

Review

Biochar-Derived Electrochemical Sensors: A Green Route for Trace Heavy Metal Detection

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Abstract

The increasing demand for rapid, sensitive, and eco-friendly methods for the detection of trace heavy metals in environmental samples, attributed to their serious threats to health and the environment, has spurred considerable interest in the development of sustainable sensor materials. Toxic metal ions, namely, lead (Pb^{2+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), arsenic (As^{3+}), and chromium, are potential hazards due to their non-biodegradable nature with high toxicity, even at trace levels. Acute health complications, including neurological, renal, and developmental disorders, arise upon exposure to such metal ions. To monitor and mitigate these toxic exposures, sensitive detection techniques are essential. Pre-existing conventional detection methods, such as atomic absorption spectroscopy (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS), involve expensive instrumentation, skilled operators, and complex sample preparation. Electrochemical sensing, which is simple, portable, and eco-friendly, is foreseen as a potential alternative to the above conventional methods. Carbon-based nanomaterials play a crucial role in electrochemical sensors due to their high conductivity, stability, and the presence of surface functional groups. Biochar (BC), a carbon-rich product, has emerged as a promising electrode material for electrochemical sensing due to its high surface area, sustainability, tunable porosity, surface rich in functional groups, eco-friendliness, and negligible environmental footprint. Nevertheless, broad-spectrum studies on the use of biochar in electrochemical sensors remain narrow. This review focuses on the recent advancements in the development of biochar-based electrochemical sensors for the detection of toxic heavy metals such as Pb^{2+} , Cd^{2+} , and Hg^{2+} and the simultaneous detection of multiple ions, with special emphasis on BC synthesis routes, surface modification methodologies, electrode fabrication techniques, and electroanalytical performance. Finally, current challenges and future perspectives for integrating BC into next-generation sensor platforms are outlined.

Keywords: biochar; electrochemical sensors; trace heavy metal ions; green electrode

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1. Introduction

Owing to rapid industrialization, huge amounts of toxic metal ions, including lead (Pb^{2+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), arsenic (As^{3+}), and chromium, are being expelled into the water system globally, resulting in heavy metal ion pollution becoming a major concern of this 21st century [1]. These persistent contaminants accumulate, leading to severe health hazards to humans and wildlife even at trace concentrations. Once released, these heavy metal ions do not deteriorate; rather, they penetrate the soil, mix with the

groundwater system, and percolate into biological systems, where they disrupt cellular function and accumulate over time [1,2].

Among analytical techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) [3,4], and X-ray fluorescence (XRF) [5,6], which are considered prime methods for heavy metal detection, their expensive instrumentation, centralized laboratories, and intricate procedures limit their use in rapid field analysis and large-scale environmental inspection. Consequently, there is an urgent need for an alternative sensing platform that also fulfills the criteria for being sustainable, economical, and portable, along with being sensitive and selective. Recent advancements in electrochemical sensors have established sensor-based systems as potent alternatives to conventional analytical methods for heavy metal ion detection. They exhibit several advantages, including high sensitivity, selectivity, quick response, and the targeted detection of analytes even at trace levels [7,8]. To further enhance their performance, these sensors rely on diverse functional materials for electrode modification. An array of functional materials has been used for electrode modification [9] to improve the sensor performance, which includes metal nanoparticles, metal oxides, metal–organic frameworks (MOF) [10], quantum (carbon) dots, graphene [11], and several carbon-based materials [12] and their derivatives. These entities were found to help increase the surface area, electron-transfer kinetics, and specific binding affinity toward metal ions, collectively exhibiting more precise and facile detection in intricate environmental samples.

The fabrication of next-generation electrochemical sensors for heavy metal ion detection necessitates the assimilation of materials that manifest high sensitivity, selectivity, and operational stability. In this context, the synthesis of cost-effective, environmentally friendly, and electrochemically active carbon nanomaterials has come into the limelight. Specifically, biomass-derived carbons, commonly named biochar (BC), tend to be a potent alternative to traditional carbon-based nanomaterials due to their inherent abilities, such as renewability, surface functionality, and tunability. These BCs were found to possess enhanced adsorption capability and electron transfer kinetics, due to their high specific surface area, porosity, and copious amounts of oxygen-containing functional groups, which are the results of pyrolysis or hydrothermal carbonization [13,14]. In addition, the mechanical robustness, thermal stability, chemical stability, and compatibility of BC when combined with nanomaterials like metal nanoparticles, MOFs, etc., make it a prominent candidate for use in advanced electrochemical sensing platforms targeting trace-level heavy metal ions [15]. The incorporation of BC-derived nanocomposites represents a significant strategy to improve the electrochemical sensing performance for the precise detection of trace heavy metal ions in water, soil, and atmospheric gases.

BC, the product of biomass pyrolysis, is a carbonaceous substance with high surface area, porosity, tunability, and stability, assisting its application in environmental monitoring and pollutant remediation [13–15]. However, raw, unmodified BC undergoes structural disintegration and reduced electrochemical performance during extended operation [16,17]. To overcome these constraints, researchers have been focusing on the fabrication of modified BC-based nanocomposites using metal/metal oxide nanoparticles. These were found to exhibit enhanced electrocatalytic performance with high sensitivity and selectivity, making them robust materials for electrochemical sensing of trace heavy metal ions [18,19]. This review aims to provide consolidated information on the emerging role of BC-derived nanocomposites in the electrochemical sensing of trace heavy metal ions using electrochemical techniques, namely cyclic voltammetry (CV), differential pulse voltammetry (DPV), square wave anodic stripping voltammetry (SWASV), and adsorptive stripping differential pulse voltammetry (DPAdSV), thereby highlighting their potential to improve sustainable environmental monitoring and remediation. For the lowest possible detection

limits, stripping voltammetry is the preferred method, especially for heavy metals like Pb^{2+} , Cd^{2+} , and Hg^{2+} . SWASV usually offers better sensitivity and faster operation than DPASV. It is often preferred when ultra-trace detection and quick analysis are needed, such as in environmental field samples. DPASV delivers excellent peak resolution and consistent background suppression, making it a better choice for routine laboratory analysis, especially when dealing with complex matrices. Both methods take advantage of the high surface area and functional groups of biochar-based electrodes, but SWASV may better utilize the full sensitivity potential of biochar modifications. The choice between SWASV and DPASV should depend on the analytical challenge. Use SWASV when the lowest detection limits are needed for rapid or field testing. Use DPASV for robustness, reproducibility, and handling complex sample matrices. Both methods work well with green, biochar-based electrodes, taking advantage of their benefits while requiring careful optimization for the best results. Ultimately, the incorporation of BC-derived nanocomposites in the electrochemical sensing of heavy metal ions marks a significant advancement towards an eco-friendly pollutant detection technology with widespread implications for ecosystem protection and public health.

2. Biochar: A Green Electrode Material

Biochar, a carbon-rich material derived from naturally occurring, renewable, and cost-effective sources such as agricultural wastes and forest residues, adheres to the principles of green chemistry, sustainability, and the circular economy [20,21]. BC production from agricultural waste or forestry by-products usually requires relatively less energy, with material costs being low. It also needs an average amount of only 1–2 mg for one working electrode, rendering it pretty cheap [22]. The much lower environmental impacts of biochar-based materials as opposed to traditional carbonaceous materials motivate their use in developing sustainable sensors [23]. Li et al. assess the life cycle assessment (LCA) of BC used in agriculture. It focuses on how BC can reduce greenhouse gas (GHG) emissions, its energy requirements for production, and its economic feasibility. The study shows that biochar can cut net GHG emissions by about 0.5 to 3.0 tons of CO_2 -equivalent per ton of biochar. This depends on the type of feedstock, production method, and application conditions. Gasification is identified as the most cost-effective approach (around \$150 to \$250 per ton). Hydrothermal carbonization (HTC) needs lower energy inputs (1.2 to 2.0 MJ/kg) but offers slightly lower carbon sequestration. BC has good carbon stability in soil, ranging from 60 to 90%. This translates to 2.2 to 3.3 tons of CO_2 -equivalent sequestered for each ton applied. However, the overall benefits depend on factors like feedstock drying, transport emissions, energy sources, and interactions between soil and BC. In conclusion, the paper emphasizes BC's strong potential as a sustainable, carbon-negative approach. It also calls for more standard methods for LCA and validation on a larger scale [24]. Nevertheless, BC sustainability depends on feedstock choice and pyrolysis conditions. Sludge or any biomass with abnormally high metal content can be a precursor to the toxic emissions of PAHs and heavy metals [25–27]. Also, algae-derived biochar electrodes have an extremely low environmental impact (~ 0.02 kgs. CO_2 -eq per functional unit), contrary to the more polluting graphene-based electrodes (~ 0.21 kgs. CO_2 -eq) [28]. Together, these bring home the point that biochar can serve as a low-carbon, energy-saving, and renewable solution for electrochemical sensor platforms, especially when complemented with optimized fabrication processes and circular resource approaches. BC-based electrochemical sensors have the merits of portability, low cost, and real-time detection, but suffer from lower sensitivity and the need for matrix-matched calibration as compared to the conventional methods like AAS and ICP-MS [29]. In comparison to nanomaterials like graphene and CNTs, biochar is less conductive but environmentally friendlier and much easier to process.

