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Review

Sustainable Biopolymer-Based Electrochemical Sensors for Trace Heavy Metal Detection 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. The 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 limitation. 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

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),

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- 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 incorporated into modified electrodes, films, or composites, forming 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, the 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.

The review further analyzes the integration of biopolymers into various sensor platforms, such as amperometric, potentiometric, and impedimetric systems, focusing on strategies like nanocomposite fabrication and surface modification to improve 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, the review assesses the real-world applicability of these sensors in environmental monitoring, industrial processes, and point-of-care diagnostics and discuss the future research directions should be realized in future to further 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(II), cobalt Co(II), Iron Fe(II), Manganese Mn(II), Mercury Hg(II), Chromium Cr(IV), Silver Ag(I), Gold Au(III), Palladium Pd(II), Platinum Pt(III), Uranium U(VI), 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 and 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 main sources of heavy metals are industries such as tanneries, pharmaceutical and chemical industries, electroplating, mining, alloy production, fertilizers, etc (See Table 1).

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2.2. Toxicological Effects

Heavy metals are among the most dangerous pollutants because they are toxic, non-biodegradable, and accumulate in ecological systems. The determination of 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, leading to bioaccumulation, can take them up. Through the food chain, they eventually become biomagnified in the human body through consumption of bioaccumulated plants and animals or contaminated water [12]. A natural mechanism for the controlled removal of heavy metals from the human body is not yet known. Therefore, trace 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 enter the environment and ecological cycles in a variety of forms along with inorganic metal ions, hydrated metal ions, hydroxyl complexes, carbonate complexes, and complexes mixed with natural substances, and are taken up and enriched by aquatic plants, animals, and microorganisms. They can also interact with several inorganic colloids, organic colloids, and organic-inorganic complexes in the water or sediment and sooner or later agglomerate and settle to the back of the water body [1].

World Health Organization (WHO) sets a guideline and recommendation regarding the maximum allowed level of various heavy metal in drinking water. Table 1 resumes 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.

Metal	WHO (mg L^{-1})	Toxicity		Anthropogenic sources	Effects	Ref
		Tolerable daily Intake (mg/per day)	Lethal dose mg kg^{-1} body weightw			
Lead (Pb)	0.05	0.025–0.052	94–158	PVCc pipes in sanitation, agriculture, recycled PVC lead paints, jewellery, lead batteries, lunch boxes	Causes Alzheimer's and senile dementia, also leads to neurodegenerative diseases, decreases IQ, kidney damage, decreased bone growth, behavioral problems, digestive problems, urinary system failure, nervous system damage	[11] [14] [15] [16]
Cadmium (Cd)	0.005	0.018–0.052	4.4–6.2	Paints, pigments, batteries, plastics and rubbers, engraving process, photoconductors and photovoltaic cells	Renal toxicity, hypertension, weight loss, fatigue, microcytic hypochromic anaemia, lymphocytosis, pulmonary fbrosis, 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, efects on digestive system, immune system, lungs, kidneys, skin and eyes, Minamata, hypertension	[18] [19]
Arsenic (Ar)	0.05	0.03	41	Wooden electricity poles that are treated with arsenic-based preservatives, pesticides, fertilizers	Causes effects on cardiovascular system, pulmonary diseases, gastrointestinal tract, genitourinary system, hematopoietic system, dermatology, foetal 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	[20] [15]
Silver (Ag)	0.1	-	-	Refning of copper, gold, nickel, zinc, jewellery and electroplating industries	Argyria, gastroenteritis, neuronal disorders, mental fatigue, rheumatism, knotting of cartilage, cytopathological efects in fbroblast, keratinocytes and mast cells	[17] [4]
Zinc (Zn)	5	15–20 16.	1–25.3	Soldering, cosmetics and pigments Respiratory disorders, metal fume fever, bronchiolar	leucocytes, neuronal disorder, prostate cancer risks, macular degeneration and impotence	[15] [9]
Copper (Cu)	1.3	10	4.0–7.2	Fertilizers, tanning and photovoltaic cells	Adreno-corticol hyperactivity, allergies, anaemia, alopecia, arthritis, autism, cystic	[20] [21]

					fbrosis, diabetes, haemorrhaging and kidney disorders	
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 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 instrumentation. The most commonly used methods are:

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 to simultaneously determine multiple heavy metals and isotopes.

Electrochemical techniques, are also used to measure heavy metals in solution by monitoring changes in electrical properties due to redox reactions of metal ions. Electrochemical methods 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. 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 [24].

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 pollution in complex environments. Electrochemical sensors are also miniaturized systems that allow the development of portable instruments capable of monitoring on site. Given the wide range of recognition element with biomolecules such as antibodies, enzyme, DNA aptamer, DNAzyme and whole cells as well as macromolecules such as molecularly imprinted polymers (MIPs), macrocycles, and biopolymers, these methods have been considered as innovative tools in metal monitoring because of their stable interaction, low detection limit, and high selectivity [25,26]. The use of bio-sourced polymers in electrochemical sensors for metal pollution detection is a rapidly growing in this field of research because is assure detection approach beside possibility of removal.

