licenses/by/4.0/>.

developed by Xu et al.,¹²⁹ and this method enhanced the sensing ability of the developed sensor with minimal interference. Silver has also attracted considerable attention

in recent years for its use as a sensing material, which was used to determine chromium through its catalytic function. In situ electroplating of a glassy carbon electrode with a silver layer

Table 6. Electrochemical Sensing of Lead Ions

technique	electrochemical platform	limit of detection	detection range	ref
SWASV	antimony film carbon paste electrode	0.8 and 0.2 $\mu\text{g L}^{-1}$	4.0–150.0 $\mu\text{g L}^{-1}$	98
SWASV	Bi–C nanocomposite	0.65 and 0.81 $\mu\text{g L}^{-1}$	1–100 ppb	99
SWASV	Au nanoparticles-carbon nano fibers	0.1 μM	0.1–1.0 μM	100
SWASV	silicon nanowires-SH/GCE	0.04 mA/nM and 0.074 $\mu\text{A/nM}$	5–250 nM	101
SWASV	Gr and the OPFP IL modified CPE	4.50×10^{-10} mol L^{-1}	0.1–30.0 ng mL $^{-1}$	168
SWASV	Nafion/ionic liquid/graphene/SPCE	0.08 ng m L^{-1}	0.1 to 100.0 ng L^{-1}	103
ASV	GCE	1.9 $\mu\text{g L}^{-1}$	5–200 $\mu\text{g L}^{-1}$	104
SWASV	MgSiO ₃ modified GCEs	0.247 nM	0.1–1.0 M	106
DPASV	hydroxyquinoline mercury drop electrode	0.03 nM	1.7–3.2 nM	169
SWASV	B-doped diamond-like carbon film	8.9 nM	2–25 $\mu\text{g L}^{-1}$	109
SWASV	Boron doped diamond films	19.3 nM	20 ppb –100 ppb	170
DPASV	boron doped diamond films	26.5 nM	up to 48 nM	110
SWASV	thiol functionalized clay modified CPE	60 nM	3×10^{-7} to 10^{-5} M	171
LSASV	TETRAM-modified graphite felt electrode	25 nM		172
SWASV	complexing polymer films	0.5 nM	10^{-8} – 10^{-6}	111
CA	GC/PEDOT:PSS	0.19 nM	2 nmol L^{-1} to 0.1 $\mu\text{mol L}^{-1}$	173
SWASV	MWCNT tower based GCE	12 nM	2–8 μM	113
SWASV	Graphene NS	10^{-11} M		114
SWASV	Cucumber like HAP	0.00423 nM	0.01–10 nM	115
DPV	Nanostructured MIP	0.6 nM	1.0×10^{-9} to 8.1×10^{-7} M	174
ASV	RGO/Bi nanocomposite	0.55 $\mu\text{g L}^{-1}$	20–120 mg L^{-1}	116
SWASV	porous MGO nanoflowers	2.1 pM	3.3–22 nM	117
SWASV	AuNP-CNT	0.546 $\mu\text{g L}^{-1}$	–22.29 ppb	175
SWASV	SnO ₂ /RGO nanocomposite	0.18 nM,	0 to 1.3 μM	118
SWASV	CdS QD modified ssDNA	7.8 pM	0.01 nM to 3.31 1.0 μM	176
EIS	PET-SPE	1 nM	50 μM to 1 mM	119
GSCP	D-LMF based carbon electrode	0.02 $\mu\text{g L}^{-1}$	0.06–0.36 $\mu\text{g L}^{-1}$	120
sequential injection analysis (SIA)-ASV	SPCNTE	0.2 $\mu\text{g L}^{-1}$	2–100 $\mu\text{g L}^{-1}$	121
SWASV	BiNPs	2 $\mu\text{g L}^{-1}$		122
SWASV	Nano-Bi	1.97 $\mu\text{g L}^{-1}$		123

has been reported in the literature to create a sensor for chromium detection at the $\mu\text{g/L}$ level by DPASV.¹³⁰ When silver electroplating was used, chromium was detected at 5.2 $\mu\text{g/L}$ concentration, 4 times higher than that of bare electrodes. In a similar manner, the decorated silver nanoparticles on biphenol biphenquinone nanoribbons were used to modify a graphite paste electrode for chromium detection.¹³¹ The silver nanoparticles improved the current density and reversibility of the developed sensor as shown in Figure 12.

Table 5 presents a quick overview of reports of electrochemical sensing of chromium that have been published in recent years.

3.4. Research on Electrochemical Sensing of Lead.

Lead ions, which are produced through lead-based paints and contaminated water, soils, and foodstuffs, are a significant contaminant due to their potential bioaccumulation and toxic effects. Lead poisoning is linked to cognitive impairment, anemia, paralysis of the skeletal muscles, and hypertension in humans. The recommended level of lead in drinking water is below 15 ppb.