Hence, it finds its greatest applicability in point-of-care or field-level preliminary screening rather than ultra-trace detection in complex matrices [30]. BC consists of a hierarchical pore system, entailing micropores (pore diameters of less than 2 nm), mesopores (2–50 nm), and macropores (greater than 50 nm), which is crucial for effective adsorption and provides abundant active sites for electrochemical reactions [31]. Usually, pyrolysis temperatures in the range of 400 to 700 °C favor the development of its pore structure [32,33]. Depending on the biomass precursor and pyrolysis temperature, a genuine biochar exhibits higher-than-average BET surface areas ranging from 200 to more than 1500 m²/g [34]. BC's skeletal density typically ranges from 1.34 to 1.96 g cm^{−3}, increasing with pyrolysis temperature, while envelope density ranges from 0.25 to 0.60 g cm^{−3} [35]. In comparison with conventional carbon nanomaterials, such as graphene and its oxide, carbon nanotubes, and fullerenes, BC exhibits numerous advantages, encompassing high surface area, porosity, and copious amounts of surface functional groups (hydroxyl, carbonyl, and amino groups) supporting efficient electron transfer kinetics along with adsorption of metal ions. BC is generally produced via thermochemical conversion of biomass in an oxygen-deficient environment, where the synthesis route significantly influences its physicochemical properties and electrochemical performance [36]. To understand how BC's properties contribute to sensor performance, it is first important to explore how it is synthesized and modified. The following are some of the reported synthesis routes for biochar manufacturing.

2.1. Synthesis of BC

2.1.1. Pyrolysis

Pyrolysis is one of the most predominantly used thermochemical techniques for BC manufacturing, involving the decomposition of organic biomass at higher temperatures (in the range of 300–800 °C), mostly in an inert or oxygen-deficient atmosphere, giving rise to solid BC, bio-oil, and syngas as products. When biomass is produced under a low heating rate, for instance, 5–10 °C per minute with sustained dwelling time (slow pyrolysis), solid BC with high carbon content and a thermally stable aromatic structure will be obtained at a higher yield, which is ideal for applications where carbon-rich nanomaterial is preferred. On the contrary, at a rapid heating rate of >100 °C per minute with minimal dwelling time, the obtained BC will be in a less solidified form with a distorted structure, whose electrochemical application can be improved through chemical activation [32,33]. The pyrolysis temperature plays an important role in the morphology and chemical characteristics of BC. Slow pyrolysis conserves functional groups, enabling higher adsorption of metal ions but with lower conductivity. On the other hand, fast pyrolysis enhances aromatization and deoxygenation, leading to improved electrical conductivity [32,33,37]. These surface functionalities also promote strong interactions with dopants or nanoparticles for further performance tuning. The inherent tunability of biochar's porosity and chemical reactivity via controlled pyrolysis parameters makes it a versatile platform for heavy metal sensing.

2.1.2. Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) is an emerging and versatile thermochemical method for BC manufacturing, particularly for high-moisture biomass under reasonably mild reaction conditions [38]. HTC operates at moderate temperatures (180–250 °C) and pressures (2–10 MPa) in aqueous conditions. The biomass is treated with water in a Teflon-lined, highly sealed, corrosion-resistant stainless-steel container under an inert atmosphere, which enables simultaneous reactions, namely hydrolysis, dehydration, decarboxylation, polymerization, and aromatization. The obtained BC will have high carbon content and enhanced surface oxygen functionality, while the aromatic structure depends on the reaction parameters (temperature, feedstock composition, and dwelling time) [39–41]. HTC-derived

biochar has been explored in diverse applications, including soil quality monitoring [42], adsorption of environmental pollutants [43–45], catalyst support [46], and as an advanced functional material for electrochemical sensing [47] and energy storage [48], which has become a promising candidate for sustainable material development and green chemistry approaches by researchers. HTC produces hydrochar with different structural and chemical properties from pyrolyzed biochar. This process usually occurs at lower temperatures, between 180 and 250 °C, in water. HTC retains a higher amount of oxygen- and nitrogen-containing functional groups like hydroxyl, carboxyl, amine, and phenolic groups [49]. These groups increase surface polarity, help coordinate metal ions, and improve the redox activity of the carbon surface. Although hydrochar generally has lower surface areas (usually less than 50 m²/g) and less developed porosity than pyrochar, its surface chemistry makes it suitable for activation or doping after synthesis [49]. HTC retains more surface oxygen functionalities than pyrolysis, but results in a lower surface area. This lower surface area can be countered with post-treatment approaches. Moreover, HTC can customize carbon surface chemistry to enhance sensing performance. This ability makes HTC useful for creating adjustable biochar for specific electrochemical applications.

Overall, both pyrolysis and HTC present exciting and complementary options for biochar synthesis. Each method has distinct advantages based on different feedstocks and application requirements. While pyrolysis is known for making stable, carbon-rich biochar with high surface area, HTC offers a low-temperature, water-based route that improves the processing of wet biomass and produces hydrochar with unique properties. Although regular biochar shows potential, its characteristics can be significantly modified through techniques like chemical activation, heteroatom doping, and adding nanostructured materials such as metal oxides or MOFs. These changes can further enhance the selectivity, sensitivity, and stability of electrochemical sensors, which will be discussed in the next section.

2.2. Modification of the Synthesized BC

The modification of synthesized BC plays a crucial role in tailoring its physicochemical properties for improved performance in the fields of electrochemical sensing, adsorption, and catalysis. BC synthesized from pyrolysis or HTC usually requires modification to enhance its surface reactivity, porosity, and conductivity [50]. Common functionalization methods include chemical activation, heteroatom doping, and the incorporation of metal/metal oxide nanoparticles/MOFs. Modification using acids or bases may incorporate oxygen-containing functional groups like hydroxyl or carboxyl, which improves the adsorption capacity of BC for the targeted analytes [50]. These modifications also help with their enhanced interaction with other carbon nanomaterials and polymeric systems. Overall, the modification of BC demonstrates enhanced sensitivity, selectivity, and stability in the electrochemical sensing of heavy metal ions, supporting its role as a sustainable, high-performing nanomaterial in advanced sensing technologies. The different modification techniques are discussed as follows.

2.2.1. Chemical Activation

Chemical activation is a commonly used method to improve the surface and structural aspects of BC, making it highly efficient in the fields of electrochemical sensing, adsorption, and catalysis. The as-obtained or synthesized BC is treated with chemical activating agents, such as potassium hydroxide (KOH), phosphoric acid (H₃PO₄), or sulfuric acid (H₂SO₄), either before or during pyrolysis. This chemical activation process increases porosity by eliminating volatile components present in the material and introduces oxygen functional groups like hydroxyl, carbonyl, etc. Moreover, the surface area of BC also increases, which

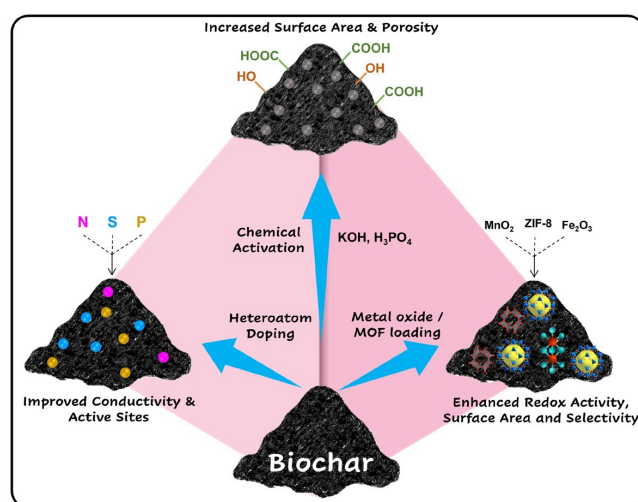
in turn improves analyte adsorption and electron transfer in electrochemical applications. The choice of activating chemicals also affects the surface chemistry of BC. For instance, KOH leads to the formation of oxygen functional groups (enhancing electrical conductivity), while H_3PO_4 increases phosphate concentration (enhancing metal ion binding) on the BC surface. Overall, chemical activation enhances the reactivity, porosity, and functional group influence in BC, converting it into a more efficient and tunable nanomaterial for environmental monitoring and sensing applications [51].

2.2.2. Heteroatom Doping

Apart from oxygen functional groups, heteroatoms like nitrogen (N), sulfur (S), phosphorus (P), or boron (B) are incorporated into the BC matrix to improve its electronic conductivity, chemical reactivity, and functional versatility in the fields of electrochemical sensing, energy storage, and catalysis. These heteroatoms are introduced either by using gas (e.g., N_2 gas) or chemicals (e.g., H_2SO_4), which alters the surface chemistry by forming defects, enhancing porosity, and generating active sites for heavy metal ion sensing. Electron-donating N increases conductivity and facilitates redox reactions, whereas S and P improve metal ion affinity via coordination or complexation mechanisms. Thus, heteroatom doping makes BC a high-performing, multifunctional nanomaterial with enhanced sensitivity, selectivity, and stability for electrochemical sensing of heavy metal ions and environmental monitoring [52].

2.2.3. Incorporation of Metal/Metal Oxide Nanoparticles

Metal nanoparticles are introduced into the BC via wet impregnation, in situ synthesis, or sol-gel techniques using a precursor. These nanoparticles act as active sites that critically enhance catalytic activity, redox behavior, and electron transfer kinetics of the BC. For instance, magnetic iron oxide (Fe_3O_4) nanoparticles impart magnetic properties to the BC, in turn enhancing electron transfer in electrochemical sensing applications [53], while noble metal nanoparticles like gold (Au) [54] improve electrocatalytic sensitivity and stability. The strong interaction between the BC matrix and the incorporated nanoparticles ensures structural integrity and uniform distribution, which is vital for reproducible electrochemical sensor performance. This synergistic combination of BC and metal nanoparticles results in hybrid systems with enhanced sensitivity, selectivity, and robustness for detecting trace levels of heavy metal ions and other environmental contaminants. The above information is condensed in the form of a figure and represented in Scheme 1.



Scheme 1. Methods for biochar modification: chemical activation, heteroatom doping, and metal oxide/MOF loading. Created using icons from www.flaticon.com (accessed on 22 July 2025).