2.5. Electrochemical Methods of Detection

Electrochemical techniques are cost effective and user friendly dependable. They can provide analytical results with lower detection limits compared to spectroscopic and optical methods. Electrochemical techniques widely used in heavy metal detection are potentiometric, amperometry, voltammetry, coulometric, impedance, and electrochemiluminescence. Voltammetry and potentiometry techniques have more used due their simplicity and the possibility to follow the redox signal of metal ions. Various techniques in voltammetry are employed to improve the sensitivity of detection and widely used are linear sweep anodic voltammetry (LSV), square wave anodic voltammetry (SWV), differential pulse anodic voltammetry (DPV). Chronoamperometry can be applied for real time monitoring of the metal ions in reel sample (Figure 1). However, detection with CV and potentiometric electrochemical methods analysis suffer from low selectivity [27].

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

Biopolymers and bio-sourced polymers modified electrodes presents interesting way for improving the attachment and stability of metal ion on the surface electrode leading to sensitivity and selectivity of detection. Another parameter in development sensor technology has recently been considered is the use of renewable sources materials.

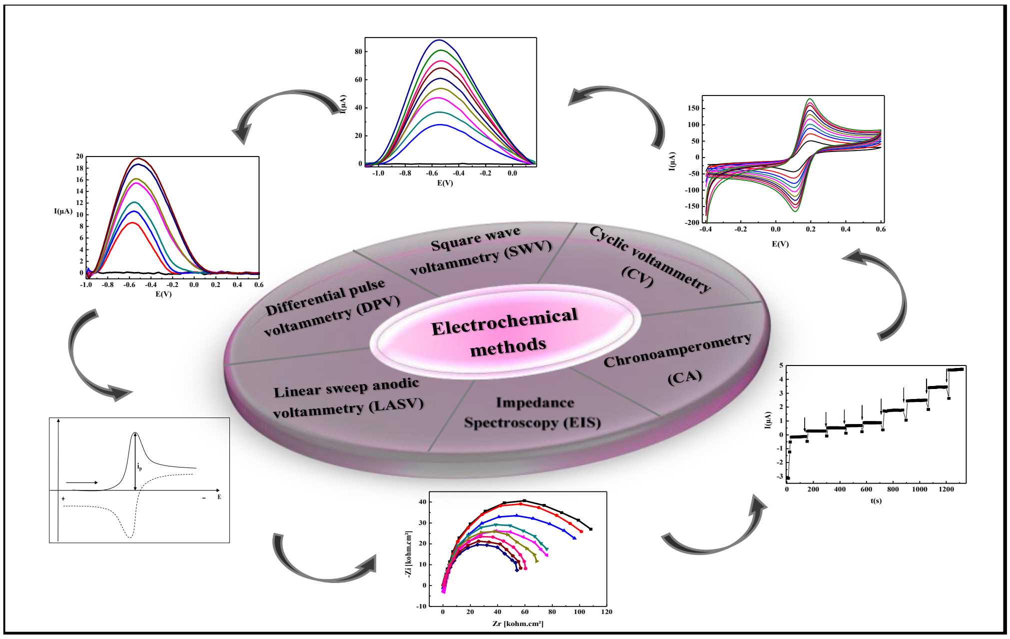

Figure 1. Presentation of the differentes electrochemical methods for heavy metal detection.

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 utilizes essential biological data, 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, 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 [28].

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:

- Biopolymers produced from renewable (biological) and biodegradable raw materials.
- Biopolymers produced from sustainable (biological), non-biodegradable raw materials.
- Biodegradable biopolymers based on fossil fuels [28].

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 structure of some synthetic biopolymers.

Advances in molecular design and polymer chemistry now allow the synthesis of synthetic biopolymers to be 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 polyhydroxybutyrate [2].

These synthetic biopolymers can be synthesized using various techniques, including esterification, dehydration, polycondensation, hydrolysis, and granulation, to achieve specific structural and mechanical properties [29].

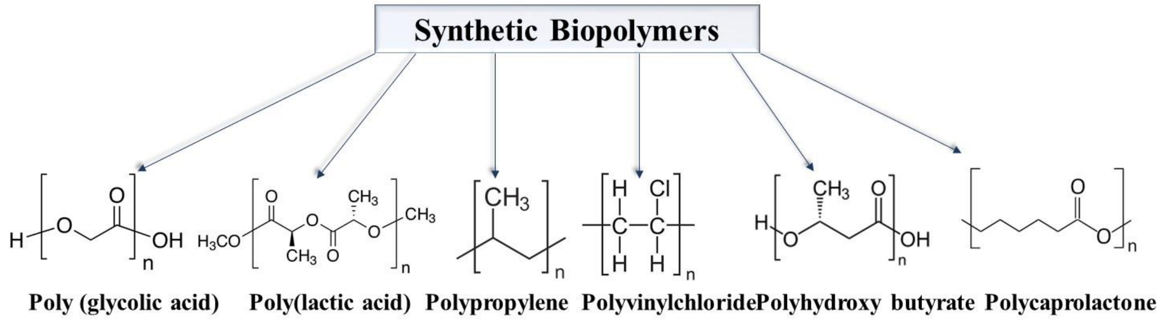

Figure 2. Examples of some structural units of synthetic and biosourced biopolymers.

3.3. Natural Biopolymers (Bio-Sourced Polymers)

Natural polymers are macromolecules produced or occurring naturally in living organisms. Although the terms "biopolymers" and "natural polymers" are sometimes used interchangeably, it is important to distinguish between them. "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, more random structures, have well-defined three-dimensional structures essential for their function [30].

