

Review

Sustainable Biopolymer-Based Electrochemical Sensors for Trace Heavy Metal Determination in Water: A Comprehensive Review

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Abstract: The growing concern over heavy metal contamination in environmental and industrial settings has intensified the need for sensitive, selective, and cost-effective detection technologies. Electrochemical sensors, due to their high sensitivity, rapid response, and portability, have emerged as promising tools for detecting heavy metals. Recent years have seen significant progress in utilizing biopolymer-based materials to enhance the performance of these sensors. Biopolymers, derived from renewable raw materials, have garnered considerable interest in both science and industry. These biopolymer-based composites are increasingly recognized as superior alternatives to conventional non-biodegradable materials because of their ability to degrade through environmental exposure. This review provides a comprehensive overview of recent advancements in biopolymer-based electrochemical sensors for heavy metal detection. It discusses various types of biopolymers and bio-sourced polymers, their extraction methods, and chemical properties. Additionally, it highlights the state of the art in applying biopolymers to electrochemical sensor development for heavy metal detection, synthesizing recent advances and offering insights into design principles, fabrication strategies, and analytical performance. This review underscores the potential of biopolymer-based sensors as cost-effective, eco-friendly, and efficient tools for addressing the pressing issue of heavy metal contamination in water and discusses their advantages and limitations. It also outlines future research directions to further enhance the performance and applicability of these sensors.

Keywords: biopolymers; electrochemical sensors; heavy metals; detection; water pollution; sustainability; environmental; green technology; polysaccharides

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1. Introduction

Heavy metal contamination in water has become a growing concern, with pollution levels rising dramatically over recent decades [1]. To mitigate the harmful effects on human health and the environment, it is essential to develop strategies, policies, technologies, and materials to control this problem [2]. Developing cost-effective, sustainable, and environmentally friendly materials is crucial to addressing these challenges [3]. Although nanomaterials have been extensively studied for sensor applications due to their unique physicochemical properties, concerns about their potential toxicological effects have shifted attention toward biopolymers [4].

Biopolymers, or bio-sourced polymers derived from renewable resources, have gained increasing importance in sensing applications. These materials, produced from plants, animals, and algae, are seeing a steady rise in production and use. Biopolymers

from renewable raw materials can be categorized into four main groups based on their chemical structure and properties:

- Proteins (e.g., gelatin and collagen), known for their high mechanical strength;
- Poly(lactic acid) and poly(hydroxyalkanoates);
- Natural rubber latex, offering flexibility and conductivity;
- Polysaccharides (e.g., cellulose, chitosan, lignin), valued for their biocompatibility, biodegradability, and versatile functional groups [5].

Biopolymers are increasingly being applied in environmental remediation, particularly in the removal of metal ions. Recent research has focused on their potential to replace synthetic materials in electrochemical sensors for detecting heavy metals, aligning with sustainability goals. These biopolymers can be included into the content of the electrode, modifying layers, films, or composites to form functionalized detection surfaces with enhanced electrochemical properties. Their chemical structures also offer opportunities for modification, such as grafting functional groups to improve performance [5].

This review summarizes recent advances in the use of low-cost biopolymers and their chemical and physical modifications to enhance metal removal and electrochemical sensing capabilities. It begins by emphasizing the importance of heavy metal detection and the limitations of traditional methods. Next, this review explores the characteristics of biopolymers, highlighting their renewability, biocompatibility, and multifunctionality, which make them ideal for sensor development. Biopolymers are categorized by their source, structure, and properties, and their roles as sensing elements in electrochemical sensors for heavy metal detection are discussed.

This review further analyzes the integration of biopolymers into various electrochemical sensor platforms, such as amperometric, potentiometric, and impedimetric systems, focusing on strategies like nanocomposite fabrication and surface modification to improve the sensor selectivity, sensitivity, and stability. It also evaluates the performance of biopolymer-based electrochemical sensors in detecting heavy metals, including lead, mercury, cadmium, arsenic, and chromium, addressing key factors such as detection limits, response times, and interference effects. Finally, this review assesses the real-world applicability of these sensors in environmental monitoring, industrial processes, and point-of-care diagnostics and discusses the research directions that should be realized in the future to improve their performance and applicability.

2. Heavy Metals

2.1. Heavy Metals Definition and Sources

Although the definition of heavy metals is controversial and not entirely clear, an element can be classified as a heavy metal if it has a much higher density than water, occurs naturally, and is present primarily in the earth's crust. Approximately 40% of the lakes and rivers of the planet have been polluted by heavy metals [6]. The main heavy metal pollutants in surface waters are Lead Pb(II), Zinc Zn(II), Cadmium Cd(II), Copper Cu(II), Nickel Ni(II), Arsenic As(III), Cobalt Co(II), Iron Fe(II), Manganese Mn(II), Mercury Hg(II), Chromium Cr(VI), Silver Ag(I), Gold Au(III), Palladium Pd(II), Platinum Pt(II), Uranium U(VI), and Cesium Cs(I). Cr(VI), Ni(II), Cd(II), Pb(II), and Hg(II) are among the most toxic ions to be found in nature, particularly in wastewater [7].

The sources of heavy metals can be natural or anthropogenic. Natural sources include interactions with meta-bearing rocks normally present in the environment and volcanic eruptions [8]. Anthropogenic sources include those associated with industrial (e.g., fossil fuel combustion, metal processing), agricultural (pesticides), and domestic activities (e.g., garbage, cleaning products) [9]. Mining is one of the most important sectors to consider, particularly because it plays a central role in the economies of both developed and developing countries. This activity releases large quantities of heavy metals, which are released through mineral extraction and transported through rivers and streams, where they may be dissolved in the water or as part of the sediments [10]. These metals typically seep into

groundwater and can also cause water shortages, prevent crop growth through soil erosion, and cause serious health problems for local animals and people [11]. The other main sources of heavy metals are also industries such as tanneries, pharmaceutical and chemical industries, electroplating, alloy production, fertilizers, etc. (see Table 1).

2.2. Toxicological Effects

Heavy metals are among the most dangerous pollutants because they are toxic, non-biodegradable, and accumulate in ecological systems. Determining heavy metals is therefore crucial for monitoring environmental quality, which is currently under pressure due to increasing pollution from industrial, agricultural, and domestic activities. When heavy metals enter and accumulate in the environment, plants and animals living in contaminated areas can take them up. Through the food chain, they eventually become biomagnified in the human body through consumption of contaminated plants, animals, and water [12]. A natural mechanism for controlling heavy metals' removal from the human body is not yet known. Therefore, traces of toxic heavy metals can have harmful effects on human health, including damage to multiple organs and the nervous system [13].

Heavy metal ions in water are involved in the environment and ecological cycles in a variety of forms, along with other inorganic metal ions, hydrated metal ions, hydroxyl complexes, carbonate complexes, and complexes mixed with natural substances. Also, they are taken up and enriched by aquatic plants, animals, and microorganisms. They can also interact with several inorganic or organic colloids and organic–inorganic complexes in the water or sediment and then settle to the bottom of the water body [1].

The World Health Organization (WHO) sets a guideline and recommendation regarding the maximum allowed level of various heavy metal in drinking water. Table 1 summarizes the main sources of heavy metals, their toxicological effects, and the permissible limits in drinking water recommended by WHO.

Table 1. Limits, sources, and effects of various heavy metal ion contaminations in human health.

Metal	WHO (mg L ⁻¹)	Toxicity		Anthropogenic Sources	Effects	Refs.
		Tolerable Daily Intake (mg/per day)	Lethal Dose mg kg ⁻¹ Body Weight			
Lead (Pb)	0.05	0.025–0.052	94–158	PVC pipes in sanitation, agriculture, recycled PVC, lead paint, jewelry, lead batteries, lunch boxes.	Alzheimer's disease and senile dementia, damage to the nervous system, also leads to neurodegenerative diseases, lower IQ, kidney damage, reduced bone growth, behavioral problems, digestive problems, urinary insufficiency.	[11,14–16]
Cadmium (Cd)	0.005	0.018–0.052	4.4–6.2	Paints, pigments, batteries, plastics rubbers, engraving process, photoconductors, and photovoltaic cells.	Renal toxicity, hypertension, weight loss, fatigue, microcytic hypochromic anemia, lymphocytosis, pulmonary fibrosis, lung cancer.	[15,17]
Mercury (Hg)	0.001	0.03	5.1–10.0	Combustion of coal, municipal solid waste incineration, and volcanic emissions.	Impaired neurologic development, effects on digestive system, immune system, lungs, kidneys, skin and eyes, hypertension.	[18,19]
Arsenic (Ar)	0.05	0.03	41	Wooden electricity poles that are treated with arsenic-based preservatives, pesticides, fertilizers.	Affects the cardiovascular system, pulmonary diseases, gastrointestinal tract, genitourinary system, hematopoietic system, dermatology, fetal and teratogenic diseases,	