Overall, modifying biochar with chemical activation, adding different atoms, and including metal oxides or MOFs significantly improves its structure and surface properties. This opens the door to new functions for specific applications. Chemical activation boosts porosity and surface area. Adding different atoms creates active sites, which improve reactivity. Loading with metal or metal oxide nanoparticles or MOFs gives it special catalytic, adsorptive, or electrochemical features. These modifications not only widen the use of biochar beyond its traditional roles but also make it a flexible and sustainable option for high-performance materials in environmental cleanup, energy storage, and sensor technologies.

3. Application of BC for Electrochemical Sensing of Heavy Metal Ions

3.1. Lead (Pb^{2+})

Lead (Pb^{2+}) is a prevalent and extremely toxic heavy metal with no significant biological function and has a clear capacity to cause multisystem health damage [55]. Its toxicity is significantly pronounced in exposed populations, such as children and pregnant women, where chronic exposure, even at a trace level concentration of $10\text{ }\mu\text{g dL}^{-1}$, can impair neurological development, behavioral disorders, and reduce IQ levels [56]. In adults, continuous exposure gives rise to hypertension, anemia, nephrotoxicity, and, in extreme cases, reproductive dysfunction [57]. The subtle behavior of Pb^{2+} , which has a biological half-life of up to a few years, lies in its ability to bioaccumulate in bones and soft tissues [57]. Environmental sources of Pb^{2+} contamination include industrial discharge, lead–acid batteries, plumbing materials, paints, ceramics, and electronic waste [58]. About 19 works have reported the electrochemical sensing and detection of Pb^{2+} ions using BC-derived electrodes as the substrate, with modification using various innovative electrode materials (Table 1).

Ouangpipat et al. prepared a BC material using *Pennisetum setosum*, a common grass species known for its rapid growth and bioaccumulative properties [59]. This was treated by the crosslink-xanthate method, focused on increasing its metal ion exchange capability by incorporating functional groups that support lead ion binding. Following the chemical treatment, the *Pennisetum* was mixed with graphite powder and mineral oil for the preparation of a carbon paste electrode (CPE), which was employed for the detection of Pb^{2+} ions. This report demonstrates the potential of biosorption-based materials in green chemistry, offering a low-cost, renewable, and potent alternative for heavy metal sensing in groundwater and canal water samples. Mojica et al. prepared a banana tissue-based BC by first removing the moisture from the tissue, followed by grinding it into a powder [60]. This powder was mixed with graphite powder and mineral oil to form a homogeneous CPE, which exhibits efficient sensing of Pb^{2+} ions owing to the intrinsic biosorptive properties of the banana tissue, which acts by providing active sites capable of complexing with Pb^{2+} ions. This work demonstrates eco-friendly and robust methods for Pb^{2+} ion sensing in water samples. Agustini et al. prepared a BC (derived from castor oil cake) and bismuth nanomaterial modified CPE for sensing Pb^{2+} ions in ceramic plates [61]. First, the castor oil cake was pyrolyzed at $300\text{ }^{\circ}\text{C}$, and the ground BC was mixed with graphite powder and mineral oil to form a CPE. To this electrode, bismuth nanoparticles were incorporated by electrochemical deposition at pH 1.5 for 30 s, forming an nBi-BchCPE modified electrode for Pb^{2+} sensing. This modified electrode was successfully utilized for the detection of Pb^{2+} ions released from overglaze-decorated ceramic dishes.

Tan et al. used cellulose extracted from *Cladophora rupestris* algae, followed by *in situ* polymerization of aniline monomer, forming a Clad-Polyaniline (PANI) composite, which was further acid-treated to ensure the PANI was present in its emeraldine form [62]. They prepared a stable, conductive paper-based electrode to electrochemically detect Pb^{2+}

ions, which may be utilized as a potent water-quality sensor. Ajab et al. utilized oil palm empty fruit bunches (OPEFB) as a precursor for preparing BC [63]. Cellulose was extracted from the precursor, which was then combined with separately synthesized hydroxyapatite (Hap), forming a cellulose-Hap composite that was further made into a CPE with graphite powder and paraffin. This fabricated electrode was found to exhibit improved surface roughness, enhanced porosity, and crystalline structures, providing surplus active sites for highly sensitive and selective sensing of Pb^{2+} in blood serum samples.

Table 1. Electrochemical sensors for the detection of Pb^{2+} ions.

Biomass Feed	Synthesis Method	Technique	E (V)	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
<i>Pennisetum setosum</i>	Crosslink-xanthate	DPASV	-0.55^a	-	0.048	Groundwater, canal water	[59]
Banana tissue	Drying	DPASV	-0.5^a	4.8–96.5	0.483	Water	[60]
Castor oil cake	Pyrolysis	DPAdSV	-0.6^a	0.005–1.0	0.001	Ceramic dishes	[61]
<i>Cladophora rupestris</i>	-	DPASV	-0.3^a	0.96–4.83	0.35	-	[62]
Oil palm empty fruit bunches	Pyrolysis	SWASV	-0.5^a	0.048–0.29	0.001	Blood serum	[63]
Bayberry kernel	Pyrolysis	CV	-0.5	48.3–3861	~ 0.0002	-	[64]
Almond shells	HTC	DPASV	-0.6^a	9.65–579.15	3.4	Tap water	[65]
<i>Acacia senegal</i>	-	DPV	-0.55^a	4.826–48.26	2.442	Plastic toys	[66]
<i>Benincasa hispida</i> + <i>Holstein Friesian</i>	HTC	DPASV	-0.63^a	2.4–482.6	0.965	Tap water, lake water	[67]
<i>Zea mays</i> L.	-	SWV	-0.5^a	0.1–5.0	0.02	Tap water	[68]
Spent coffee grounds	Pyrolysis	DPAdSV	-0.48^a	0.128–2.44	0.004	Gunshot residues Hair dye	[69]
<i>Litsea cubeba</i>	Pyrolysis	DPASV	-0.2^b	14.5–4.8	0.000005	Paddy water	[70]
<i>Centella Asiatica</i>	Pyrolysis	CV	-0.07^a	-	-	-	[71]
Tea residue	Pyrolysis	DPASV	-0.6^a	0.386–5.791	0.002365	River water, farmland water	[72]
Coconut husk	HTC	DPASV	-0.55^a	0.06–0.14	0.022	Tap water	[73]
Yerba-mate tea extracts	HTC	SWV	-	0.027–0.034	0.012	-	[74]

a—vs. Ag/AgCl; b—vs. SCE; LOD—limit of detection.

Li et al. developed an N-doped wormlike mesoporous carbon material from bayberry kernels as a BC precursor and melamine as the N source [64]. The kernels were subjected to *in situ* pyrolysis at a range of temperatures from 500 to 900 °C using an ethanol–Nafion solution to obtain a homogeneous dispersion. This dispersion was coated onto a glassy carbon electrode (GCE), followed by curing with an infrared lamp. The composite pyrolyzed at 900 °C exhibited a unique interconnected mesoporous “blood vessel-like” structure with abundant graphitic carbon, quaternary, and pyridinic-N sites, which paved the way for enhanced electrochemical sensing of Pb^{2+} ions. The fabricated electrode was found to possess a high surface area, excellent conductivity, and fast charge-transfer kinetics, which enabled highly sensitive and selective detection of Pb^{2+} over a wide range of concentrations. Similar to the previous report, Baikeli et al. fabricated an N-doped activated nanoporous carbon obtained from almond shells [65]. The cleaned and ground almond shells were carbonized at 450 °C under N_2 atmosphere, followed by KOH activation and subsequent pyrolysis at 600 °C to obtain the desired carbon. The “as-obtained” nanoporous carbon underwent

HTC in the presence of urea at 180 °C to yield N-doped carbon having a high surface area with pores. This N-doped carbon was dispersed in a water–isopropanol–Nafion solution and made into a homogeneous suspension for drop-casting over a GCE. The modified electrode exhibited improved conductivity and a high electroactive surface area, which in turn displayed enhanced electron transfer kinetics, making it an efficient material for sensitive and selective detection of Pb^{2+} in real tap water samples.

Sivan et al. reported the green synthesis of titanium oxide (TiO_2) nanoparticles using gum arabic as the biotemplate, followed by calcination at 500 °C [66]. The TiO_2 nanoparticles were drop-casted over a previously fabricated CPE (using graphite powder and silicone oil) and were used for electrochemical sensing of Pb^{2+} . The modified electrode displayed enhanced electrochemical sensing performance and was extended to real-sample analysis in plastic toys. Similar to [64], Xu et al. reported the fabrication of a wormlike N-doped carbon framework using *Benincasa hispida* (wax gourd) as the carbon source and *Holstein Friesian* (cattle milk) as the N source [67]. The wax gourd was first subjected to HTC at 180 °C, and subsequently pyrolyzed at 800 °C in the presence of milk and N_2 atmosphere. The obtained BC was dispersed in a 1 wt% Nafion solution and drop-casted over a pretreated GCE, subjecting it to electrochemical measurements after drying under an infrared lamp. This fabricated electrode exhibited superior conductivity, abundant active sites, and excellent electrochemical sensing of Pb^{2+} ions, which was further extended to the detection of Pb^{2+} ions in tap and lake water samples.

Radotić et al. derived BC from maize stems, where the cell walls were extracted via sequential extraction using methanol [68], sodium chloride, Triton-X 100, water, acetone, and methanol, which gave rise to clean biomass rich in cellulose, hemicellulose, and lignin. Unlike the previously reported literature, no pyrolysis was involved, yielding a low-energy, eco-friendly, non-pyrolyzed BC for the electrochemical sensing of heavy metal Pb^{2+} and non-heavy metal Cu^{2+} ions. Oliveira et al. utilized spent coffee grounds as the carbon source by pyrolyzing them at temperatures between 300 and 700 °C [69] and subsequently activating them with nitric acid under reflux at 60 °C for three hours to enrich the surface with oxygen functional groups. The CPE was fabricated by mixing the activated BC with graphite powder and mineral oil, further subjecting it to the electrochemical sensing of Pb^{2+} ions. The presence of oxygen functional groups in an abundant quantity aided in the facile, sensitive, and selective detection of Pb^{2+} ions when compared with a non-activated BC-based CPE and was used to detect Pb^{2+} ions in gun residues and hair dye.