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 [31].

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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) [31].

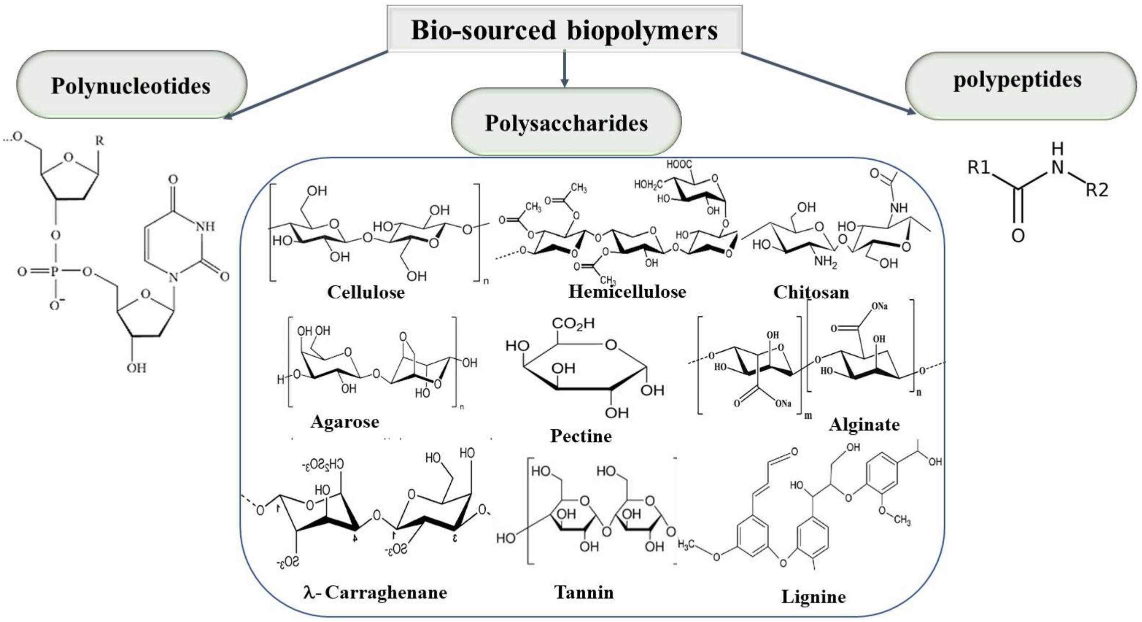

Figure 3. Structure of biosourced polymers.

3.4. Properties of Bio-Sourced Polymers

Biopolymers 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 biopolymers is their chemical and structural diversity, as they are sourced from plants and living organisms.

Biopolymers such as chitosan, alginate, cellulose, pectin, gelatin, and acacia gum are widely used in the development of biosensors due to their inherent properties [32]. They are especially valued for:

- 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 [33].

These properties make biopolymers an ideal matrix for sensor applications, particularly in the development of selective and sensitive sensors for heavy metal detection. Additionally, biopolymers possess functional groups such as hydroxyl, amine, and carboxyl groups that allow them to bind chemically and physically to various molecules [34,35].

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

Various carbohydrate-based biopolymers have been extensively used for the removal of heavy metals from water. Among these, adsorbents made from chitosan, lignin, carboxymethylcellulose, and alginate have shown high efficiency. These biopolymers contain numerous functional groups that act as adsorbents, improving the removal of heavy metals from water samples by chelating metal ions and forming complexes [7].

Several technologies have been explored for the removal of heavy metals from water. For instance, ion exchange [36], coagulation-flocculation [37], precipitation, and membrane filtration [38],have been studied 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. Over the years, various natural polysaccharides, such as cellulose, hemicellulose, chitosan, and lignin [39–41], along with phenolic compounds (lignin) [42,43], chelators, activated carbon, and clay, have been used as adsorbents for removing heavy metals [44].

To achieve high removal efficiency, adsorption relies on the attraction of heavy metal ions present in wastewater by an adsorbent with a porous structure and a large surface area. Active functional groups found in natural or synthetic biopolymers (such as aromatic, phenolic, alcoholic, carbonyl, methoxy, carboxyl, and amino groups) serve as adsorption sites for heavy metal ions [45] [46]. 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 process of decontamination.

Table 2 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 2. Summary of the metal ion types, maximum adsorption capacity, and adsorption mechanism of the Biopolymers.

Biopolymers used for removal	Metal ions	Adsorption capacity (mg g⁻¹)	Ref
Nano-sized TiO_2/ carboxymethyl chitosan hemicellulose composites	Ni(II) Cd(II)	32.2	[47]
	Cu(II) Hg(II)	27.6	
	Mn(VII)	13.5	
	Cr(VI)	9.4	
		4.8	
		4.3	
Phosphorylated cellulose microsphere	Pb(II)	139.38	[48]
Porous carboxymethyl chitosan (PCMC)	Co(II)	46.25	[49]
Cellulose/N-isopropylacrylamide-glycidyl methacrylate Cell- *g* -NIPAM- *co* -GMA	Ni(II)	74.68	[50]
	Cu(II) Pd(II)	82.92	
		119.76	
Carboxymethylated cellulose fiber (CMF)	Cu(II)	23.48	[51]
Glucan/chitosan (GL/CS) hydrogels	Cu(II)	342	[52]
	Co(II)	232	
	Ni(II)	184	
	Pb(II)	395	
	Cd(II)	269	
Chitosan/calcium alginate/bentonite composite hydrogel	Pb(II)	434.89	[53]
	Cu(II)	115.30	
	Cd(II)	102.38	
Carboxylated chitosan/carboxylated nanocellulose hydrogel beads	Pb(II)	334.9	[54]
Cellulose nanofiber and sodium alginate	Pb(II)	318.47	[55]
Picea smithiana sawdust	Pb(II) Cr(VI)	6.35	[56]
	Cd(II)	3.37	