					anorexia, brown pigmentation, hyperpigmentation, local edema, and skin cancer.	
Chromium (Cr)	0.05	0.013–0.099	-	Leather industry, tanning, and chrome plating industries.	Gastrointestinal diseases, hepatic encephalopathy, respiratory and cardiovascular problems, renal and endocrine systems defects, hematological, ocular problems.	[15,20]
Silver (Ag)	0.1	-	-	Refining of copper, gold, nickel, zinc, jewelry, and electroplating industries.	Argyria, gastroenteritis, neuronal disorders, mental fatigue, rheumatism, knotting of cartilage, cytopathological effects in fibroblast, keratinocytes, and mast cells.	[4,17]
Zinc (Zn)	5	15–16.2	1–25.3	Soldering, cosmetics and pigments, respiratory disorders, metal fume fever, bronchiolar.	leucocytes, neuronal disorder, prostate cancer risks, macular degeneration, and impotence.	[9,15]
Copper (Cu)	1.3	10	4.0–7.2	Fertilizers, tanning, and photovoltaic cells.	Adrenocortical hyperactivity, allergies, anemia, alopecia, arthritis, autism, cystic fibrosis, diabetes, hemorrhaging, and kidney disorders.	[20,21]
Nickel (Ni)	0.07	0.089–0.231	-	Coal burning, diesel and fuel oil burning, tobacco smoking, wind dust, volcanic activity, garbage burning, cheap jewelry, stainless steel appliances.	Dermatitis, pulmonary fibrosis, asthma, respiratory and cardiovascular diseases, immune system failure, carcinogenic, DNA damage.	[22,23]

2.3. Conventional Methods for Heavy Metal Detection

It is essential to frequently determine and measure the concentration of heavy metals in tap water to ensure human safety. The selected technique must be sensitive enough to detect low concentrations of these metals accurately [17]. Although meeting all these criteria is challenging, the development and combination of various techniques have enabled accurate detection of heavy metals [3].

Conventional methods for determining heavy metals involve sample treatment, analytical techniques, and heavy instrumentation. The most commonly used methods are as follows:

- Atomic Absorption Spectroscopy (AAS);
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS);
- Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES);
- Flame Atomic Emission Spectroscopy (FAES);
- X-Ray Fluorescence (XRF), primarily used for solid sample analysis such as soil and sediments.

Colorimetric methods are less common but are still used for detecting specific heavy metals.

ICP-MS and ICP-AES are the most widely used methods because of their high sensitivity and the ability of simultaneous determination of multiple heavy metals and isotopes. Table 2 summarizes a comparison of traditional heavy metal detection methods with their advantages and disadvantages [24,25].

Table 2. Advantages and disadvantages of traditional heavy metal detection methods.

Method	Advantages	Disadvantages
Atomic Absorption Spectroscopy (AAS)	High sensitivity and specificity, simple sample preparation, wide range of applications.	Requires individual measurements for each element, susceptible to interference from other elements.
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)	Simultaneous multi-element analysis, high sensitivity and precision, wide linear dynamic range.	Complex instrumentation, expensive, requires skilled operators.
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Extremely high sensitivity, excellent detection limits, isotopic analysis capability.	
Colorimetric Methods	Simple, inexpensive, and rapid.	Low sensitivity, susceptible to interference, limited dynamic range.

Electrochemical techniques are also used to measure heavy metals in solution by monitoring the change in electrochemical properties of redox reactions of metal ions. Electrochemical methods also offer the advantages of simultaneous determination, high sensitivity, and cost-effectiveness, while also being environmentally friendly.

2.4. Electrochemical Sensors

Electrochemical sensors have emerged as powerful tools for environmental analysis control. They offer several advantages over traditional methods, including on-site detection, rapid response, and low cost. Electrochemical sensors can detect various pollutants, including metals, pharmaceuticals, agrochemicals, and illicit drugs [26].

The development of electrochemical sensors for the detection of metal pollution in the environment has received considerable attention in recent years. Such sensors can be used to detect low levels of metal pollutants in complex environments. Electrochemical sensors are also miniaturized systems that allow the development of portable instruments capable of monitoring the contamination on site. Sensors for metal ions detection can use a wide range of recognition elements, including biomolecules and macromolecules such as antibodies, enzymes, DNA aptamers, DNazymes, and whole cells, as well as molecularly imprinted polymers (MIPs), macrocycles, and biopolymers. The use of recognition elements for capturing heavy metals have been considered as innovative tools in metal monitoring because of their stable interaction, low detection limit, and high selectivity [27,28]. The use of bio-sourced polymers in electrochemical sensors for metal detection is rapidly gaining traction in this field of research due to their potential properties. Biopolymers also offer the dual advantages of reliable detection and the potential for removal of metal pollutants.

2.5. Electrochemical Methods of Detection

Electrochemical techniques are cost effective, user friendly, and dependable. They can provide analytical results with lower detection limits compared to spectroscopic and optical methods. Electrochemical techniques, which are widely used in heavy metal detection, include potentiometry, amperometry, voltammetry, coulometry, impedance, and electrochemiluminescence. Voltammetry and potentiometry techniques are preferred due to their simplicity and capacity to track the redox signals of metal ions. Various techniques in voltammetry are employed to improve the sensitivity of detection and are widely used, such as linear sweep anodic stripping voltammetry (LSASV), square wave anodic stripping voltammetry (SWASV), and differential pulse anodic stripping voltammetry (DPASV). Chronoamperometry (CA) can be applied for real-time monitoring of the metal ions in real samples (Figure 1). However, detection with cyclic voltammetry (CV) and potentiometric electrochemical analysis methods suffer from low selectivity [29].

Electrochemical detection could be improved by modified electrodes where a selection of scaffold of metal ions improves their stability on the surface and then their sensitivity and selectivity of electrochemical signal detection.

Biopolymers and bio-sourced polymers modified electrodes present an interesting way to improve the attachment and stability of metal ions on the surface of the electrode, leading to an increased sensitivity and selectivity of detection. Another parameter in the development of sensor technology that has recently been considered is the use of renewable-source materials.

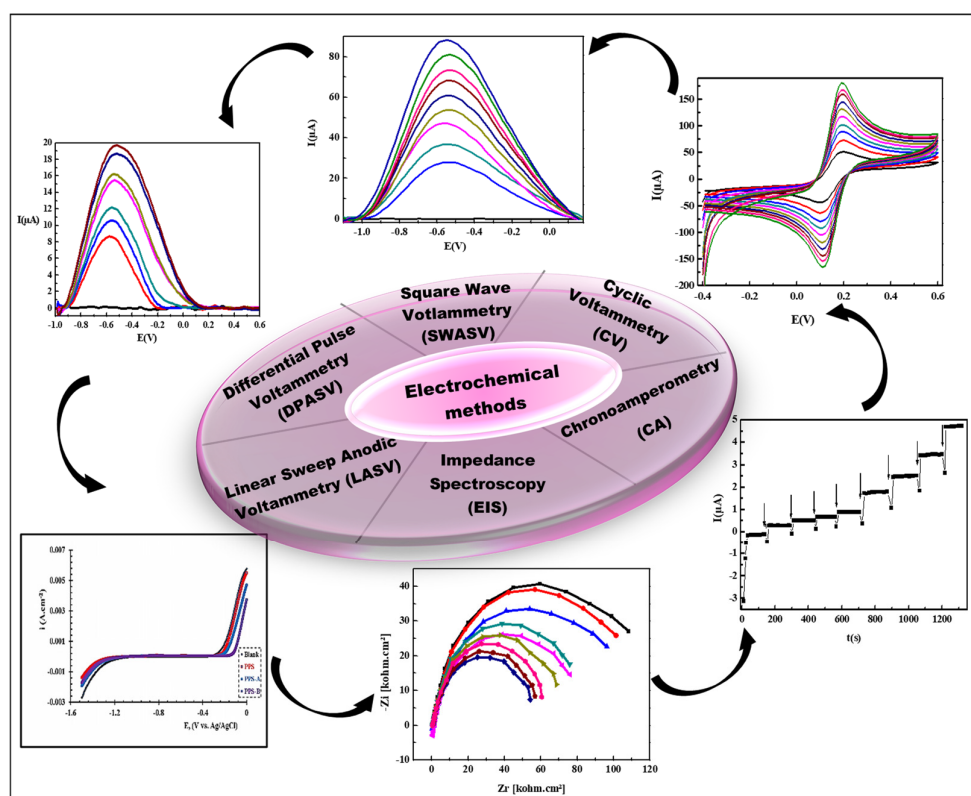


Figure 1. Presentation of the different electrochemical methods for heavy metal detection.

3. Polymers and Biopolymers as Sensing Layers

3.1. Definition and Characteristics

Polymers play a crucial role in the biological world as well as in today's industry. Some natural polymers, such as proteins and nucleic acids, possess and utilize their essential biological properties, while other polymers, such as polysaccharides, contribute to cellular functions and serve as structural components in living systems.

Biopolymers are a versatile category in their own right. The terms biodegradable polymers and biopolymers (or biologically based polymers) are sometimes used interchangeably in the literature, but there is a significant difference between the two types of polymers. Biodegradable polymers are materials whose chemical and physical properties deteriorate and completely degrade when exposed to microorganisms and aerobic and anaerobic processes. Bio-based polymers are a raw material-related term applied to polymers from renewable sources. Raw materials are defined as renewable if they are renewed by natural processes at a comparable rate or faster than they are consumed [30].