Zou et al. reported the fabrication of a bismuth nanocluster-decorated porous activated BC, similar to the previous work [70]. The BC was prepared using *Litsea cubeba* shells via chemical activation with KOH and subsequent carbonization at 800 °C under N_2 atmosphere. This process was found to give rise to an oxygen-functional-group-rich BC (activated), to which bismuth nitrate was added and reduced using sodium borohydride (Figure 1). The synthesized nanocomposite was drop-casted on a GCE, which exhibited enhanced electrochemical activity towards Pb^{2+} ion detection due to its high surface area with abundant oxygen-rich sites, and was further subjected to paddy water analysis. Similar to the previous work, a molybdenum oxide nanoparticle-based BC was prepared by Mamatha et al. for the electrochemical detection of Pb^{2+} ions. The *Centella asiatica* plant was used as the carbon source [71]. It was dried into a fine powder (using an autoclave) before the addition of molybdenum nitrate, followed by heating in a muffle furnace at 600 °C to form molybdenum oxide nanoparticles. These nanoparticles were mixed with graphite powder and silicone oil for CPE preparation and were found to exhibit enhanced redox behavior for the electrochemical detection of Pb^{2+} in alkaline media.

Su et al. reported a green and efficient electrochemical sensor for detecting Pb^{2+} in real water samples using *in situ* electrochemically reshaped nano-BC (ErNBC) made from

tea residue [72]. The BC was created by heating it to 300 °C and reshaping it directly on the electrode surface through CV. This ErNBC showed a significant reduction in particle size, improved conductivity, better hydrophilicity, and increased oxygen content. The modified GCE/ErNBC demonstrated excellent electrochemical performance for lead detection, achieving a low detection limit of 0.49 µg/L, which is well below the standards set by the WHO and China. To improve predictive capabilities, the authors integrated machine learning models, including linear regression, K-nearest neighbor (KNN), and random forest, with electrochemical data. The random forest model performed the best, and the sensor was validated using river and farmland water. This work highlights the value of waste-derived nanomaterials for environmental sensing. It also shows the potential of combining green sensor development with machine learning for effective and sustainable heavy metal detection.

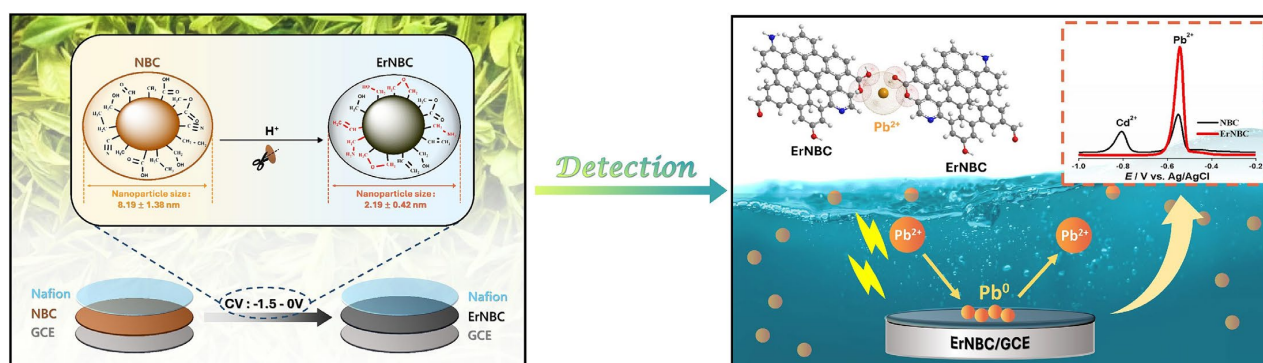


Figure 1. Schematic illustration of the fabrication and application of electrochemically reduced nitrogen-doped biochar (ErNBC) for electrochemical detection of heavy metals. Reproduced with permission from [72]. © 2024 Elsevier B.V.

Similar to previous reports on N-doped BC-based nanocomposites, Sharma et al. fabricated N and S co-doped mesoporous carbon from coconut husk waste [73]. First, the coconut husk was chemically activated using H_2SO_4 and pyrolyzed at 1200 °C under an N_2 atmosphere. Second, thiourea (S source) and melamine (N source) were added and subjected to HTC, which resulted in the formation of abundant functional groups. When drop-casted on a GCE, this displayed enhanced conductivity and electrocatalytic activity. This work presents a straightforward, scalable approach for electrode fabrication using biomass-derived doped carbon materials, resulting in eco-friendly and highly sensitive electrochemical sensors. Similar to previous reports, nanoscale zero-valent iron particles were synthesized using Yerba mate tea extract by Mampane et al. [74], where ferrous sulfate solution was mixed with the tea extract, followed by heating at a range of temperatures from 25 to 85 °C, which resulted in highly stable iron oxide nanoparticles with minimal agglomeration at 25 °C. The nanoparticles were drop-casted over Au screen-printed electrodes, which exhibited enhanced electrochemical activity with low charge transfer resistance and strong redox behavior, making them a suitable material for the electrochemical sensing of Pb^{2+} ions.

The works reviewed so far clearly show the potential of BC-derived materials as a sustainable and effective base for electrochemical sensors. Using various biomass sources and innovative modification methods, which include chemical functionalization, heteroatom doping, nanomaterial integration, and even in situ electrochemical reshaping, researchers have created strong, sensitive, and selective platforms for detecting key heavy metal ions, especially Pb^{2+} . These studies promote green chemistry by using plentiful waste biomass. They also lead to practical, low-cost, and eco-friendly solutions for monitoring

heavy metals in different complex mixtures, further improved by emerging methods like machine learning.

3.2. Cadmium (Cd^{2+})

Cadmium (Cd^{2+}) is a highly toxic and non-essential heavy metal responsible for environmental and human health concerns. Human exposure causes renal dysfunction, skeletal demineralization, pulmonary damage, and carries high cancer risks for the prostate and lungs. It is considered a Group 1 carcinogen by the International Agency for Research on Cancer. It predominantly settles in the kidneys and liver, having a biological half-life of more than one to three decades [75]. Cd^{2+} accumulation in the environment comes from mining, electroplating, the usage of phosphate fertilizers, battery manufacturing, pigment (dye) production, and improper disposal of e-waste [76]. Several approaches have been carried out for its qualitative and quantitative detection, with electrochemical sensors playing a major role. Recently, BC-incorporated electrochemical sensors have gained researchers' interest, and the reported works are discussed as follows (Table 2).

Table 2. Electrochemical sensors for the detection of Cd^{2+} ions.

Biomass Feed	Synthesis Method	Technique	E (V)	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
Green tea extract	Bioextraction	DPASV	-0.75^a	0.05–6.0	0.00101	River water, drinking water	[77]
Sour tea extract	Sol-gel	DPV	-0.9^a	0.02–20	0.00110	Milk, chocolate	[78]
Orange peel	Biological method	SWV	-0.95^a	10–1000	0.00047	-	[79]
<i>Plumeria alba</i>	HTC	DPSV	-0.82^b	0.00996–149.45	8.9×10^{-6}	River water, tap water, rice	[80]
<i>Plumeria alba</i>	Freeze drying	DPSV	-0.82^b	0.0747–9.96	4.98×10^{-5}	-	[81]

a—vs. Ag/AgCl; b—vs. SCE; DPSV—differential pulse stripping voltammetry.

Incebay et al. prepared BC using dry green tea leaves as the source via Soxhlet extraction with ethanol at 30 °C for 2.5 h [77]. The obtained extract was washed repeatedly with ethanol to remove insoluble impurities, leaving behind a clean, bioactive material rich in polyphenols, alkaloids, proteins, and other biofunctional materials. This was then functionalized using multiwalled carbon nanotubes, and this nanocomposite was drop-casted over GCE and further utilized for the electrochemical sensing of Cd^{2+} in river water and drinking water samples. Similar to this work, Jangi and Khoobi used sour tea extract as a natural source for preparing sodium aluminate nanostructures by mixing aluminum nitrate nonahydrate, sodium sulfate, and sour tea extract at 50 °C [78]. To this, ethylenediamine was added to adjust the pH to 10–12, followed by heating at 100 °C to form a gel-like material, which was then calcined at 900 °C for three hours to produce the desired sodium aluminate nanostructures. The obtained gel was then incorporated into a carbon paste matrix and used for the electrochemical sensing of Cd^{2+} ions in milk and chocolate samples.

Rani et al. reported the fabrication of nanoceria (CeO_2 nanoparticles)-based BC using orange peel extract [79], where the orange peels were washed, cut into small pieces, and extracted with deionized water at 90 °C for two hours. Similar to the previous work, the extract was added dropwise to cerium nitrate hexahydrate under continuous magnetic stirring for three hours at a pH between 6.3 and 7.2. The formed nanoceria was separated, washed, and dried at 80 °C for ten hours, followed by calcination at 600 °C for four hours.

This process sustained only the natural antioxidants, namely ascorbic acid, flavonoids, polyphenols, and organic acids, which were responsible for reducing the cerium ions to highly crystalline, cubic nanoceria that exhibited highly sensitive and selective detection of Cd^{2+} ions.