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Sodium alginate@ polyethyleneimine-carbon dots	Pb(II)	380.39	[57]
Hemicellulose based hydrogel	Pb(II)	5.88	[58]
microwave-functionalized cellulose	Pb(II)	295.20	[59]
	Cd(II) Ni(II)	151.51	
		72.80	
Thiol-functionalized cellulose nanofiber	Cu(II)	49.0	[60]
	Cd(II) Pb(II)	45.9	
		22.0	
Unctionalized lignin-based hybrid magnetic nanoparticles	Pb(II)	150.33	[61]
	Cu(II)	70.69	
Three-dimensional porousgraphene/lignin/sodium alginate nanocomposite (denoted as 3D PG/L/SA)	Cd(II) Pb(II)	79.88	[62]
		226.24	
Chitosan/Nanoclay composite	Cu(II)	176	[63]
	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	[64]
Chitosan/ 4-hydroxy-3-methoxybenzaldehyde (VAN)-Epichlorohydrin (Fe_3O_4@CTS-VAN)	Cr(VI)	188.68	[65]
Modified xylan hemicellulose/ HA3	Pb(II)	193	
	Cd(II)	182	
	Cu(II)	66	[66]
Modified xylan hemicellulose/ HS50	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 (Figure 4). This efficiency can be partly attributed to the composition of the biomass, particularly the ratio of its key components: cellulose, hemicellulose, and lignin. Each of these components plays a critical role in the adsorption process, with functional groups providing binding sites for metal ions. A considerable body of 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 [67].

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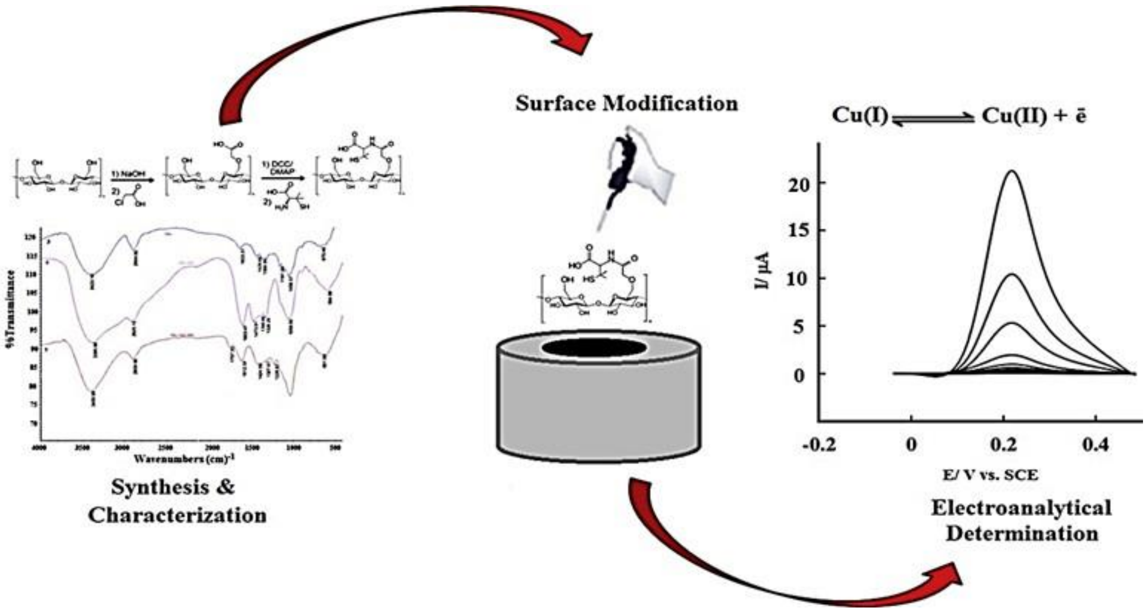

Figure 4. Nanocellulose functionalized with d-penicillamine used as electrochemical transducers for copper detection(reproduced from ref 74 with permission from publisher Elsevier).

In this section, we discuss 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 unique 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 [68].

5.1. Cellulose and Cellulose Composite-Based Sensors

Cellulose, one of the most common polysaccharides, is widely used in biosensors. It is an oxygen-rich polysaccharide composed of glucose units linked by oxygen bonds[69]. Plants produce cellulose in a fibrous form, which strengthens cell walls. Cellulose has a fibril structure that provides high resistance, allowing it to form durable polysaccharide-based walls. Its carbon structure enables cellulose to be both crystalline and amorphous, which makes it an attractive material for sensor applications.

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 [70]. 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 the use of cellulose and its derivatives in constructing electrochemical sensors for heavy metals. For example, sodium carboxymethylcellulose has been used to modify glassy carbon electrodes (GCE) for detecting cadmium ions using differential pulse anodic stripping voltammetry (DPV). 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 [71].