The definition of biopolymers is based on two different criteria: the source of the raw materials and the biodegradability of the polymer. They can be the following:

- Biopolymers produced from renewable (biological) and biodegradable raw materials.
- Biopolymers produced from sustainable (biological), non-biodegradable raw materials.
- Biodegradable biopolymers based on fossil fuels [30].

3.2. Synthetic Biopolymers

Synthetic biopolymers are polymers that have either been chemically synthesized from synthetic monomers or modified from natural polymers, enabling them to degrade naturally without leaving harmful residues in ecosystems. Due to their advantages over natural polymers in terms of stability and flexibility for a wide range of applications, synthetic biopolymers have garnered significant attention in recent years. These biopolymers are favored over conventional synthetic polymers due to their environmental safety and biodegradability. Figure 2 shows the structure of some synthetic biopolymers.

Advances in molecular design and polymer chemistry now allow the synthesis of synthetic biopolymers tailored to meet specific needs. Synthetic biopolymers are generally divided into two categories:

- Non-biodegradable synthetic biopolymers, which resist environmental degradation and contribute to waste (e.g., polyamide, polyvinylchloride, polypropylene)
- Biodegradable synthetic biopolymers, which break down when exposed to environmental factors, such as poly(glycolic acid), poly(lactic acid), polycaprolactone, and polyhydroxy butyrate [2].

These synthetic biopolymers can be synthesized using various techniques, including esterification, dehydration, polycondensation, hydrolysis, and granulation, to achieve specific structural and mechanical properties [31].

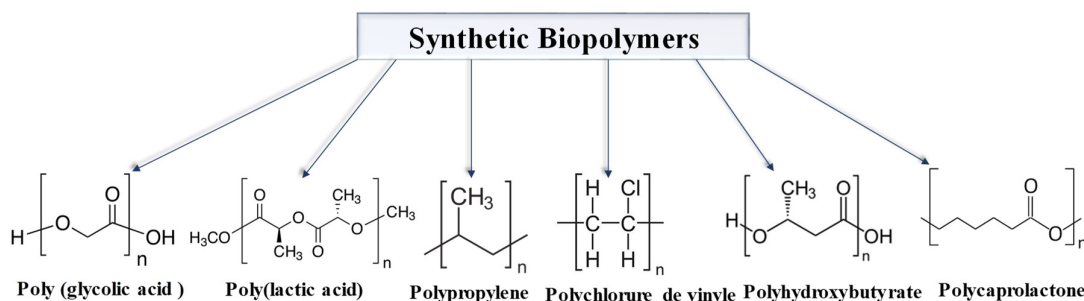


Figure 2. Examples of some structural units of synthetic biopolymers.

3.3. Natural Biopolymers (Bio-Sourced Polymers)

Natural polymers are macromolecules produced or occurring naturally in living organisms. “Biopolymers” is a broad term that includes both biodegradable and bio-based polymers, regardless of whether they are natural or manufactured. Natural polymers are derived from bacteria, plants, or animals.

Natural polymers are formed by covalently bonding monomer units. The specific monomers and their arrangement determine the properties of the polymer. Biopolymers, unlike synthetic polymers with simpler, random structures, have well-defined three-dimensional structures, which is essential for their function [32].

Natural polymers are classified into three main categories based on their monomer units:

- Polynucleotides: polymers composed of nucleotide monomers (e.g., RNA, DNA);
- Polypeptides: polymers made of amino acids (e.g., proteins);
- Polysaccharides: polymers made of carbohydrates (e.g., cellulose, hemicellulose, pectin) [33].

Polysaccharides consist of monosaccharide units linked by glycosidic bonds, which can be either linear or branched. Similarly, polynucleotides are made of nucleotide units linked by phosphodiester bonds, and polypeptides are chains of amino acids linked by peptide bonds (see Figure 3) [33].

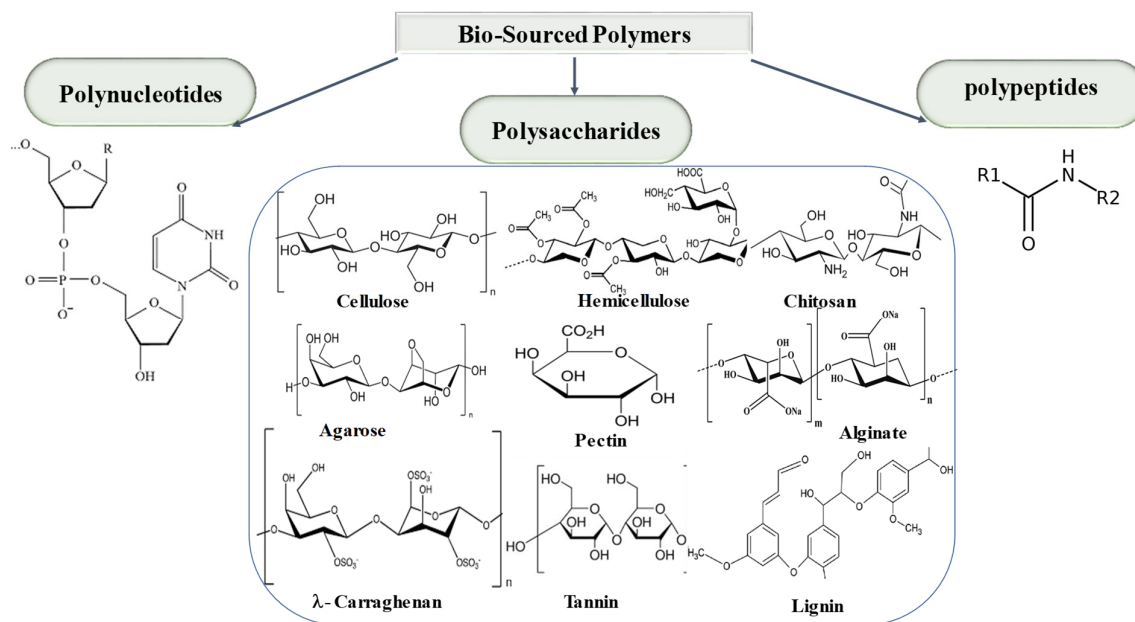


Figure 3. Structure of bio-sourced polymers formed with three family polynucleotides, polysaccharides and polypeptides.

3.4. Properties of Bio-Sourced Polymers

Bio-sourced polymers are environmentally friendly because they can be broken down into elemental units through natural processes using enzymes or microorganisms. The final products of this decomposition can re-enter the environment, leaving a minimal carbon footprint. Another advantage of bio-sourced polymers is their chemical and structural diversity, as they are sourced from various plants and living organisms.

Bio-sourced polymers such as chitosan, alginate, cellulose, pectin, gelatin, and acacia gum are widely used in the development of biosensors due to their inherent properties [34]. They are especially valued for these properties, such as the following:

- **Biocompatibility:** ability to interact harmoniously with biological systems.
- **High adsorption capacity:** enhanced ability to absorb or adsorb molecules.
- **Hydrophilicity:** affinity for water, which can improve performance in sensing applications.
- **Relative thermostability:** ability to withstand moderate thermal variations [35].

These properties make the biopolymers an ideal matrix for sensor applications, particularly in the development of selective and sensitive detection of heavy metals. Additionally, biopolymers possess functional groups such as hydroxyl, amine, and carboxyl groups that allow them to bind chemically and physically to various molecules [36,37].

4. Application of Biopolymers for the Removal of Heavy Metals from Water

Several technologies have been explored for the removal of heavy metals from water, for instance, ion exchange [38], coagulation–flocculation [39], precipitation, and membrane filtration [40], using biomaterials. Although these techniques reduce the concentration of residual metal ions in treated wastewater, their high operating costs, material costs, and limited absorption efficiency have restricted their large-scale application. Research

shows that using low-cost adsorbents for heavy metal removal is both effective and economically viable. Various carbohydrate-based biopolymers have been extensively used for the removal of heavy metals from water [7]. Over the years, various natural polysaccharides, such as cellulose, hemicellulose, and chitosan [41–43], along with phenolic compounds (lignin) [44,45], chelators, activated carbon, and clay, have been used as adsorbents for removing heavy metals [46]. These biopolymers contain numerous functional groups that interact with metal ions by chelating metal ions and forming complexes improving the removal of heavy metals from water. To achieve high removal efficiency, adsorption relies on the attraction of the heavy metal ions present in wastewater by an adsorbent with a porous structure and a large surface area. The active functional groups found in natural biopolymers (such as aromatic, phenolic, alcoholic, carbonyl, methoxy, carboxyl, and amino groups) serve as adsorption sites for heavy metal ions [47,48]. Due to their abundance and accessibility, bio-sourced polymers are also cost-effective, making them a practical choice for long-term adsorption system design and maintenance, and can now be applied in some processes of decontamination.