Liang et al. reported the fabrication of two electrochemical sensors for Cd^{2+} detection using *Plumeria alba* flower extract (PAFE) [80,81]. In the first study [80], PAFE was mixed with iron (III) chloride hexahydrate and sodium acetate and subjected to one-pot HTC of iron (III) oxide nanoparticles (at 180 °C for 9 h). Using the same experimental conditions, the reduction of graphene oxide to reduced graphene oxide (rGO) was also performed, resulting in the formation of iron oxide-anchored rGO sheets. The product was separated magnetically, washed, and freeze-dried for 72 h to form a BC with high structural uniformity and electrochemical activity, targeting Cd^{2+} ions. On the contrary, the second report [81] aimed at the synthesis of rGO with iron oxide anchoring, where graphene oxide (synthesized by the modified Marciano method) was reduced using different weight ratios of PAFE under reflux at 110 °C for 8 h at pH 5 (Figure 2). The obtained product was found to be N-doped rGO, which exhibited higher electrochemical performance due to rich restored conjugation and N doping. The BC obtained from the first study was found to possess multifunctionality, namely magnetism and sensing, whereas the second BC was found to possess pure electrochemical activity with higher sensitivity.

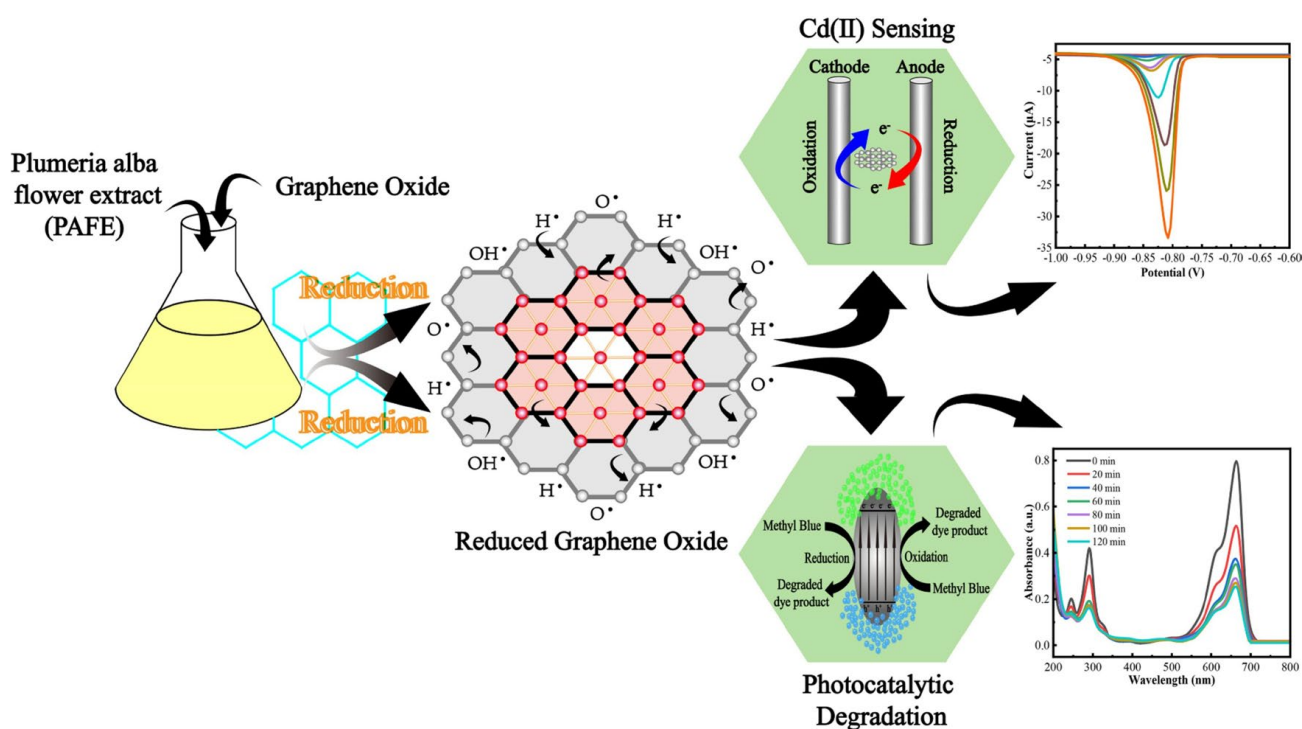


Figure 2. Schematic representation of green synthesis of rGO using PAFE and its electrochemical sensing of Cd(II) ions. Reproduced with permission from [81]. © 2025 Elsevier B.V.

The works presented together show the flexible and significant use of plant-based bioresources in making effective electrochemical sensors for detecting Cd^{2+} . These studies highlight new ways to turn natural extracts and biomass into useful materials, either directly as BC or as templates and reducing agents for creating nanostructures, such as carbon nanotubes, sodium aluminate, nanoceria, and iron oxide-anchored graphene. This green chemistry method produces sensors with improved electrochemical performance, displaying remarkable sensitivity and selectivity for Cd^{2+} in different complex samples, including

environmental waters and food products. The findings highlight the strong potential of sustainable, biomass-focused methods for improving heavy metal detection technologies.

3.3. Mercury (Hg^{2+})

Mercury (Hg^{2+}) is considered one of the most hazardous environmental pollutants, known for its neurotoxic, nephrotoxic, and immunotoxic effects. Among its several forms, divalent mercury, Hg (II), and methylmercury exhibit severe threats to human health owing to their high bioavailability and bioaccumulation potential. Hg^{2+} has the capability to penetrate the blood–brain barrier and placenta, which is responsible for causing irreversible neurological damage, developmental delays, and cognitive impairment in fetuses and children, whereas it causes tremors, memory loss, kidney dysfunction, and cardiovascular diseases in adults [82]. Coal combustion, artisanal gold mining, chloralkali industries, and improper disposal of Hg^{2+} from mercury-containing products, such as thermometers, fluorescent lamps, barometers, and dental fillings, are some of the key sources of environmental Hg^{2+} pollution [83]. The Hg^{2+} , released into the environment, undergoes methylation in the aquatic systems, gets converted to the toxic methylmercury, and subsequently enters the food chain via aquatic species [84]. The determination of Hg^{2+} ions is quite challenging due to their low concentration, complex matrices, and co-existing interferents, which create difficulty in their selective and sensitive detection. Despite these challenges, electrochemical sensors have garnered significant attention for the detection of Hg^{2+} ions. The rich porosity, surface morphology, and tunability of BC help in the rapid adsorption of Hg^{2+} ions present in the samples, making them a green and efficient solution for environmental Hg^{2+} monitoring. The works reported so far in the literature are discussed as follows (Table 3).

Table 3. Electrochemical sensors for the detection of Hg^{2+} ions.

Biomass Feed	Synthesis Method	Technique	E (V)	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
<i>Litsea cubeba</i>	HTC	DPASV	+0.2 ^b	0.000448–4.487	0.00015	Paddy water, apple	[85]
<i>Litsea cubeba</i>	HTC	DPASV	+0.2 ^b	4.99×10^{-6} –4.987	1.50×10^{-6}	Lettuce	[86]
Honeycomb polypore	HTC	DPV	+0.2 ^b	0.05–2	0.002309	Lake water, tap water, sewage water	[87]
<i>Magnolia soulangeana</i> leaves	Pyrolysis	DPASV	+0.12 ^a	0.0005–3.49	0.00015	Lake water	[88]

a—vs. Ag/AgCl ; b—vs. SCE.

Zou et al. reported two electrochemical sensors for the detection of Hg^{2+} using BC derived from *Litsea cubeba* wood, similar to that reported for Pb^{2+} ions [85,86]. In the first study [85], the BC was synthesized by activation pyrolysis at high temperatures (500–800 °C), yielding a highly porous, honeycomb-like structure. On this structure, bismuth molybdate nanosheets were grown *in situ* via the solvothermal reaction of bismuth nitrate and sodium molybdate. In the second study [86], the precursor was initially activated using KOH, followed by impregnation pyrolysis at high temperatures (600–800 °C), which led to the formation of surface oxygen groups, mesopores, and micropores (Figure 3). Subsequently, a copper precursor, such as copper nitrate or sulfate, was reduced to form copper oxide (Cu_2O) nanoparticles. The former work enabled dual sensing and photocatalytic remediation, whereas the latter exhibited excellent electrochemical activity, making it ideal for ultra-trace Hg^{2+} ion sensing.

Hareesha et al. synthesized a highly porous BC from honeycomb polypore biomass waste using a thermal activation method [87]. The shade-dried biomass waste was crushed, washed with concentrated H_2SO_4 and water (to remove impurities), followed by pre-

carbonization at 200 °C for three hours and subsequent chemical activation via soaking in sodium hydroxide (NaOH) for 12 h. The obtained mass was subjected to HTC at 300 °C for four hours, washed, filtered, and oven-dried to obtain NaOH-activated porous carbon nanosheets. These nanosheets were then mixed with graphite powder and Nafion to fabricate the electrodes. These electrodes were found to possess high porosity, conductivity, and an enhanced electroactive surface area, which exhibited improved electrocatalytic performance in both Hg^{2+} ion sensing and water splitting reactions. This fabricated electrode was found to be highly suited for eco-friendly multifunctional energy and sensing applications.