Bacterial cellulose, which is produced by certain bacteria, has also been employed in heavy metal sensing due to its highly porous network and large surface. A notable example is a electrochemical sensor developed by Qin et al. to detect cadmium (Cd(II)) and lead (Pb(II)) in drinking water. This sensor used a glassy carbon electrode (GCE) modified by a composite material which combined carbonated bacterial cellulose (CBC) with gamma-alumina (γ-AlOOH) and differential pulse voltammetry (DPV) 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 μg/L for Cd(II) and 0.1 μg/L for Pb(II). The authors compared these results to those obtained through the more established method of inductively coupled plasma mass spectrometry (ICP-MS), and demonstrated the sensor's reliability and accuracy [72].

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 eucalyptus-derived for detecting traces of Cd(II), Cu(II), Pb(II), and Hg(II) using differential pulse anodic stripping voltammetry (DPV). 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) [73].

The combination of cellulose derivatives as scaffold with others components such biomolecules or nanomaterials leads to improvement of sensing properties towards heavy metals detection. Many examples are cited with various cellulose derivatives and their association with carbon nanomaterials as well as metal oxide. For example, nanocellulose has also been combined with biomolecules to further enhance detection sensitivity. Taheri et al. demonstrated that a nanocellulose composite modified with d-penicillamine (DPA-NC) significantly improved the detection of copper ions (Cu(II)) in tap and river water (Figure 4). A pencil-shaped graphite electrode modified with DPA-NC exhibited improved amperometric detection of Cu(II) through square wave voltammetry (SWV), with a sensitivity of 0.2 μA/μmol and a detection limit of 0.048 pM [74]. This result demonstrated the ability of sensors based on biopolymers for the integration in handheld devices and detection in reel samples.

In the same way, the association of carboxymethylcellulose (CMC) with carbon nanomaterials has been explored for detection of cadmium and lead. A study by Prya et al. has focused on the simultaneous detection of trace levels of cadmium (Cd(II)) and lead (Pb(II)) using a nanocomposite made from porous graphene, CMC, and fondaparinux a penta-saccharide to form a composite (PrGO/CMC/Fonda). This nanocomposite, when deposit on GCE and detection of various heavy metal are performed using square wave anodic stripping voltammetry showed a high sensitivity, with 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 metal ions immobilization [75].

Cellulose nanocrystals, also known as nano-whiskers (CNW), 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. was 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 facilitated the electrochemical detection of mercury in water samples, achieving a limit of detection (LOD) of 0.0052 μM and a wide dynamic linear range of 2.5–200 μM [76].

Additionally, metal oxides nanomaterials are also associated with cellulose to improve the conductivity of the nanocomposite. Padmalaya et al. developed a cellulose-based composite using cellulose acetate, a major cellulose ester, 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 an LOD of 0.41 μM and a sensitivity of 3.11 μA/μM within a linear concentration range of 0.1–0.5 mM. The conductive nature of zinc oxide, along with its stability and the hydroxyl groups in cellulose acetate's structure, endowed the nanocomposite with electrical and chemical properties well-suited for lead detection [77].

Cellulose can also serve as electrode and supporting matrix for the immobilization of chelating agent of metal ions. For example, hierarchical porous metal organic framework zeolitic imidazolate frameworks (ZIF-8) were integrated into cellulose paper for removal and detection of metal ions (Figure 5). The modified cellulose were used as working electrodes for the selective electrochemical detection of lead ions (Pb(II)) with an LOD of 8 μM [78].

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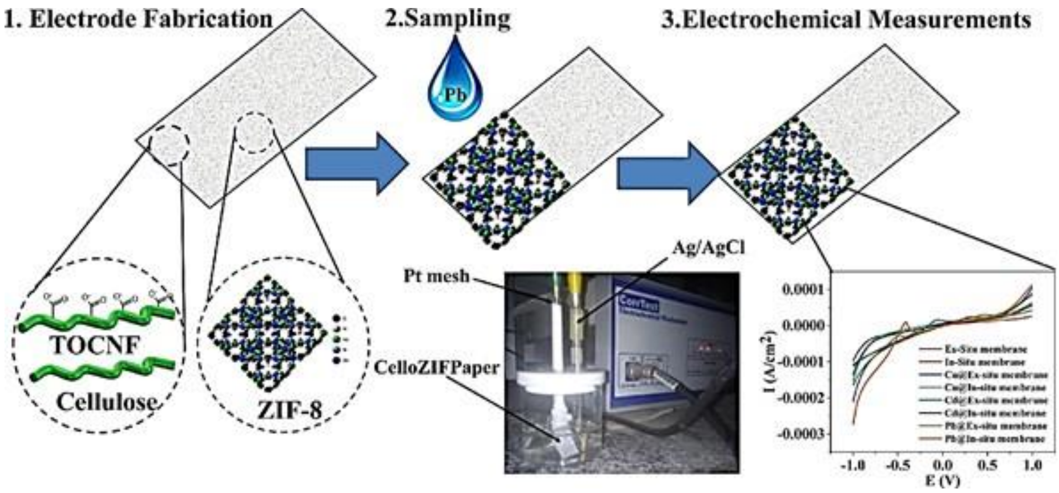

Figure 5. Schematic representation of electrode fabrication, sampling from cellulose, and electrochemical measurements of CelloZIFPaper for detection of lead ions. The inset camera image shows the setup of the cell electrodes and potentiostat. Reproduced from ref 78.