Table 3 summarizes the most recent studies on adsorption efficiency, highlighting the use of natural and synthetic biopolymers and their composites with organic and inorganic materials for metal removal. Special attention is given to polysaccharide-based biopolymers, such as lignocellulose, cellulose, hemicellulose, chitosan, and alginate.

Table 3. Summary of the polymers and biopolymers developed for metal ion removal with the value of the maximum adsorption capacity.

Biopolymers Used for Removal	Metal Ions	Adsorption Capacity (mg g ⁻¹)	Ref.
Nano-sized TiO ₂ /carboxymethyl chitosan hemicellulose composites	Ni(II)	370.4	[49]
	Cd(II)	555.6	
	Cu(II)	526.3	
	Hg(II)	18.6	
	Mn(VII)	29.9	
	Cr(VI)	32.1	
Phosphorylated cellulose microsphere	Pb(II)	139.38	[50]
Porous carboxymethyl chitosan (PCMC)	Co(II)	46.25	[51]
Cellulose/N-isopropylacrylamide-glycidyl methacrylate Cell-g-NIPAM-co-GMA	Ni(II)	74.68	[52]
	Cu(II)	82.92	
	Pd(II)	119.76	
Carboxymethylated cellulose fiber (CMF)	Cu(II)	23.48	[53]
Glucan/chitosan (GL/CS) hydrogels	Cu(II)	342	[54]
	Co(II)	232	
	Ni(II)	184	
	Pb(II)	395	
	Cd(II)	269	
Chitosan/calcium alginate/bentonite composite hydrogel	Pb(II)	434.89	[55]
	Cu(II)	115.30	
	Cd(II)	102.38	
Carboxylated chitosan/carboxylated nanocellulose hydrogel beads	Pb(II)	334.9	[56]
Cellulose nanofiber and sodium alginate	Pb(II)	318.47	[57]
Picea smithiana sawdust	Pb(II)	6.35	[58]
	Cr(VI)	3.37	
	Cd(II)	2.87	
Sodium alginate@ polyethyleneimine-carbon dots	Pb(II)	380.39	[59]
Hemicellulose-based hydrogel	Pb(II)	5.88	[60]

Microwave-functionalized cellulose	Pb(II)	5.43	[61]
	Cd(II)	3.14	
	Ni(II)	2.77	
Thiol-functionalized cellulose nanofiber	Cu(II)	49.0	[62]
	Cd(II)	45.9	
	Pb(II)	22.0	
Lignin-based hybrid magnetic nanoparticles	Pb(II)	150.33	[63]
	Cu(II)	70.69	
Three-dimensional porous graphene/lignin/sodium alginate nanocomposite (denoted as 3D PG/L/SA)	Cd(II)	79.88	[64]
	Pb(II)	226.24	
Chitosan/nanoclay composite	Cu(II)	176	[65]
	Ni(II)	144	
Chitosan/Two-Dimensional Metal-Organic Frameworks (Ni ₃ (HITP) ₂) and MXene (Ni ₃ (HITP) ₂ /MXene/CS)	Pb(II)	448.93	[66]
Chitosan/4-hydroxy-3-methoxybenzaldehyde (VAN)-Epichlorohydrin (Fe ₃ O ₄ @CTS-VAN)	Cr(VI)	188.68	[67]
Xylan hemicellulose modified with sulfonic acid 30% content HA3	Pb(II)	193	[68]
	Cd(II)	182	
	Cu(II)	66	
Xylan hemicellulose modified with sulfonate 50% content of Xylan	Pb(II)	273	
	Cd(II)	143	
	Cu(II)	45	

5. Applications of Bio-Sourced Polymers in Electrochemical Sensing of Heavy Metals

Lignocellulosic biomass has emerged as a promising tool for heavy metal detection. This efficiency can be partly attributed to the composition of the biomass, particularly the ratio of its key components: cellulose, hemicellulose, and lignin. Each component plays a critical role in the adsorption process, with functional groups providing binding sites for metal ions. Considerable research has explored the potential of lignocellulosic biomass in developing electrochemical sensors based on modified electrodes incorporating biopolymers and bio-sourced polymers derived from this biomass [69].

This section discusses several relevant electrochemical sensors for heavy metal detection based on polysaccharide derivatives (e.g., cellulose, sodium alginate, chitosan, chitin, and pectin) and polyphenols. We also explore their association with other organic and inorganic nanomaterials.

Polysaccharides are long chains of monosaccharides linked by glycosidic bonds, and their specific sugar types and linkages define their properties, such as solubility and rigidity. Additionally, the linear or branched structure of a polysaccharide influences these characteristics. Among these polymers, cellulose and its composites stand out due to their stability, conductivity, and affinity for heavy metals, making them particularly valuable for designing electrochemical sensors for heavy metal detection [70].

5.1. Cellulose and Cellulose Composite-Based Sensors

Cellulose, one of the most common polysaccharides in plants, is widely used in biosensors. It is an oxygen-rich polysaccharide with glucose units linked by oxygen bonds [71]. Plants produce cellulose in a fibrous form, which strengthens cell walls. Cellulose has a fibril structure with high resistance, allowing it to form durable polysaccharide-based walls. Its carbon structure enables cellulose to be both crystalline and amorphous.

Cellulose can be modified to produce conductive forms, such as carboxymethylcellulose (CMC), cellulose nanocrystals (CNC), and cellulose nanofibers (CNF); all possess

high adsorption capacities and porous surfaces [72]. Hydroxyethyl cellulose, while not directly used for heavy metal uptake, is employed as a supporting matrix or immobilization platform in sensor systems.

Several studies have reported using cellulose and its derivatives to construct heavy metal electrochemical sensors. For example, sodium carboxymethylcellulose has been used to modify GCE to detect cadmium ions using DPASV. Under optimal conditions, the proposed CMC/GCE sensor showed a strong linear response to cadmium ions and achieved a detection limit of 0.75 nM [73].

Bacterial cellulose has also been employed in heavy metal sensing due to its highly porous network and large surface. A notable example is an electrochemical sensor developed by Qin et al. to detect cadmium Cd(II) and lead Pb(II) in drinking water. This sensor used a GCE modified by a composite combining carbonated bacterial cellulose (CBC) with gamma-alumina (γ -AlOOH) and used DPASV for detection. The unique structure of this composite provided a highly porous network and strong affinity for heavy metals, resulting in detection limits of 0.17 μ g/L (1.5 nM) for Cd(II) and 0.1 μ g/L for Pb(II) (0.48 nM). The authors compared these results to those obtained through the more established method of ICP-MS, demonstrating the sensor's reliability and accuracy [74].

Cellulose nanofibers have also emerged as a highly sensitive material for detecting heavy metals due to their ability to adsorb large amounts of metal ions. Zinoubi et al. reported the development of a GCE modified with nanocellulose fibers derived from eucalyptus for detecting traces of Cd(II), Cu(II), Pb(II), and Hg(II) using DPASV. This modified electrode CNF/GCE demonstrated high sensitivity, stability, and low detection limits of 5 nM for Cd(II) and Hg(II) and 0.5 nM for Cu(II) and Pb(II) [75].

Combining cellulose derivatives as scaffolds with other components, such as biomolecules or nanomaterials, leads to improved heavy metal sensing properties. Many developed sensors include various cellulose derivatives with carbon nanomaterials or metal oxide. For example, nanocellulose has been combined with biomolecules to enhance sensors sensitivity. Taheri et al. demonstrated that a nanocellulose composite modified with d-penicillamine (DPA-NC) significantly improves the detection of Cu(II) in tap and river water (Figure 4). A pencil-shaped graphite electrode modified with DPA-NC exhibited amperometric detection of Cu(II) measured by SWASV, with a sensitivity of 0.2 μ A/ μ mol and a detection limit of 0.048 pM [76]. This result demonstrated the ability of sensors based on biopolymers to detect the presence of metal ions in real samples.

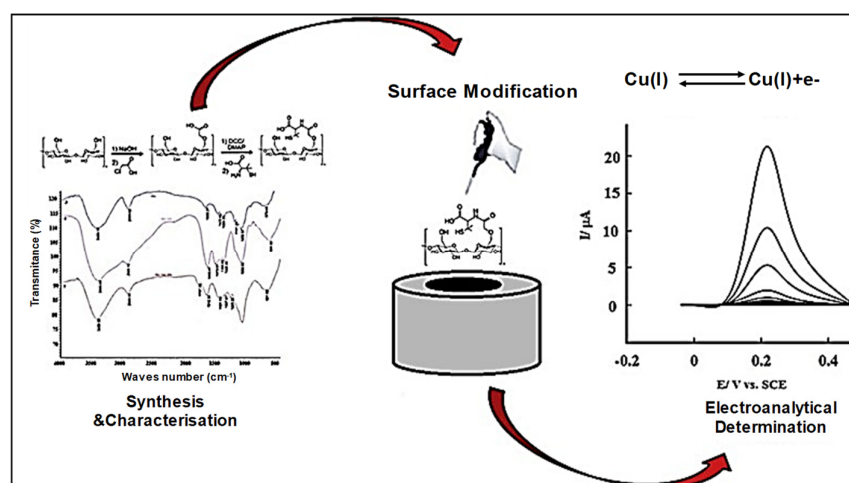


Figure 4. Nanocellulose functionalized with d-penicillamine used as electrochemical transducers for copper detection, the scheme shows the composition of the nanocomposite and them the deposition on surface electrode by drop casting followed by detection of copper using SWASV for electroanalytical determination (reproduced with permission from Taheri et al., *J. Phys. Chem. Solids*, publisher Elsevier2018, ref. [76]).