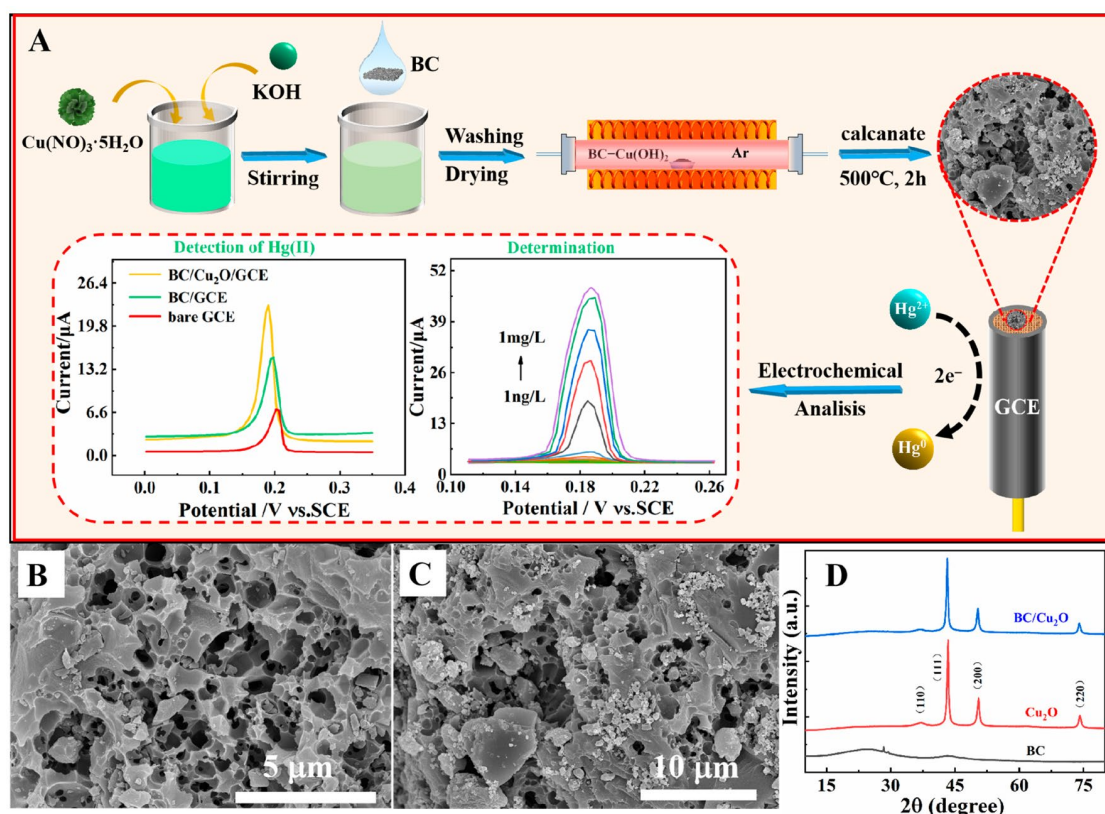


Figure 3. (A) Schematic illustration of the fabrication of BC/Cu₂O/GCE for electrochemical sensing of Hg(II) ions. (B,C) SEM images and (D) XRD analysis of the synthesized BC/Cu₂O. Reproduced with permission from [86]. © 2023 by the authors. Licensee MDPI, Basel, Switzerland.

Zou et al. reported the development of a high-performance electrochemical sensor made from 3D hollow nickel–cobalt layered double hydroxide (NiCo-LDH) nanocages anchored on porous BC [88]. The BC was obtained from *Magnolia soulangeana* leaves and synthesized using a ZIF-67 MOF template-assisted method. The 3D NiCo-LDH/PBC hybrid had a large surface area, many electroactive sites, and excellent electrical conductivity. This allowed for highly sensitive and simultaneous detection of trace levels of Cu²⁺ and Hg²⁺. This work demonstrates the potential of using MOF-derived 3D hollow structures along with sustainable carbon materials in electrochemical sensing platforms.

The studies show how versatile and effective BC-derived materials are for high-performance electrochemical sensing of Hg²⁺ ions. By using different biomass sources and various preparation methods, such as templating with MOFs, high-temperature activation, and chemical functionalization, researchers have created BC-based composites. These include materials like bismuth molybdate, copper oxide, or NiCo-LDH nanocages, along with porous carbon nanosheets. These advancements produce materials with specific porosities, improved conductivity, and many active sites. This leads to highly sensitive and selective platforms that can also be multifunctional, enabling dual sensing, photocatalytic,

or energy applications for detecting low levels of mercury in numerous environmental and biological samples. This research highlights the important role of sustainable biomass in improving electrochemical sensing technologies for environmental monitoring and public health.

3.4. Simultaneous Detection of Heavy Metal Ions

The simultaneous determination of heavy metal ions is significant for environmental monitoring, food safety, and public health, as these ions frequently co-exist and cause synergistic toxic effects. Conventional methods often require sequential analysis, which is time-consuming, requires trained personnel, and may fail to capture the dynamic interactions among the heavy metal ions. In contrast, simultaneous detection ensures rapid, economical, and thorough screening, which comprehensively analyzes heavy metal ions. This is highly valuable for detecting Pb^{2+} , Cd^{2+} , and Hg^{2+} , as they have overlapping toxic thresholds and collectively cause neurotoxicity, nephrotoxicity, and carcinogenic effects even at trace levels [89].

Electrochemical sensors incorporating BC and advanced nanomaterials offer high sensitivity, selectivity, and portability for real-time field analysis. Thus, the development of robust BC-based electrochemical sensors capable of simultaneously detecting heavy metal ions is necessary for monitoring heavy metal contamination in health and the environment. The BC-based electrochemical sensors reported so far in the literature for the simultaneous detection of heavy metal ions are discussed in the following sections (Table 4).

Table 4. Electrochemical sensors for the simultaneous detection of heavy metal ions.

Biomass Feed	Synthesis Method	Technique	E (V)	Target Ions	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
Castor oil cake	Ball milling	DPAdSV	-0.6^a -0.8^a	Pb^{2+} Cd^{2+}	0.05–10 0.25–50	0.0098 0.069	Water	[90]
Castor oil cake	Pyrolysis	DPAdSV	-0.6^a -0.75^a 0.0^a	Pb^{2+} Cd^{2+} Cu^{2+}	-	-	-	[91]
Corn flour	Hydrolysis	SWASV	-0.4^a -0.6^a	Pb^{2+} Cd^{2+}	0.5×10^{-6} – 10×10^{-6} 10×10^{-6} – 100×10^{-6}	1.72×10^{-6} 1.58×10^{-6}	Lake water	[92]
Bacterial cellulose	Freeze drying	DPASV	-0.6^a -0.8^a	Pb^{2+} Cd^{2+}	0.0096–0.4825 0.0178–0.8896	0.001592 0.003380	Tap water Waste water	[93]
<i>Trichoderma asperellum</i>	Ball milling	DPASV	-0.6^a -0.8^a	Pb^{2+} Cd^{2+}	-	0.01 0.1	Water	[94]
OPEFB	Thermolysis	SWASV	-0.5^a -0.8^a 0.0^a -1.1^a	Pb^{2+} Cd^{2+} Cu^{2+} Zn^{2+}	0.0483–0.2413 0.0889–0.4448 0.157–0.787 0.153–0.765	0.00053 0.00098 0.00173 0.00168	Tap water Blood serum Palm oil mill effluent	[95]
Pomelo peels	Thermolysis	SWASV	-0.6^b -0.8^b 0.0^b	Pb^{2+} Cd^{2+} Cu^{2+}	0.025–0.500 0.025–0.500 0.025–0.500	0.00919 0.0209 0.01478	Water	[96]
Kelp	Freeze drying	SWASV	-0.6^b -0.8^b	Pb^{2+} Cd^{2+}	0.01–0.5 0.00445–0.4448	0.01138 0.0233	-	[97]
Spent coffee grounds	Thermolysis	DPASV	-0.4^a -0.65^a	Pb^{2+} Cd^{2+}	30–189 30–269	90 89	-	[98]
<i>Platanus</i>	Microwave-assisted solvothermal pyrolysis	SWASV	-0.55^a -0.8^a	Pb^{2+} Cd^{2+}	0.0024–0.2413 0.0178–0.4448	0.000627 0.000712	Tap water Lake water	[99]
<i>Posidonia oceanica</i>	Pyrolysis	SWASV	-0.55^b -0.8^b	Pb^{2+} Cd^{2+}	0.0096–0.2413 0.01–0.45	0.001005 0.001713	Drinking water	[100]

Table 4. Cont.

Biomass Feed	Synthesis Method	Technique	E (V)	Target Ions	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
Peanut shell	Pyrolysis	DPASV	−0.5 ^a −0.75 ^a	Pb ²⁺ Cd ²⁺	0.1–8 0.06–9	0.008250 0.016	Domestic sewage	[101]
Peanut shell	Pyrolysis	SWASV	−0.55 ^a −0.7 ^a	Pb ²⁺ Cd ²⁺	0.2413–2.413 0.4448–4.448	0.063 0.182	Seawater	[102]
<i>Magnolia grandiflora</i>	Pyrolysis	DPASV	−0.55 ^b +0.13 ^b	Pb ²⁺ Hg ²⁺	0.000014–4.826 0.000015–4.985	0.00000483 0.00000499	River water Paddy water	[103]
Gum arabic	-	DPASV	−0.6 ^a +0.1 ^a −0.1 ^a −1.1 ^a	Pb ²⁺ Hg ²⁺ Cu ²⁺ Zn ²⁺	24.13–1448.55 4.99–997.0 157.4–4723.0 30.58–2293.5	20.26 4.48 151.15 29.06	Farm water	[104]
Orange peel Lemon peel	Bioreduction	SWV	−0.9 ^a +0.05 ^a	Cd ²⁺ Hg ²⁺ Cd ²⁺ Hg ²⁺	2.2–12 2.95–11.8 0.17–1.5 0.12–1.2	0.0270 0.0253 0.0096 0.0135	-	[105]
Banana root bulb	Pyrolysis	DPASV	−0.8 ^a +0.1 ^a	Cd ²⁺ Hg ²⁺	0.01–2 0.06–1.5	0.008 0.003	Lake water	[106]
<i>Mangifera indica</i>	Thermolysis	DPV	−0.75 ^a −0.55 ^a 0.0 ^a +0.25 ^a	Cd ²⁺ Pb ²⁺ Cu ²⁺ Hg ²⁺	0.09–4.8 0.09–5.7 0.09–4.8 0.09–0.99	24.4 0.0057 23.2 0.0246	-	[107]
<i>Hordeum vulgare</i> L.	Thermolysis	DPASV	−0.5 ^a −0.75 ^a +0.1 ^a	Pb ²⁺ Cd ²⁺ Hg ²⁺	0.0002–0.014 0.01–0.085 0.001–0.0115	0.000069 0.001820 0.000237	River water Tap water	[108]
Walnut shell	Pyrolysis	SWV	−0.55 ^b −0.75 ^b 0.0 ^b +0.3 ^b	Pb ²⁺ Cd ²⁺ Cu ²⁺ Hg ²⁺	0.001–0.075 0.001–0.075 0.005–0.075 0.005–0.075	0.000175 0.000086 0.000246 0.000383	River water Soil	[109]
Oak, pine, and peach wood	Pyrolysis	SWV	−0.5 ^a −0.78 ^a 0.22 ^a	Pb ²⁺ Cd ²⁺ Hg ²⁺	0.5–6.0 0.5–6.0 0.5–6.0	0.366 0.09 0.489	Lake water Cucumber	[110]
Starch	HTC	SWASV	−0.6 ^a −0.85 ^a +0.25 ^a	Pb ²⁺ Cd ²⁺ Hg ²⁺	0.25–2 0.25–2 0.25–2	0.00191 0.00138 -	Tap water River water	[111]
<i>Cinnamomum camphoras</i> (L.)	HTC	SWASV	−0.55 ^b −0.75 ^b +0.2 ^b	Pb ²⁺ Cd ²⁺ Hg ²⁺	0.00001–7 0.0001–5 0.0001–3	0.000003 0.000036 0.000011	Tap water Lake water	[112]