Table 3 summarizes the sensors developed based on others cellulose derivatives and composites with others materials and highlights the methods of detection used as well as the limit of detection and linear range.

Table 3. Biopolymers based on cellulose and hemicellulose obtained from various sources with different polymeric materials as a sensor for heavy metals.

Electrode	Method	Analyte	LOD	Linear range	Ref
Au/ Agarose-Hemicellulose	SWV	Pb(II)	1.3 fM	1μM-1fM	[25]
Pyromellitic dianhydride-grafted cellulose nanofibrous	DPV	Pb(II)	0.048 μM	-	[79]
GCE/ Cellulose nanofiber	DPV	Cd(II)	5 nM	0.1nM-10μM	[73]
		Cu(II)	0.5 nM		
		Pb(II)	0.5 nM		
		Hg(II)	5 nM		
Penicillamine functionalized nano-cellulose modified pencil graphite electrode	SWV	Cu(II)	0.048 pM	0.2-50 pM	[74]
PA_6/ cellulose nanowhiskers /rGO	DPV	Hg(II)	5.2 μM	2,5 - 75 μM	[76]
AuNPs/Cellulose nanofiber/GCE	SWV	Cd(II)		0.1-1.0 μM	[80]
		Pb(II)	0.1 μM		
		Cu(II)			
γ-AlOOH-carbonated bacterial cellulose	DPV	Cd(II)	0.17 μg. L^{-1}	0.5- 250	[72]
		Pb(II)	0.10 μg. L^{-1}	μg. L^{-1}	
Lignocellulosic biomass/CPE :	SWV	Pb(II)		0.1-100	[81]
- Cellulose/CPE		Cu(II)	0,01 μM -0,08	0.1-20	
		Pb(II)	mM	0.1-50	
Xylane/CPE		Cu(II)		0.1-20	
Hydroxyethylcellulose-CA	EIS	Pb(II)	0,39 mg L^{-1}	-	[82]

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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 found wide applications in environmental remediation, particularly in water treatment[83]. Its biocompatibility and ability to bind metal ions make it suitable for use in electrochemical sensors for heavy metal detection.

Sodium alginate's mechanical properties can be improved by forming composites with other materials. For example, the combination of alginate with chitosan, another biopolymer, can result in stable hydrogels that can be easily deposited on sensor surfaces. The richness of functional groups such as carboxyl (-COOH) and nitrogen-containing groups in these biopolymers allows for 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 DPV. The sensor achieved a linear detection range between 1 and 100 µM, with a detection limit of 0.9545 µM [84].

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 the large surface area and high conductivity of SWCNTs, 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 differential pulse anodic stripping voltammetry (DPV). The sensor achieved detection limits of 0.1 nM for Pb(II), 31 nM for Cd(II), and 1 nM for Cu(II) [85].

5.3. Chitosan-Based Sensors

Chitosan is a linear biopolymer composed of randomly arranged D-glucosamine and N-acetyl-D-glucosamine units linked by β(1-4) glycosidic bonds. Its structure contains amine ($-NH_2$) groups at the C2 carbon, along with numerous hydroxyl (-OH) groups, which impart strong hydrophilic properties to the molecule. Chitosan is derived by deacetylating chitin in an alkaline medium [86], 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. The presence of primary amino groups ($-NH_2$) has 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 [87].

Chitosan membranes or films form effective matrices for sensing heavy metals due to the 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 SWV, 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 [88].

Another study by Hadnine et al. developed an electrochemical sensor based on a carbon paste electrode modified with a chitosan-based chelating thiourea and glutaraldehyde. This composite, used for the detection of mercury ions and showed sensitivity to Hg(II) ions in the range of 5 nM to 1 µM, with a detection limit of 1.61 nM [89]. 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

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chitosan hydrogel, which was deposited on a GCE. This electrode was investigated for detecting trace amounts of Pb(II) and Cd(II) using SWV. The sensor exhibited a detection limit of 0.07 ppb for Pb(II) and 5.06 ppm for Cd(II) [90].

Chitosan's ability to form composites with metals 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 in tap water [91]. This work demonstrates the potential of the chitosan to be printed and gives electrode with high efficiency in detection. However, the stability of these devices during the time and in hard conditions still need further development.

Chitosan can also be combined with magnetic materials, such as Fe_3O_4 nanoparticles, to improve detection performance. Zhou et al. synthesized Fe_3O_4-chitosan nanoparticles through a one-step in situ co-precipitation method. These nanoparticles were used as a sensosr for Pb(II) ions using SWV, achieving high sensitivity of 50.6 μA/μM and a detection limit of 0.0422 μM [92].

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 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/MoO_3/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 MoO_3 allow for a tunable electronic range, while the nanostructured oxides provide active surface sites for metal ion binding [93].

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, respectively [94].

The use of ion-imprinting techniques has 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 glassy carbon electrode (CS/GO-IIP) for highly sensitive 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 [95].

In similar work, Yin et al. created an electrochemical sensor based on a covalent organic framework (COF) combined with calcium lignosulfonate (CLS)-modified multiwalled carbon nanotubes (MWCNTs) and Nafion for the simultaneous analysis of Cu(II), Pb(II), and Cd(II). The COF's 3D porous structure and abundance of amino groups allow it to efficiently accumulate heavy metal ions. The MWCNTs enhanced the sensor's conductivity, while 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 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 [96].