In the same way, the association of carboxymethylcellulose (CMC) with carbon nanomaterials has been explored for the detection of cadmium and lead. A study by Prya et al. has demonstrated the simultaneous detection of trace levels of Cd(II) and Pb(II) using a nanocomposite made with porous graphene, CMC, and fondaparinux, a penta-saccharide, to form a composite (PrGO/CMC/Fonda). After deposition on GCE, this nanocomposite allows the detection of various heavy metals using SWASV with a high sensitivity and detection limits of 0.28 nM for Cd(II) and 0.17 nM for Pb(II). The composite's components worked synergistically to improve electron transfer and immobilization of metal ions [77].

Cellulose nanocrystals, known as nano-whiskers (CNWs), are rod-like nanoparticles derived from cellulose fibers through various mechanical and chemical treatments. CNWs are often used in combination with other nanomaterials for enhanced functionality. They can be obtained from cellulose via conventional acid hydrolysis of white cotton fibers. Teodoro et al. combined cellulose nanocrystals with reduced graphene oxide (rGO) and polyamide 6 through an electrospinning synthesis approach, creating a hybrid composite designed for electrochemical mercury detection. This composite exhibited improved charge transfer properties, as evaluated by cyclic voltammetry, due to the excellent electrical properties of graphene. The nanocomposite allows the electrochemical detection of mercury in water samples, achieving a limit of detection of 0.52 μM and a wide dynamic linear range of 2.5–200 μM [78].

Additionally, metal oxide nanomaterials are also associated with cellulose to improve the conductivity of the nanocomposite. Padmalaya et al. developed a cellulose-based composite using cellulose acetate, in combination with zinc oxide. This nanocomposite served as an electrochemical sensor for cadmium quantification. Square wave voltammetry was employed to assess cadmium presence, with a LOD of 0.41 μM within a linear concentration range of 0.1–0.5 mM. The conductive nature of zinc oxide, its stability, and the hydroxyl groups in the cellulose acetate's structure endowed the nanocomposite with electrical and chemical properties well-suited for lead detection [79].

Cellulose can also serve as an electrode and supporting matrix for the immobilization of chelating agents of metal ions. For example, hierarchical porous metal organic framework zeolitic imidazolate framework (ZIF-8s) was integrated into cellulose paper for removal and detection of metal ions (Figure 5). The modified cellulose was used in working electrodes for the selective electrochemical detection of lead ions (Pb(II)) with an LOD of 8 μM [80].

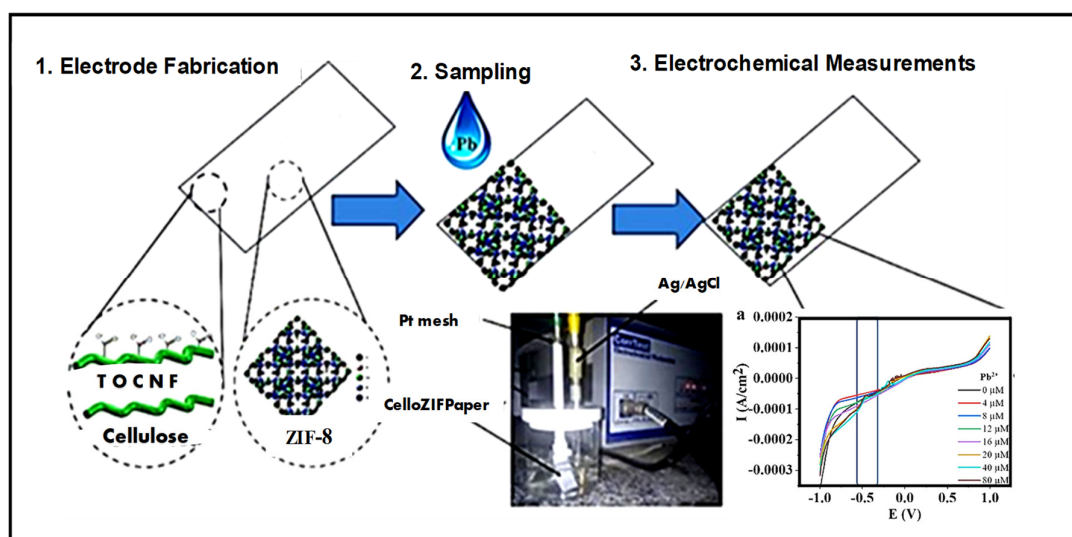


Figure 5. Schematic representation of electrode fabrication, sampling from cellulose, and electrochemical measurements of CelloZIFPaper for detection of lead ions. The inset camera image shows the setup of the cell electrodes and potentiostat. Reproduced with permission from Abdelhamid et al., Chem. Eng. J.; publisher by Elsevier 2022 ref. [80].

Table 4 summarizes the sensors developed based on other cellulose derivatives and composites with other materials and highlights the methods of detection used as well as the limit of detection and linear range.

Table 4. Different polymeric materials as the modifying layers of the sensors for heavy metals determination.

Electrode	Method	Analyte	LOD	Linear Range	Applications	Ref
Au/Agarose-Hemicellulose	SWASV	Pb(II)	1.3 fM	1 μ M–1 fM	Tap, spring, and sea water	[27]
GCE/Cellulose nanofiber	DPASV	Cd(II)	5 nM	0.1 nM–10 μ M	Sea water	[75]
		Cu(II)	0.5 nM			
		Pb(II)	0.5 nM			
		Hg(II)	5 nM			
Penicillamine functionalized nano-cellulose modified pencil graphite electrode	SWASV	Cu(II)	0.048 pM	0.2–50 pM	Tap and river water	[76]
PA6/Cellulose nanowhiskers /rGO	DPASV	Hg(II)	0.52 μ M	2.5–75 μ M	River and tap water	[78]
AuNPs/Cellulose nano-fiber/GCE	SWASV	Cd(II)	0.1 μ M	0.1–1.0 μ M	-	[81]
		Pb(II)				
		Cu(II)				
γ -AlOOH-carbonated bacterial cellulose	DPASV	Cd(II)	1.5 nM	4.4–2200 nM	Drinking water	[74]
		Pb(II)	0.5 nM	2–1200 nM		
Carbon nanodots Dot (CNDS)	DPASV	Hg(II)	124 nM	-	Drinking water	[82]
		Pb(II)	551 nM			
Hydroxyethylcellulose-CA	EIS	Pb(II)	1.8 nM	-	Leachates from detonation chamber dust (DCD) and galvanic sludge from the plating industry (GS)	[83]

Au: gold; PA6: Polyamide 6; rGO: reduced graphene oxide; AuNPs: gold nanoparticles; CPE: screen-printed electrode; CA: citric acid.

5.2. Alginate-Based Sensors

Sodium alginate (SA) is a linear polyanionic polysaccharide derived from brown algae, consisting of α -L-guluronic acid (G) and β -D-mannuronic acid (M) residues linked by glycosidic bonds [7,8]. Due to its abundance, antibacterial properties, and high ionic absorption capacity, sodium alginate has wide applications in environmental remediation, particularly in water treatment [84]. Its biocompatibility and ability to bind metal ions make it suitable for electrochemical sensors for heavy metal detection.

Sodium alginate's mechanical properties can be improved by forming composites with other materials. For example, combining alginate with chitosan, another biopolymer, can result in stable hydrogels easily deposited on sensor surfaces. The richness of these biopolymers' functional groups such as carboxyl (-COOH) and nitrogen-containing groups allows selective heavy metal detection. This is demonstrated in the work of Chen et al. where a nanocomposite of sodium alginate and chitosan was applied to a glassy carbon electrode (GCE) for the detection of copper ions (Cu(II)) using DPASV. The sensor achieved a linear detection range between 1 and 100 μ M, with a detection limit of 0.9545 μ M [85].

To further enhance performance and electron transfer ability, sodium alginate can be combined with carbon-based materials such as single-walled carbon nanotubes (SWCNTs). This approach leverages SWCNTs' large surface area and high conductivity, leading to improved adsorption and faster sensor response times. Thus, Chrouda et al. demonstrated a biopolymer sensor based on sodium alginate decorated with SWCNTs for the detection of Pb(II), Cd(II), and Cu(II) using DPASV. The sensor achieved detection limits of 0.1 nM for Pb(II), 31 nM for Cd(II), and 1 nM for Cu(II) [86].