A conducting-polymer-coated nanostructured porous gold electrode and peptide probe have been used to create a novel electrochemical sensor for lead ions.¹⁶¹ The reduced peak of the porous gold electrode had an increased electrode surface area due to the porous nanostructure. The sensor can detect 1 nM lead ions in low-pH conditions with a large linear dynamic detection range between 1 nM and 10 mM. This sensor exclusively detects lead ions without cross-reactivity. Salih et

al.¹⁶² proposed an electrochemical sensor for lead ion detection, which was made from a carbon paste electrode modified with polydiaminonaphthalene and bismuth film. The prepared sensor was characterized and tested with cyclic voltammetry. Results showed that the sensor had an electroactivity that detected lead in an acidic medium, and under the best conditions a linear range was found for concentrations from 0.5 to 50 $\mu\text{g/L}$ with a detection limit of 0.3 $\mu\text{g/L}$ as shown in Figure 13.

Liu et al.¹⁶³ used 8-17 DNAzyme as a recognition element for the fabrication of lead ion sensors by including the TdTase-mediated base extension principle. This electrochemical sensor shows great sensitivity with a low detection limit of 0.043 nmol/L. In a similar manner, an electrochemical sensor for lead ion detection based on a carboxy-functionalized graphene modified electrode was proposed.¹⁶⁴ In this work 8-17 DNAzyme was used as the recognition element and H₂O₂ catalyzed by an iron-doped metal–organic framework as a signal probe. This developed sensor showed high selectivity to lead ions due to the advantages of graphene and excellent catalytic capability with a wide linear range of 10^{-3} – 10^{-7} mol/L and a minimum detection level of 1.7×10^{-14} mol/L. Moreover, 8-17 DNAzyme and GR-5 DNAzyme were combined in a study into one amplification system to create a sensitive and selective lead ion sensor.¹⁶⁵ The detection limit was 0.048 pmol/L using dual lead ion-DNAzyme assisted feedback amplification.

The electrochemical detection of lead ion was also investigated with a silica modified glassy carbon electrode.¹⁶⁶

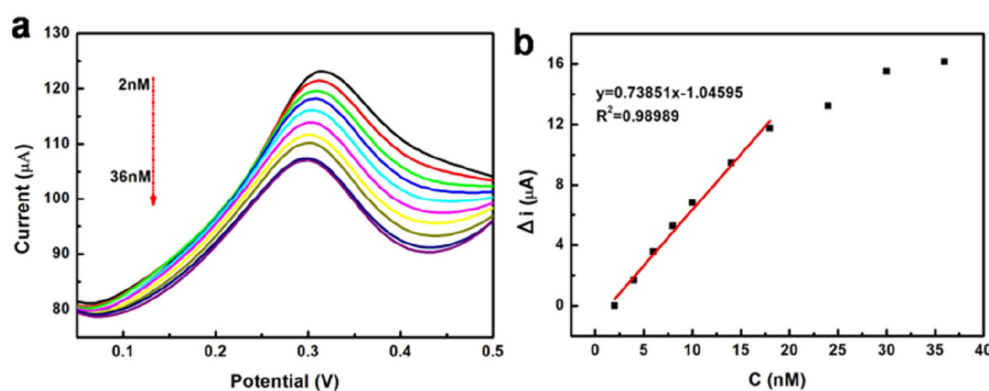


Figure 14. (a) DPV curve of zinc oxide/reduced graphene oxide/polypyrrole for different mercury ion concentrations. (b) Corresponding calibration curve of mercury ion concentrations. Reprinted with permission from ref 182. Copyright 2018 Elsevier.

Table 7. Electrochemical Sensing of Mercury Ions

technique	electrochemical platform	limit of detection	detection range	ref
SWASV	chemically modified CPE	0.05 ng m L ⁻¹	1.5–1000 ng m L ⁻¹	102
Amperometry	nanoCB SPE	5 nM	0.05–14.77 ppm	185
SWASV	Gr and OPFP IL modified CPE	3.86×10^{-10} mol L ⁻¹	1.25×10^{-9} – 2.00×10^{-7} mol L ⁻¹	168
SI-ASV	BDD-TFE	0.04 ng m L ⁻¹	0.1–30.0 and 5.0–60.0 ng mL ⁻¹	186
SWASV	NH ₃ -pn-MWCNTs	0.1439 nM	0.02–0.6 M	105
SWASV	MgSiO ₃ modified GCEs	0.375 nM	0.8–2.0 M	106
SWASV	B-doped DLC	4.99 nM	2–25 µg/L	109
DPASV	BDD	11.5 nM	up to 5 nM	110
EIS	β-ketoimine calix ¹⁰² arene on ITO	0.1 nM		187
SWASV	complexing polymer films	100 nM	5×10^{-8} to 5×10^{-6}	111
conductometry	invertase, mutarotase, glucose oxidase	25 nM	0.1–100 µM	188
amperometry	invertase, mutarotase, glucose oxidase	10 nM		189
DPV	AuNP amplified DNA-Gold electrode	0.5 nM	1–100 nM	190
SWASV	SnO ₂ /reduced graphene oxide nanocomposite	0.28 nM	0–1.3 µM	118
DPV	DNA duplexes containing multiple T–Hg ²⁺ –T base pairs	0.2 nM	0–80 nM	191

The SWASV method was used for the characterization of the modified electrodes. The results show that lead ions exhibit good oxidation peaks and a high peak current in 0.1 M acetate buffer. Similarly, a silver–gold alloy nanoparticle aptamer modified glassy carbon electrode for sensing lead was developed and these alloy nanoparticles were electrodeposited by a double pulse method on electrodes. The results showed that the proposed electrochemical sensor detected over a linear range of 0.01–10 µg/L with a detection limit of 0.03×10^{-2} µg/L.¹⁶⁷

Table 6 presents a quick overview of reports of electrochemical sensing of lead ions that have been published in recent years.