Researchers also combine chitosan with conductive polymers to create composite materials that offer enhanced sensitivity, selectivity, and charge transfer capabilities, improving sensor performance and design robustness. Since chitosan is non-conductive, it has been paired with various conductive polymers. 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 [97].

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, with a detection limit of 13.77 ppm and minimal interference from other cations and anions [98].

The literatures data regarding chitosan-based sensors for heavy metals detection is very large and Table 4 summarizes some relevant papers regarding the detection of heavy metal where detection is performed in reel samples for water environment control.

Table 4. summarizes relevant sensors based on chitosan for heavy metal detection.

Electrode	Method	Metal	LOD	Linear range	Ref
Thymine-Hg^{2+}-Thymine/ AuNPs/Chitosane (Aptamère/ $(AuNPs/CS)_2$/GCE)	DPV	Hg(II)	0,005 nM	0,01-500 nM	[99]
GC/Chitisane–(Bi–CX)	SWV	Pb(II) Cd(II)	0.07 ppb 5.06 ppm	0.2–2 ppb 11.2–124 ppm	[90]
AuNPs/CS-Aptamer/GCE	DPV	Cd(II)	0,04995 pM	0.001-100 nM	[100]
Amino-functionalized graphene/chitosan (NH_2–G/CS)	DPV	Cu(II)	0.064 μM L^{-1}	0.4- 40 μM	[101]
CS/AuNPs/GR/GCE	DPV	Cd(II)	16.2nM	0.1-0.9 μM	[102]
Biochar-nanodiamond-chitosan electrode ND-BC-CS	SWV	Cd(II) Pb(II)	0.11 μM 0.056 μM	1.0-75 μM 0.25-6 μM	[103]
Chitosan-graphene oxide composites polymer CS/GO-IIP	DPV	Cu(II)	0.15 μM	0.5 – 100μM	[95]
rGO/MoS_2/CS (GCE)	SWV	Pb(II)	0.0016 μM	0,005-2.0 μM	[104]
NiO-CS/CPE	EIS	Pb(II)	0.3 μM	1μM-0.1mM	[105]

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 that have a high affinity for metal ions. Polyphenols can be monomers, polymers, or complexes, with molecular weights ranging 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 for Cu(II), 35 ng/L for Cd(II), and 11 ng/L for Pb(II)[106].

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 polyphenol-polyvinyl chloride membrane, using polyphenols extracted from acorn shells. The modified electrode

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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 [107].

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 [108]. The integration of 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 not only enhance conductivity but also 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 [109].

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 effective material for heavy metal ion sensing. The underlying mechanism of lignin interaction with heavy metals—comprising chelation, ion exchange, adsorption, and surface modification—suggests that lignin and similar biopolymers could serve as versatile agents in a broad range of environmental sensing applications. This versatility is particularly important for developing cost-effective, biodegradable materials for heavy metal removal and sensing, aligning with the growing demand for sustainable environmental technologies [110].

Moreover, the research by Xin Bao et al. emphasizes the use of naturally occurring polyphenols from tea in fabricating rGO-ZVI-P composites, which showed remarkable sensitivity toward Hg(II) detection. The application of green chemistry methods, such as using tea polyphenols as reducing agents, aligns with a sustainable approach to sensor development, reducing the need for harsh chemicals while enhancing material performance. The synergy between zero-valent iron (ZVI) and reduced graphene oxide (rGO) offers an efficient platform for ion accumulation and electron transfer, with a sensitivity of 41.42 μA/μM and 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 to improve detection performance [111].

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[112].

Pectin, a polysaccharide rich in carboxyl groups, can be associated with other nanomaterials for the sensing of 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 presence of carboxylic acid groups in 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 [113].

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 the presence of amine functionalities. The combination of polypyrrole with pectin has been shown to significantly enhance detection performance. For example, Arulraj et al. fabricated an electrochemical sensor using a composite of pectin, polypyrrole, and graphene (PPy/Pct/GR) for detection of mercury (Hg(II)). The sensor demonstrated excellent performance, with a sensitivity of 28.64 µA/µM and a detection limit as low as 4 femtomolar (fM)[114].

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 (SWV), 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 [115].

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. The alternating layers of agar, carrageenan, and polyaniline (PANI) 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)) [116].

Table 5 provides a summary of 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 5. summaries of sensors of heavy metal obtained with polyphenols derivatives.