5.3. Chitosan-Based Sensors

Chitosan is a linear biopolymer composed of randomly arranged D-glucosamine and N-acetyl-D-glucosamine units linked by $\beta(1-4)$ glycosidic bonds. Its structure contains amine ($-NH_2$) groups at the C2 carbon, and numerous hydroxyl ($-OH$) groups, which impart strong hydrophilic properties to the molecule. Chitosan is derived by deacetylating chitin in an alkaline medium [87], leading to amino groups. The chitosan is particularly valuable due to the free amine groups that are active sites for chemical reactions as well as metal chelation. Primary amino groups ($-NH_2$) have been extensively exploited for heavy metal ion detection due to the favorable acid–base interaction between these electron-rich amino ligands and electron-deficient heavy metal ions. Thus, chitosan is widely used across various industries, including wastewater treatment and environmental monitoring [88].

Chitosan membranes or films form effective matrices for sensing heavy metals due to their strong mechanical strength, hydrophilic properties, and ability to bind metals through chelation. Various studies have demonstrated the effectiveness of chitosan as a sensing material for detecting heavy metals.

For example, a flat carbon electrode coated with chitosan has been used to detect zinc (Zn(II)) and lead (Pb(II)) without any prior extraction or treatment. Using SWASV, two distinct peaks were obtained at various potentials corresponding to Zn(II) and Pb(II), with detection limits of 0.6 and 1 ppb, respectively [89].

Another study by Hadnine et al. developed an electrochemical sensor based on a carbon paste electrode modified with chitosan-based chelating thiourea and glutaraldehyde. This composite is used to detect mercury ions and showed sensitivity to Hg(II) ions in the range of 5 nM to 1 μ M, with a detection limit of 1.61 nM [90]. The synergistic effect of thiourea's sulfur atoms and chitosan's nitrogen and hydroxyl groups contributed to the sensor's sensitivity.

Chitosan has also been employed as a matrix for immobilizing other molecules. Fort et al. developed a modified electrode using doubly doped mesoporous carbon xerogel confined within a chitosan hydrogel, deposited on a GCE. This electrode was investigated to detect trace amounts of Pb(II) and Cd(II) using SWASV. The sensor exhibited a detection limit of 0.07 ppb (0.07 nM) for Pb(II) and 5.06 ppm (5 μ M) for Cd(II) [91].

Chitosan's ability to form composites with metal nanomaterials has enhanced the sensitivity of heavy metal sensors. For instance, Pathak et al. developed a flexible electrochemical sensor based on a copper–chitosan nanocomposite. The sensor, fabricated through a low-cost screen-printing technique, was used to detect Pb(II) ions in water samples. The sensor exhibited a detection limit of 0.72 ppb (0.72 nM) in tap water [92]. This work demonstrates the potential of the chitosan to be printed and gives electrodes with high detection efficiency. However, the stability of these devices over time and in challenging conditions still needs further development.

Chitosan can also be combined with magnetic materials, such as Fe₃O₄ nanoparticles, to improve detection performance. Zhou et al. synthesized Fe₃O₄-chitosan nanoparticles through a one-step in situ co-precipitation method. These nanoparticles were used as a sensor for Pb(II) ions using SWASV, achieving a detection limit of 0.04 μ M [93].

Chitosan and metal oxides are widely employed in fabricating electrochemical sensors for heavy metal detection. The oxygen atoms in metal oxides can donate electron pairs, forming covalent bonds with transition metals, and their porous structure further

increases the available surface area, enhancing metal ion interaction. For example, Shang et al. presented a novel strategy that utilizes nickel oxide, molybdenum oxide, and chitosan to construct a 3D Ni/NiO/MoO₃/chitosan interface, acting as a sensing element for Cu(II). The electrochemical response arises from a reduction in barrier height at the interface due to Cu(II) uptake, with a linear detection range of 0–25 µM and a low detection limit of 5.69 nM. Chitosan (CS) demonstrates excellent Cu(II) adsorption capacity due to its abundance of reactive hydroxyl and carboxyl groups. Additionally, the wide band gaps of NiO and MoO₃ allow for a tunable electronic range, while the nanostructured oxides provide active surface sites for metal ion binding [94].

Chitosan can also be combined with carbon nanomaterials, such as carbon nanotubes or graphene, as a sensing layer for heavy metal detection. These carbon nanomaterials offer several advantages: increased surface area, enhanced electrical conductivity, and the ability to be functionalized with chemical groups that selectively attract certain heavy metals. For instance, a composite of chitosan, reduced graphene oxide (rGO), and poly-L-lysine (PLL) was developed through electropolymerization, achieving detection limits for Cd(II), Pb(II), and Cu(II) at 0.01, 0.02, and 0.02 µg/L (0.09, 0.1, 0.3 nM), respectively [95].

Ion-imprinting techniques have gained attention in the selective detection of metal ions. Wei et al. developed an electrochemical sensor based on a chitosan–graphene oxide composite with a polymer-modified GCE (CS/GO-IIP) for Cu(II) detection via an immersion coating method. Cu(II) ions were imprinted by chemical crosslinking with epichlorohydrin after the CS/GO/Cu(II) composite was applied to the glassy carbon electrode. A linear response was observed from 0.5 to 100 µM, with a detection limit of 0.15 µM [96].

In similar work, Yin et al. developed an electrochemical sensor composed from a covalent organic framework (COF), calcium lignosulfonate (CLS)-multiwalled carbon nanotubes (MWCNTs), and nafion for the simultaneous analysis of Cu(II), Pb(II), and Cd(II). The nanocomposite porous and 3D structure with the abundance of amino groups allows the efficient accumulation of heavy metal ions. The MWCNTs enhanced the sensor's conductivity, while the CLS's hydrophilic groups prevented MWCNT aggregation. Under optimal conditions, this sensor demonstrated broad linear responses for Cu(II), Pb(II), and Cd(II) within the ranges of 0.6–63.5, 2.1–207.2, and 1.1–112.4 µg/L, respectively, and low detection limits of 0.2, 0.7, and 0.4 µg/L (3 nM, 3.3 nM, 3.5 nM) [97].

Researchers also combine chitosan with conductive polymers to form composite materials with enhanced sensitivity, selectivity, and charge transfer capabilities, improving sensor performance and design robustness. Since chitosan is a non-conductive material, it has been paired with various conductive polymers to improve its electron transfer ability. Xu et al. reported a chitosan–polypyrrole hybrid polymer used in constructing sensors for Pb(II) detection in wastewater, effectively measuring Pb(II) concentrations via electrochemical methods [98].

Chitin, like chitosan, is a long-chain, biodegradable biopolymer that can be sourced from crustaceans. The NHCO group in each glucose ring of chitin facilitates metal ion trapping via complexation. Singh et al. demonstrated a chitin-based sensor with a chemically interactive polyaniline electrode grafted with chitin (Cs-g-PANI) for copper ion detection. The electrode's potentiometric response to Cu(II) ions followed the Nernst relationship within a range of 1 to 103 ppm (103 µM), with a detection limit of 13.7 ppm (13.7 µM) and minimal interference from other cations and anions [99].

The literature data regarding chitosan-based sensors for heavy metals detection are extensive. Table 5 summarizes some relevant papers regarding the detection of heavy metals where detection is performed in real samples for water environment control.

Table 5. The summary of the relevant sensors based on chitosan for heavy metal determination.

Electrode	Method	Metal	LOD	Linear Range	Application	Ref.
Thymine-Hg ²⁺ -Thymine/AuNPs/Chitosane (Aptamer/(AuNPs/CS) ₂ /GCE)	DPASV	Hg(II)	0.005 nM	0.01–500 nM	Tap water	[100]
GC/Chitosane-(Bi-CX)	SWASV	Pb(II)	0.07 nM	0.2–2 nM	Drilled well water	[91]
		Cd(II)	5.06 µM	11.2–124 µM		
AuNPs/CS-Aptamer/GCE	DPASV	Cd(II)	0.05 pM	0.001–100 nM	Tap water	[101]
Amino-functionalized graphene/chitosan (NH ₂ -G/CS)	DPASV	Cu(II)	0.064 µM ⁻¹	0.4–40 µM	Tap water	[102]
CS/AuNPs/GR/GCE	DPASV	Cd(II)	16.2 nM	0.1–0.9 µM	River water, tap water, and pure milk	[103]
Biochar-nanodiamond-chitosan electrode ND-BC-CS	SWASV	Cd(II)	0.11 µM	1.0–75 µM	-	[104]
		Pb(II)	0.056 µM	0.25–6 µM		
Chitosan-graphene oxide composites (CS/GO-IIP)	DPASV	Cu(II)	0.15 µM	0.5–100 µM	Tap and river water	[96]
rGO/MoS ₂ /CS (GCE)	SWASV	Pb(II)	1.6 nM	0.005–2.0 µM	Tobacco leaves	[105]
NiO-CS/CPE	EIS	Pb(II)	0.3 µM	1 µM–0.1 mM	Waste water	[106]

5.4. Polyphenols as Sensing Platforms

Polyphenols, also known as phenolic compounds, are characterized by at least one aromatic ring in their structure, which bears a variable number of hydroxyl (OH) groups with high affinity for metal ions. Polyphenols can be monomers, polymers, or complexes, with molecular weight up to 9000 Daltons. Due to their unique properties, polyphenols hold promise for heavy metal detection applications.