a—vs. Ag/AgCl; b—vs. SCE; OPEFB—oil palm empty fruit bunches.

3.4.1. Lead and Cadmium

Suguihiro et al. developed a castor oil cake-derived BC-modified carbon paste electrode (CPE) for the simultaneous detection of Pb²⁺ and Cd²⁺ ions [90]. The castor oil cake was pyrolyzed under different conditions, including heating rate (5–10 °C min^{−1}), temperature range (300–350 °C), and duration (30–60 min). The BC prepared at 300 °C for 60 min with a 10 °C min^{−1} heating rate exhibited the most desired surface functional groups, such as hydroxyl, carboxyl, and nitrogen (N) groups, which in turn enhanced the adsorption of heavy metal ions upon combination with CPE. In a subsequent study [91], the same research group modified the experimental conditions for BC synthesis (pyrolysis temperature = 200–600 °C; heating rate = 5 °C per minute). This modification enhanced the electrocatalytic sensing performance of the BC-CPE and extended the electrochemical sensing capabilities to include Cu²⁺, in addition to Pb²⁺ and Cd²⁺ ions. The change in synthesis conditions resulted in the BC possessing greater aromaticity and higher carbon content. These two studies highlight the significance of optimizing pyrolysis conditions for altering the physical and chemical properties of the target BC.

Zeinu et al. reported the synthesis of bismuth oxide-doped BC for the simultaneous detection of Pb^{2+} and Cd^{2+} ions [92]. Corn flour was first activated with KOH, followed by drying and pre-carbonization at 500 °C under an N_2 atmosphere. This material was then refluxed with H_2O_2 to incorporate oxygen functional groups and to adsorb bismuth from the subsequently added bismuth nitrate, along with carbonization from 500 to 900 °C. The BC carbonized at 900 °C with bismuth modification possessed enhanced graphitization and porosity. This modified BC was then combined with a glassy carbon electrode (GCE) for the electrochemical detection of Pb^{2+} and Cd^{2+} at picomolar levels. Qin et al. synthesized a bacterial cellulose-based BC using a one-step carbonization approach [93]. The freeze-dried bacterial cellulose was subjected to direct carbonization at a temperature of 800 °C for five hours under an N_2 atmosphere. This technique produced a fluffy, lightweight, amorphous carbon nanofiber with a high level of interconnectivity. The obtained carbon was combined with Nafion and coated over a GCE for the electrochemical sensing of Pb^{2+} and Cd^{2+} ions. Similar to the previous work, a fungal biomass-derived BC was prepared by Dali et al. using *Trichoderma asperellum* strains extracted from metal-contaminated soils [94]. The dried fungal biomass, rich in functional groups like carboxyl, hydroxyl, amine, and imidazole, was made into a fine powder using a ball mill. This powder was then mixed with carboxyl-functionalized single-walled carbon nanotubes to improve the surface area and conductivity, and was drop-casted over a GCE to simultaneously detect Pb^{2+} and Cd^{2+} ions.

The same group of scientists from [63] utilized the same oil palm empty fruit bunch (OPEFB)-derived BC (under the same experimental conditions) for the simultaneous detection of Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} [95]. The former study focused more on clinical/biomedical applications by detecting Pb^{2+} in blood serum, whereas the latter focused more on environmental/industrial applications by simultaneously detecting the aforementioned ions in palm oil mill effluent. Zhang et al. used waste pomelo peels as the BC source, decorating them with palladium nanoparticles via a multi-step process [96]. First, the pomelo peels were dried at 80 °C and chemically activated using KOH for 24 h, followed by carbonization at 700 °C for 3 h under an argon atmosphere, which produced porous activated carbon. To this, palladium chloride was added, followed by a second thermal treatment at 900 °C for 3 h under an argon atmosphere, enabling uniform dispersion of palladium nanoparticles over the activated carbon. The obtained modified BC was found to possess a highly graphitic nature and porosity, which enhanced the simultaneous sensing of Pb^{2+} , Cd^{2+} , and Cu^{2+} ions with nanomolar-level detection limits. Following the bacterial cellulose [93] and fungal biomass [94]-derived BC reports, a study on an algal (kelp)-derived BC was carried out by the same group of scientists [97]. Dried kelp was immersed in KOH for chemical activation and freeze-dried for 48 h, followed by carbonization at 900 °C for three hours under an argon atmosphere. This resulted in improved graphitic nature, surface functionality, and enhanced electrochemical performance towards the simultaneous detection of Pb^{2+} and Cd^{2+} ions.

Aldrete et al. utilized spent coffee grounds as the biomass feedstock [98], which underwent extensive pretreatment via washing, drying, milling, and was finally enriched with carboxylic functional groups through the addition of citric acid. The obtained BC was mixed with graphite powder to form an electrode paste, which was then used for the simultaneous detection of Pb^{2+} and Cd^{2+} ions. Zhu et al. reported the incorporation of bismuth nanoparticles onto *Platanus* seeds-derived BC [99]. Initially, the *Platanus* seeds were ultrasonically washed, vacuum-dried, and pre-carbonized at 600 °C under an N_2 atmosphere. This was followed by chemical activation with KOH and high-temperature pyrolysis at 900 °C, which resulted in a lotus-root-shaped porous BC. The BC was further subjected to microwave-assisted solvothermal deposition of bismuth nanoparticles from bismuth oxide,

followed by carbothermal reduction at 500 °C, producing the desired bismuth-decorated BC for the simultaneous detection of Pb^{2+} and Cd^{2+} ions.

A nanoscale zero-valent iron nanoparticle-decorated BC was synthesized by Djebbi et al. using the marine biomass *Posidonia oceanica* [100]. The marine biomass was ultrasonically washed, dried, powdered, soaked in KOH solution, and carbonized at 700 °C under an N_2 atmosphere, followed by acid-washing and drying (Figure 4). Simultaneously, the iron nanoparticles were synthesized and incorporated onto the BC through liquid-phase reduction with sodium borohydride. The obtained nanocomposite was found to possess a high surface area and conductivity, making it suitable for the simultaneous detection of Pb^{2+} and Cd^{2+} ions.

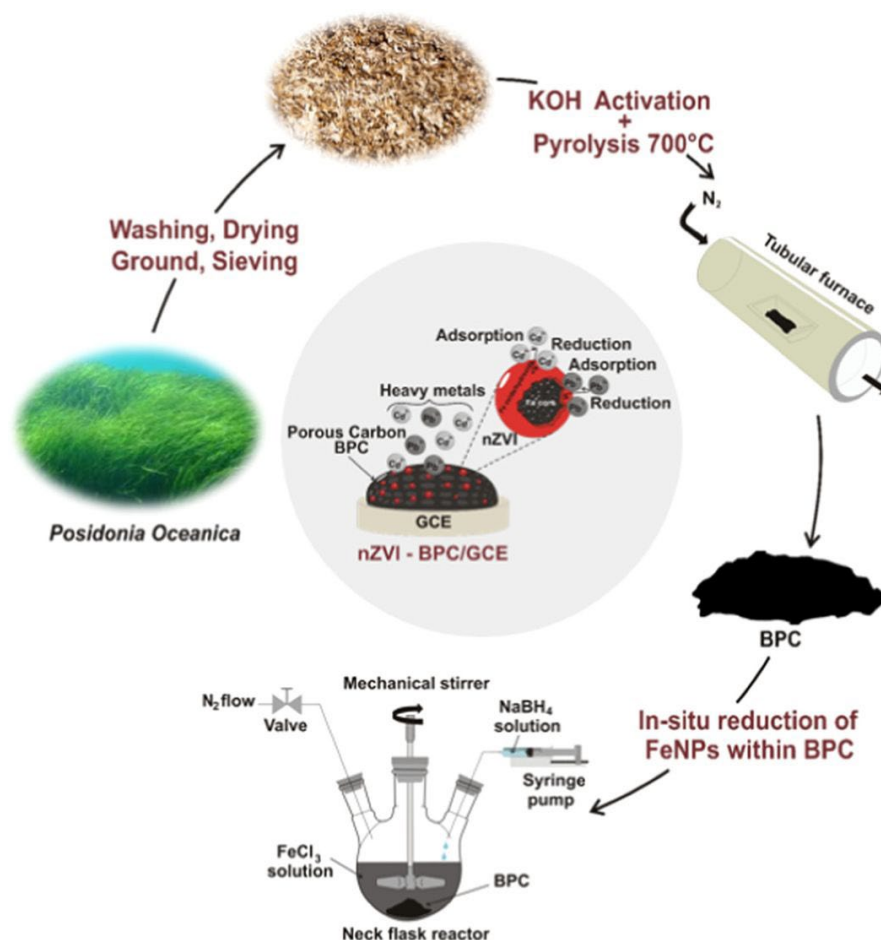


Figure 4. Schematic representation of synthesis and application of nanoscale zero-valent iron-biochar composite obtained using *Posidonia oceanica* for simultaneous detection of $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ ions. Reproduced with permission from [100]. © 2022 American Chemical Society.