Electrode	Method	Analyte	LOD	Linear range	Ref
Tea polyphenols mediated zero-valent iron/reduced graphene oxide nanocomposites (rGO-ZVI-P)	SWV	Hg(II)	1.2 nM	-	[111]
Tannic acid capped gold nanoparticle (AuNP@TA) complexes	SWV	Hg(II)	100.0 fM	100.0 fM-100.0 nM	[108]
Sodium alginate(SA) and chitosan (CS)SA-CS/GCE	DPV	Cu(II)	0.9545 µM	1–100 µM	[84]
Sodium alginate-chitosan/GCE SA-CS/GCE	DPV	Cu(II)	0.9545 µM	1–100 µM	[84]
Sodium alginate-decorated single-walled carbon nanotube	DPV	Pb(II) Cd(II) Cu(II)	0.1 nM 31 nM 1 nM	-	[85]
AuNP-biopolymer-coated carbon SPE sensor	SWV	Hg(II)	1,69 ppb	10-100 ppb	[117]
Grafted *Tricholoma* mushroom polysaccharide-silver composite nanoparticles (TMPSGP-Ag NPs)	CA	Zn(II)	0.53 nM	< 1 nM	[118]
Cork–graphite electrodes	DPV	Pb(II)	0.3 µM	1–25 µM	[119]

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Bi/AgNP/Nafion- SPGE with Pectin of Citrofortunella Microcarpa	ASV	Pb(II)	267.6 ppt	-	[120]
β -cyclodextrin (β -CD)-graphene hybrids (AuNPs-CD-GS)	DPV	Cd(II) Pb(II)	24 .8μg L^{-1} 10.6 μg L^{-1}	40 - 1200 μg L^{-1}	[121]
Green nanoparticles based on gum Arabic	DPV	Zn(II) Hg(II) Pb(II) Cu(II)	1.9 ppb 0.9 ppb 4.2 ppb 9.6 ppb	2-150 PPb 1-100 PPb 5-300 PPb 10-300 PPb	[122]

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

These studies underscore the role that sustainable, biopolymer-based materials can play 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. The use of 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 advantage s of biopolymers is related to its biodegradability and sustainability.

As 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 of advantage of biopolymers also, 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 or chitosan from seafood waste, pectin from agriculture 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 easily modification or combination with other materials is also advantage of this biopolymers. Biopolymers can be combined with nanomaterials like 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.

The 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, there are also limitations that 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. To overcome this, biopolymers often require integration with conductive materials such carbon nanotubes or graphene

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which can complicate the fabrication process and increase costs. In addition, the potential for degradation in harsh conditions could be a limitation in their applications. While biopolymers are biodegradable, this can also be a limitation. In harsh 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 compared to synthetic polymers, especially in environments prone to microbial growth or moisture. This 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 inconsistent 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 requires 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, challenges related to conductivity, durability, and production consistency must be addressed to fully leverage their benefits. 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 further improve their performance and applicability:

- ✓ Explore news methods for biopolymers production for example using biological methods such as bacterial or enzymatic process that can enhances reproducibility between the batch of source
- ✓ Enhanced 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.
- ✓ Enhance sensor stability and durability as long-term sensor stability remains a challenge for their use in monitoring during long period. Thus, future research should aim to enhance the durability of biopolymer-based sensors under different environmental conditions such as (pH fluctuations, temperature variations, salinity), ensuring consistent performance in real-world applications. This can be obtained by developing cross-linking techniques or nanocomposite formulations that enhance the mechanical and chemical stability of biopolymer sensors under prolonged exposure to harsh environments.
- ✓ Real-time sensing and multi-metal detection is a big challenge for monitoring the water contamination as various metal are presents. Current sensors often target specific metals, but future research should aim to develop sensors capable of simultaneously detecting multiple heavy metals in real time.
- ✓ The exploration of new biopolymer sources could lead to materials with novel properties that enhance sensor performance. Future research could explore: Investigating biopolymers from algae, fungi, or microorganisms, which 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.
- ✓ Improve their scalability and commercialization approach using adaptable methods for large production is also a big challenge. Although biopolymer-based sensors show great potential in laboratory settings, their scalability for mass production and commercialization remains a challenge. Further research should focus on cost-effective manufacturing processes and material sourcing to facilitate widespread adoption of these sensors.

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- ✓ Integrating biopolymer-based sensors with IoT and wireless technologies can significantly enhance their capabilities for environmental monitoring, enabling real-time data collection, remote accessibility, and scalable deployment. This can be obtained by connected biopolymer-based sensors to IoT systems to provide continuous, real-time monitoring of heavy metal concentrations in environmental samples like water and soil. These sensors, when paired with wireless modules (such., Bluetooth, Wi-Fi), can transmit data to cloud platforms, where it can be accessed remotely by environmental scientists, regulatory bodies. This allows for faster responses to pollution events, as data is readily available for analysis and decision-making. The lightweight, flexible nature of biopolymer sensors makes them ideal for deployment in difficult-to-access or remote areas. Wireless connectivity ensures that data from these locations can be transmitted without requiring direct physical access, which is particularly valuable in environmental monitoring. With a network of wireless biopolymer-based sensors, a comprehensive map of contamination can be created, supporting large-scale environmental assessment and remediation strategies.
- ✓ Biopolymer-based sensors are generally low power, making them compatible with energy-efficient wireless protocols. When combined with solar-powered or other renewable energy sources, these sensors form sustainable, self-sufficient monitoring systems can be well-suited for long-term environmental monitoring. This also helps reduce the ecological impact of continuous heavy metal monitoring operations.
- ✓ The integration of low-cost, printed biopolymer sensors with IoT reduces the need for expensive infrastructure traditionally associated with environmental monitoring. Printed biopolymer sensors can be designed for single-use or periodic replacement, making them economically viable for large-scale deployments where sensors may need regular updates due to potential degradation in outdoor environments. Such disposable sensors, integrated with IoT, make it feasible to implement dense sensor networks, providing higher spatial resolution in environmental data.

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, 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 tackling the pressing issue of heavy metal contamination in aquatic environments. As 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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