One example is the use of tannins, a type of polyphenol, for developing composite materials. Bouraoui et al. modified a gold electrode with tannin extracted from pomegranate peel (*Punica granatum* L.) to detect heavy metals in water. The adjacent hydroxyl groups in the tannin's aromatic ring allowed for chelation of metal ions. Using square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS), the modified electrode demonstrated detection limits of 6 ng/L (0.094 nM) for Cu(II), 35 ng/L (0.31 nM) for Cd(II), and 11 ng/L (0.05 nM) for Pb(II) [107].

Polyphenols from various plants have been explored for metal ion detection. Zazoua et al. studied sensors based on a boron-doped diamond electrode modified with a polyphenol-polyvinyl chloride membrane using polyphenols extracted from acorn shells. The modified electrode demonstrated sensitivity to Cd(II), Pb(II), and Ni(II), with detection limits of 0.0221 nM, 0.25 nM, and 0.00424 nM, respectively [108].

The combination of polyphenols with nanomaterials can further improve sensing performance. Suherman et al. reported an electrochemical sensor based on a screen-printed electrode modified with gold nanoparticles capped with tannic acid (AuNP@TA). This sensor demonstrated an exceptionally low detection limit of 100.0 fM for Hg(II), far below the World Health Organization (WHO) allowable limit for mercury in drinking water [109]. Integrating phenolic compounds with carbon-based materials exemplifies an innovative approach to enhancing the performance of electrochemical sensors, especially for applications in heavy metal detection. The unique properties imparted by these composites—such as increased conductivity, stability, sensitivity, and specific ion detection sites—make them particularly valuable for environmental monitoring, where rapid and accurate heavy metal detection is critical.

For example, the work by Gonçalves et al. underscores the effectiveness of lignin-polyurethane copolymer composites in achieving high selectivity and stability in Cu(II) ion detection. The MWCNTs enhance conductivity and introduce a robust framework that

retains essential mechanical and viscoelastic properties, demonstrating the feasibility of creating durable sensors for field applications. The presence of polyphenolic groups in lignin, attributed to tannins, adds another layer of functionality by improving specificity towards target metal ions. This multi-functional approach could pave the way for designing materials that respond selectively to specific pollutants while maintaining structural integrity over extended periods, an essential factor for practical use in real-world environmental monitoring [110].

Similarly, Mahfoud et al. demonstrated the role of lignin derived from olive pits combined with polyvinyl chloride for Pb(II) detection. The low detection limit achieved (5 nM) through electrochemical impedance spectroscopy (EIS) highlights the potential of lignin as a sustainable and efficient material for heavy metal ion sensing. The underlying mechanism of lignin interaction with heavy metals chelation, ion exchange, adsorption, and surface modification suggest that lignin and similar biopolymers could serve as versatile agents in various environmental sensing applications. This versatility is crucial for developing cost-effective, biodegradable materials for heavy metal removal and sensing, aligning with the growing demand for sustainable environmental technologies [111].

Moreover, the research by Xin Bao et al. emphasizes the use of naturally occurring polyphenols from tea in fabricating composites with zero-valent iron (ZVI) and reduced graphene oxide (rGO) (rGO-ZVI), which showed remarkable sensitivity toward Hg(II) detection. Applying green chemistry methods, for synthesis by using tea polyphenols as reducing agents, aligns with a sustainable approach for sensor development by reducing the environmentally damaging chemicals while enhancing material performance. The synergy between zero-valent iron (ZVI) and reduced graphene oxide (rGO) offers an efficient ion accumulation and electron transfer platform, with a detection limit of 1.2 nM, making it highly effective for mercury detection in aqueous environments. This approach suggests a pathway for developing sensors with rapid response times and high accuracy for a range of heavy metals, leveraging natural compounds as mediating agent to improve detection performance [112].

5.5. Other Biopolymers in Heavy Metal Detection

Starch, a widely consumed carbohydrate and a staple of the human diet consists of two distinct polysaccharides: amylose and amylopectin. Amylose is a linear polysaccharide with D-glucose units linked by (1–4) glycosidic bonds, while amylopectin is highly branched with similar D-glucose backbones but features about 5% (1–6) linkages. These structural features of starch have significant implications for various properties, including its potential in sensor applications [113].

Pectin, a polysaccharide rich in carboxyl groups, can be associated with other nanomaterials for sensing heavy metals. In a study by Murilo Alves et al. (2021), a citrus pectin-modified carbon paste electrode (PEC/CPE) was used for the sensitive electrochemical detection of copper in biofuels. The carboxylic acid groups in the pectin increased the current response by 32% compared to the unmodified electrode. Using differential pulse anodic stripping voltammetry, the analytical curve for copper detection showed a linear range from 50 nM to 0.01 M, with a detection limit of 25 nM and a quantification limit of 83 nM [114].

To address the low conductivity of biopolymers, they can be copolymerized with conductive polymers to create composites with novel and beneficial properties. Polypyrrole, a conducting polymer, is particularly suitable for such applications because of its stability, conductivity, and amine functionalities. Combining polypyrrole with pectin has been shown to enhance detection performance significantly. For example, Arulraj et al. fabricated an electrochemical sensor using a composite of pectin, polypyrrole, and graphene (PPy/Pct/GR) for the detection of mercury (Hg(II)). The sensor demonstrated excellent performance, with a detection limit as low as 4 fM [115].

Another promising biopolymer for metal sensing applications is walnut shell biochar (WS-BC), which is both environmentally friendly and readily available. El Hamdouni et

al. incorporated biochar derived from walnut shells into a carbon paste electrode (CPE) and electrochemically deposited polytyrosine on the surface of the biochar-doped electrode. This modified platform was tested for the detection of Cd(II), Pb(II), Cu(II), and Hg(II) ions in water and soil samples using square wave voltammetry (SWASV), achieving excellent sensitivity with detection limits of 0.086 nM, 0.175 nM, 0.246 nM, and 0.383 nM for Cd(II), Pb(II), Cu(II), and Hg(II), respectively [116].

Biopolymers extracted from red algae, such as agar and carrageenan, have also shown potential in heavy metal detection. De Oliveira Farias et al. applied a novel method to create thin films of these polysaccharides using layer-by-layer self-assembly. Alternating agar, carrageenan, and polyaniline (PANI) layers were coated onto tin-doped indium oxide (ITO) electrodes. Cyclic voltammetry revealed that these films enhanced electrochemical resistance in acidic media, allowing for the electrochemical detection of chromium (Cr(VI)) [117].

Table 6 summarizes various biopolymers derived from natural sources, combined with different polymeric materials, and their applications in heavy metal sensing. This table highlights the versatility of these biopolymers and their composites, demonstrating their wide-ranging potential for improving the sensitivity, selectivity, and efficiency of electrochemical sensors for heavy metal detection.

Table 6. The summary of the sensors based on polyphenols derivatives for heavy metal determination.

Electrode	Method	Analyte	LOD	Linear Range	Application	Ref.
Tea polyphenols mediated zero-valent iron/reduced graphene oxide nanocomposites (rGO-ZVI-P)	SWASV	Hg(II)	1.2 nM	-	River	[112]
Tannic acid capped gold nanoparticle (AuNPs@TA) complexes	SWASV	Hg(II)	100.0 fM	100 fM–100 nM	Tap	[109]
Crosslinked Sodium alginate (SA) and chitosan (CS)SA-CS/GCE	DPASV	Cu(II)	0.95 µM	1–100 µM	Tap/river	[85]
Sodium alginate-decorated single-walled carbon nanotube	DPASV	Pb(II)	0.1 nM	-	Tap	[86]
		Cd(II)	31 nM			
		Cu(II)	1 nM			
AuNPs-biopolymer-coated carbon SPE sensor	SWASV	Hg(II)	1.7 nM	10–100 nM	Landfill leachate.	[118]
Grafted <i>Tricholoma</i> mushroom polysaccharide–silver composite nanoparticles (TMPSPG-Ag NPs)	CA	Zn(II)	0.5 nM	1 nM	River	[119]
Cork–graphite electrodes	DPASV	Pb(II)	0.3 µM	1–25 µM	Tap Ground “produced water” (a brackish water)	[120]
Bi/AgNPs/Nafion-SPGE with Pectin of <i>Citrofortunella Microcarpa</i>	ASV	Pb(II)	267 nM	-	River	[121]
β-cyclodextrin (β-CD)-graphene hybrids (AuNPs-CD-GS)	DPASV	Cd(II)	0.21 µM	0.035–10 µM	River	[122]
		Pb(II)	0.05 µM	0.2–6 µM		
		Zn(II)	1.9 nM	2–150 nM		
Green nanoparticles based on gum Arabic	DPASV	Hg(II)	0.9 nM	1–100 nM	Lake	[123]
		Pb(II)	4.2 nM	5–300 nM		
		Cu(II)	9.6 nM	10–300 nM		

5.6. Discussion: Pros and Cons of Using Biopolymers in Heavy Metal Detection

These studies underscore sustainable, biopolymer-based materials' role in environmental heavy metal detection. The ability of these composites to detect trace levels of heavy metals in complex matrices, such as soil and water, is crucial for environmental health, as even low concentrations of heavy metals can accumulate and pose severe risks to ecosystems and human health. Using abundant natural resources, such as lignin from agricultural by-products or tea polyphenols, also addresses sustainability concerns, as these materials can be sourced without adverse environmental impact.