3.5. Research on Electrochemical Sensing of Mercury.

Mercury is one of the most dangerous contaminants to the environment, which originates from natural resources like geothermal or volcanic eruptions or with human activities. Mercury ions are very toxic in any form and can potentially damage the normal functioning of the immune system, brain nervous system, etc. Even though mercury in its metal form is rather safe, it produces adverse effects in its chemical form. The recommended level of mercury ions in drinking water is below 2 ppb.

The electrochemical sensing of mercury ions in aqueous solution was investigated using gold nanoparticle modified glassy carbon and indium–tin oxide electrodes.¹⁷⁷ This modification was carried out in two methods: electrochemical

reduction of hydronetrachlorogold and electric adsorption of gold nanoparticles that are stabilized by citrate. This sensing method was evaluated in terms of stripping potential, and results show that this method achieves a detection limit of 1 µM/L of mercury.

Gold nanoparticle modified screen-printed electrodes have also been utilized extensively for mercury detection in groundwater.¹⁷⁸ They can detect sub-ppb mercury levels in various water samples via microextraction with ionic liquids.^{179,180} Gupta et al.¹⁸¹ developed a nanostructured hexagon of bismuth by electrochemical deposition on indium–tin oxide for electrochemical sensing of mercury ions. The characterization was done by using square wave anodic stripping voltammetry, and the results show that the nanostructured electrodes are very sensitive to mercury ions at 0.74 ppb.

An electrochemical sensor for detecting mercury ions was investigated using a zinc oxide/reduced graphene oxide Schottky barrier as a recognition element and polypyrrole as an adsorption factor.¹⁸² In this work, DPV was used to do characterization and showed a linear range of 2–18 nM for mercury ion concentration as shown in Figure 14.

In a study, a carbon paste electrode was modified with ethylenediamine tetraacetic acid for detecting mercury ion in aqueous medium.¹⁸³ Square wave voltammetry was used to do the characterization, and the results showed a linear range of $(5–35) \times 10^{-4}$ mol/L for mercury ion with a detection limit of

16.6×10^{-9} mol/L. For the electrochemical detection of mercury ion, a platinum incorporated dealuminated modenite decorated modified glassy carbon electrode was used in a study.¹⁸⁴ In this work, cyclic voltammetry and differential pulse voltammetry were used to do the characterization, and the mesostructured properties of the modified electrode were utilized. The proposed modified electrode showed a greater peak current response for the detection of mercury ion with a low detection limit of 3.4 nM and a great sensitivity of $11.25 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ with a wide linear range of 0.1–220 μM .

Table 7 presents a quick overview of reports of the electrochemical sensing of mercury ions that have been published in recent years.

4. CONCLUSION

One of the greatest threats to the environment is the pollution of heavy metal ions. The toxicity of HMIs has been linked to a wide range of adverse health effects in a variety of organisms. This led researchers to investigate and develop methods for detecting ions from an aqueous medium. Electrochemical sensing methods are considered to be more advantageous when compared with an analytical approach because of their accuracy, faster response, and operating principle. Electrochemical approaches have been classified based on the signals used for electrical measurements like potentiostatic, galvanostatic, impedance measurement, and electrochemiluminescence techniques. Many types of materials like carbon-based materials, polymers, metal oxides, and nanomaterials have been used for developing sensing platforms; especially nanomaterials have been extensively used because of their unique properties. Due to their large surface area to volume ratio, high catalytic activity, and strong adsorption ability, nanomaterials can be coupled with electrochemical techniques for high sensitivity, fast response time, and sensing of multiple analytes with low detection limits. This review explored how different interface materials have been used to modify the conventional type electrodes like screen-printed, graphite, and glassy carbon electrodes for the detection of metal ions of arsenic, cadmium, chromium, lead, and mercury. However, it remains challenging to simplify the design and techniques of electrochemical measurements for HMI detection and the miniaturization of the involved electrochemical sensors. Future research should focus on developing portable, high-throughput devices like multichannel paper chips, universal probes for simultaneous detection of multiple heavy metal ions, and more nanosensors that can remove and analyze heavy metal ions. Large numbers of nanosensors for heavy metal ion detection are expected as the technology advances, offering applications in environmental monitoring, food security, and disease diagnosis.

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Notes

The authors declare no competing financial interest.

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