The advantages of biopolymers are related to their biodegradability and sustainability.

Biopolymers are typically derived from renewable resources; they are biodegradable and environmentally friendly, reducing the ecological footprint associated with sensor production and disposal. This is especially important for environmental applications, where sustainable monitoring solutions are preferable. In addition, the high metal binding affinity of biopolymers is an advantage compared to synthetic macrocycles, as they offer various functional groups (hydroxyl, amine, carboxyl groups) that can readily bind to metal ions through chelation or adsorption. This natural affinity for metal ions enhances their ability to detect heavy metals, even at trace levels, making them highly sensitive in low-concentration environmental settings.

One advantage of biopolymers is their low toxicity and green synthesis ability regarding conventional-based sensors, which can involve harmful synthetic chemicals. The cost-effectiveness is also an advantage of biopolymers, as many biopolymers are by-products of agricultural or industrial processes (e.g., lignin from paper production, chitosan from seafood waste, or pectin from agricultural waste), making them relatively low-cost materials. This cost-effectiveness is advantageous when producing large-scale sensors for widespread environmental monitoring. The surface functionalization flexibility and their easy modification or combination with other materials are also advantages of these biopolymers. Biopolymers can be combined with carbon nanomaterials or metal oxides to enhance conductivity, selectivity, and sensitivity. This versatility allows for the development of custom sensors that are tailored to detect specific heavy metals in complex environmental samples.

Printing compatibility is an advantage for their application as devices, as many biopolymers, such as lignin, chitosan, and cellulose, can be processed into printable inks, enabling sensor fabrication via low-cost techniques like screen printing, inkjet printing, or roll-to-roll printing. This printing compatibility leads to significant cost savings by enabling large-scale, efficient production processes. Furthermore, the flexibility of printed biopolymer-based sensors makes them ideal for developing lightweight, portable devices suitable for environmental applications.

However, while the biopolymers present numerous advantages, some limitations need to be addressed for broader applications and commercialization. The low electrical conductivity is a limitation, as many biopolymers, such as polysaccharides, are non-conductive or have limited conductivity, which can impede electron transfer and reduce sensor efficiency. Biopolymers often require integration with conductive materials such as carbon nanotubes or graphene, which can complicate the fabrication process and increase costs. In addition, the potential for degradation in complex conditions could be a limitation in their applications. While biopolymers are biodegradable, this can also be a limitation. In challenging environmental conditions (high temperatures, extreme pH, or prolonged exposure to water), biopolymers may degrade, which could limit their durability and lifespan as sensors. In addition, biopolymers can have a shorter shelf life than synthetic polymers, especially in environments prone to microbial growth or moisture. This short shelf life can lead to decreased long-term sensor stability, making it necessary to store or use biopolymer-based sensors under controlled conditions. The variable quality and consistency of bio-sourced biopolymers can be a limitation, as the properties of biopolymers can vary depending on their source and extraction methods, leading to incon-

sistent sensor performance. Standardizing biopolymer quality can be challenging, as natural variations might affect metal binding affinity, mechanical strength, and stability. In addition, the fabrication and functionalization processes to modify biopolymers or to improve their conductivity and selectivity require multiple fabrication processes, such as functionalization or integration with nanomaterials. These additional steps can increase the time, expertise, and resources needed to produce biopolymer-based sensors, which may limit scalability for widespread environmental deployment.

While biopolymers present a promising, eco-friendly alternative for electrochemical heavy metal detection in environmental applications, conductivity, durability, and production consistency must be addressed to leverage their benefits fully. The development of hybrid materials and improvements in biopolymer processing can help mitigate these limitations, making biopolymer-based sensors a viable option for sustainable and effective environmental monitoring.

6. Future Research Directions

While current developments in biopolymer-based electrochemical sensors are promising, there are several key areas where future research should focus to improve their performance and applicability further:

1. Exploring new methods for biopolymer production using biological methods such as enzymatic or bacterial production that can give reproducible biopolymers.
2. Enhancing biopolymer functionalization by exploring more efficient methods of functionalizing biopolymers to improve their metal ion binding capacities. This could include advanced chemical modification techniques and the development of new biopolymer–nanomaterial composites.
3. Sensor stability and durability: Long-term sensor stability remains a challenge, and future research should aim to enhance the durability of biopolymer-based sensors under different environmental conditions, ensuring consistent performance in real-world applications by developing cross-linking techniques or nanocomposite formulations. These modifications should enhance the mechanical and chemical stability of biopolymer sensors under prolonged exposure to challenging environments (pH fluctuations, temperature variations, salinity) and evaluate the degradation rates of biopolymer-based sensors, optimizing their durability while maintaining biodegradability.
4. Real-time sensing and multi-metal detection: Current sensors often target specific metals, but future research should aim to develop sensors capable of simultaneously detecting multiple heavy metals in real-time.
5. Exploring wireless sensor networks and portable detection systems can provide real-time data transmission for the remote monitoring of aquatic environments. This would provide a more comprehensive solution for environmental monitoring.
6. Developing new biopolymer sources: Exploring less common biopolymer sources could lead to materials with novel properties that enhance sensor performance, and future research could explore the following:
 - Investigating biopolymers from algae, fungi, or microorganisms may offer unique structural advantages or metal-binding capacities.
 - Using genetic engineering or synthetic biology to design biopolymers with optimized electrochemical properties and metal ion selectivity.
 - Assessing the environmental impact of harvesting new biopolymer sources to ensure they align with sustainability goals.
7. Scalability and commercialization: Although biopolymer-based sensors show great potential in laboratory settings, their scalability for mass production and commercialization remains challenging. Further research should focus on cost-effective manufacturing processes and material sourcing to facilitate the widespread adoption of these sensors.

8. Integrating biopolymer-based sensors with internet of things (IoT) and wireless technologies significantly enhances their capabilities for environmental monitoring. Connecting these sensors to IoT systems makes continuous, real-time monitoring of heavy metal concentrations in water and soil possible. Wireless modules enable remote data transmission to cloud platforms, facilitating a faster response to pollution events and informed decision-making. These sensors' lightweight and flexible nature allows their deployment in remote and inaccessible areas, while wireless connectivity ensures data transmission without direct physical access. This enables the creation of comprehensive contamination maps, supporting large-scale environmental assessment and remediation efforts. Additionally, integrating low-cost, printed biopolymer sensors with IoT systems reduces infrastructure costs and enables large-scale, dense sensor networks for improved spatial resolution in environmental data.
9. Biopolymer-based sensors are generally low-power, making them compatible with energy-efficient wireless protocols like LoRaWAN and NB-IoT. When combined with solar-powered or other renewable energy sources, these sensors form sustainable, self-sufficient monitoring systems that can be well-suited for long-term environmental monitoring. This also helps reduce the ecological impact of continuous heavy metal monitoring operations.

7. Conclusions

In recent years, significant advances have been made in the development of biopolymer-based electrochemical sensors for detecting heavy metals in aquatic environments. These sensors offer numerous advantages over conventional methods, including cost-effectiveness, eco-friendliness, and high sensitivity. By utilizing natural, renewable resources, biopolymers provide an excellent alternative to synthetic materials, aligning with the global push toward sustainability and environmental protection.

Biopolymers, such as cellulose, chitosan, alginate, and other polysaccharides, have shown considerable potential in enhancing the performance of electrochemical sensors. These materials exhibit high adsorption capacities and can be functionalized with nanomaterials, further improving their ability to detect trace amounts of heavy metals. Additionally, their chemical versatility allows for modifications that enhance sensor stability, sensitivity, and selectivity.

The integration of biopolymers with nanomaterials, such as carbon nanotubes, graphene, and metallic nanoparticles, has opened new pathways for improving sensor performance. These hybrid materials combine the high surface area, conductivity, and mechanical strength of nanomaterials with the biocompatibility and biodegradability of biopolymers. As a result, sensors based on biopolymer–nanomaterial composites are becoming increasingly effective for detecting metal ions such as lead (Pb), cadmium (Cd), mercury (Hg), and copper (Cu), with low detection limits and high selectivity.

Despite these advances, there are still challenges that need to be addressed. The scalability of biopolymer-based sensors for large-scale industrial applications remains a key area of focus. Additionally, the long-term stability and reproducibility of the sensors under various environmental conditions must be further investigated. Future research should focus on optimizing biopolymer synthesis, improving electrode modification techniques, and exploring new biopolymer sources for sensor development.

In conclusion, biopolymer-based electrochemical sensors represent a promising solution for the detection of heavy metal contamination in aquatic environments. As the research continues to evolve, these sensors are expected to play a crucial role in environmental monitoring, industrial applications, and public health protection.

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