Xu et al. [101] reported a peanut shell-derived BC for a zeolitic imidazolate framework. In their method, the peanut shells were washed, dried, powdered, pre-carbonized at 300 °C, chemically activated using KOH, carbonized at 700 °C under a nitrogen atmosphere, and finally treated with H_2SO_4 to incorporate in situ self-assembly of the zeolitic imidazolate framework. This material exhibited high sensitivity and selectivity towards the simultaneous detection of Pb^{2+} and Cd^{2+} ions. In all the aforementioned reports, the significance of optimizing the pyrolysis temperature and chemical activation with KOH was evidenced by the high electrochemical performance obtained during the simultaneous detection of Pb^{2+} and Cd^{2+} ions.

Mosquera-Ortega et al. described an affordable, scalable way to create flexible plastic electrodes using BC from peanut shells, which is a plentiful agricultural byproduct [102].

They produced the BC in a custom kiln and modified it with chitosan and NaOH to improve its porosity, water affinity, and surface features. They then incorporated these chitosan-BC composites into plastic electrode films through a straightforward casting method using blends of polyvinyl chloride and graphite. This process allows for large-scale production under normal conditions. They further enhanced performance by depositing bismuth, achieving ultra-low LODs for lead and cadmium, well below the World Health Organization and Environmental Protection Agency regulatory limits. Additionally, the fabrication process followed the principles of green analytical chemistry, earning a higher AGREE score (0.75) than traditional pyrolysis methods. This study showed that peanut shell BC could be a sustainable and versatile base for eco-friendly heavy metal sensors of the future.

3.4.2. Lead and Mercury

A zirconium MOF-incorporated BC, designated as UiO-66-NH₂/BC, was prepared by Zou et al. [103]. The BC precursor, *Magnolia grandiflora* fruit, was washed, dried, powdered, chemically activated using KOH, and pyrolyzed at 800 °C under an N₂ atmosphere, yielding a BC with a high surface area and rough porous texture (Figure 5). The zirconium MOF was added to the BC via a layer-by-layer approach on a GCE, offering enhanced simultaneous electrochemical detection of Pb²⁺ and Hg²⁺ ions. Separately, Elamin et al. reported a BC using gum arabic (a natural biopolymer) as a green reducing and stabilizing agent for synthesizing platinum nanoparticles [104]. Chloroplatinic acid (a platinum precursor) and gum arabic were mixed and stirred at 60 °C for 24 h, which enabled the in situ reduction and encapsulation of platinum nanoparticles by the gum arabic biopolymer. Screen-printed electrodes modified with this nanocomposite were used for the simultaneous detection of Pb²⁺ and Hg²⁺ ions.

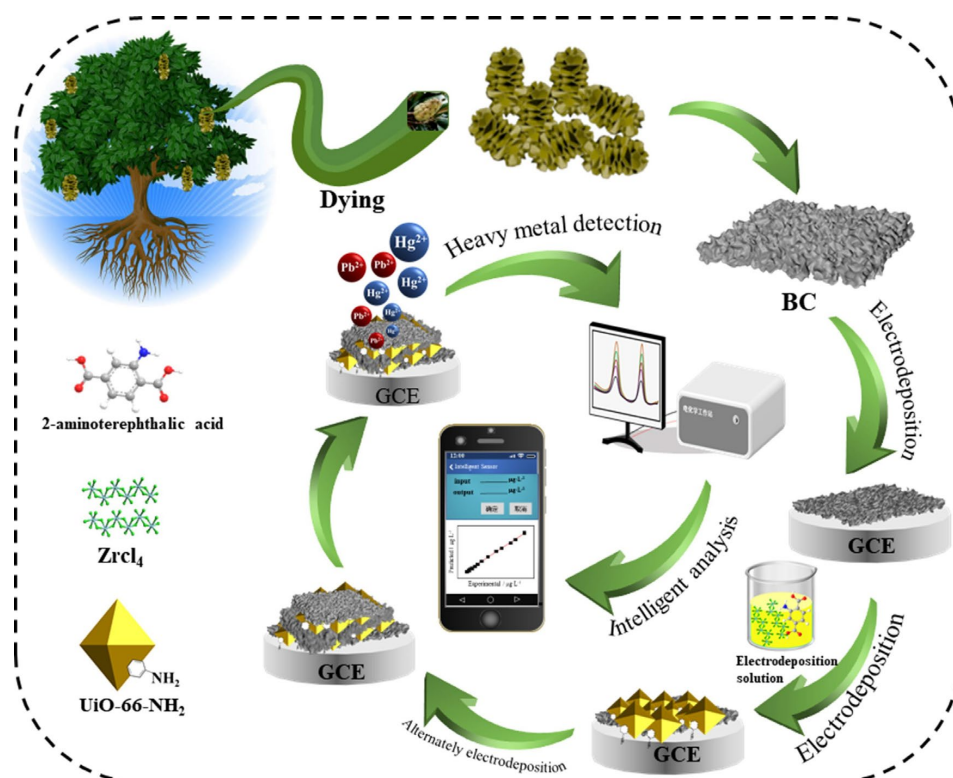


Figure 5. Schematic illustration of the synthesis and application of UiO-66-NH₂/BC-modified GCE for simultaneous detection of Pb(II) and Hg(II) ions. Reproduced with permission from [103]. © 2021 Elsevier B.V.

3.4.3. Cadmium and Mercury

Citrus fruit peel (lemon and orange) extracts were used by Okpara et al. for the formation of copper and zinc oxides from their respective precursors [105]. The salt solutions of copper and zinc precursors were heated from 60 to 100 °C with continuous magnetic stirring. To these, the citrus peel extracts were added, followed by NaOH to adjust the pH to a basic medium, enabling faster reduction and stabilization of the Cu₂O and zinc oxide nanoparticles. The obtained material was washed, centrifuged, and oven-dried (>200 °C), after which polyaniline (PANI) was incorporated before its modification onto a screen-printed electrode. The fabricated modified electrode exhibited the simultaneous detection of Cd²⁺ and Hg²⁺ ions with high sensitivity and selectivity. Doloi et al. fabricated a silver oxide nanoparticle-decorated zirconium MOF nanocomposite using banana root bulb as a natural reducing agent for silver oxide [106]. First, a zirconium MOF was prepared using the solvothermal route with zirconium chloride and benzene dicarboxylic acid as precursors (Figure 6). Second, to this MOF, silver nitrate was added and boiled, followed by the addition of banana root bulb extract, which led to the in situ reduction and formation of silver oxide nanoparticles on the MOF. This was then annealed at 100 °C to obtain the desired nanocomposite. This nanocomposite-based electrochemical sensor exhibited the simultaneous detection of Cd²⁺ and Hg²⁺ ions.

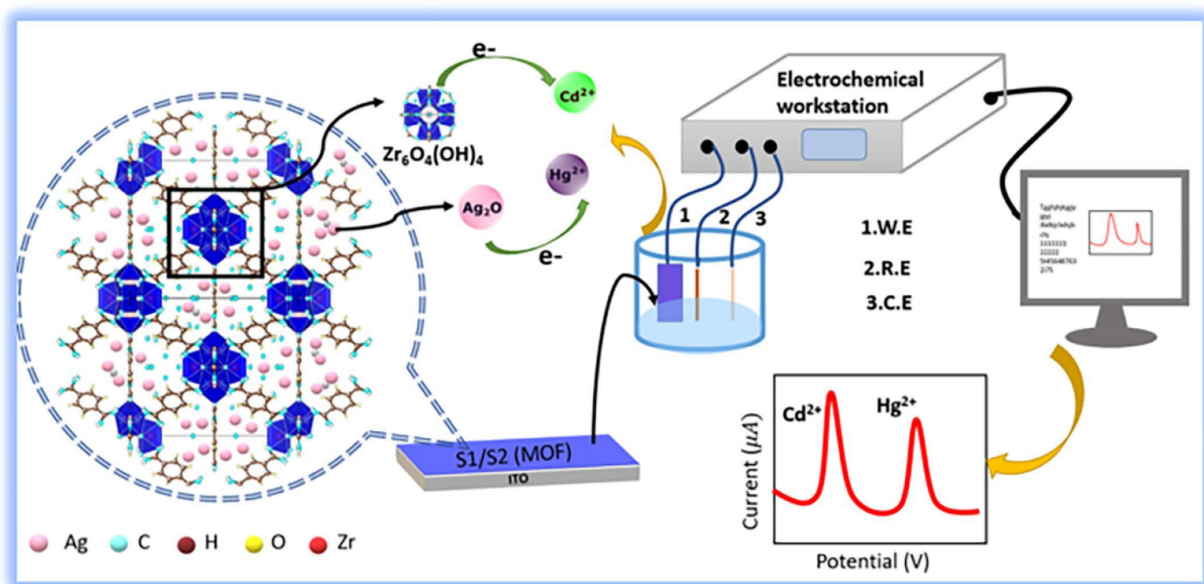


Figure 6. Schematic representation of a banana root bulb-derived MOF-based electrochemical sensing platform for the simultaneous detection of Cd(II) and Hg(II) ions. Reproduced with permission from [106]. © 2023 Elsevier Ltd., Amsterdam, The Netherlands.

3.4.4. Lead, Cadmium, and Mercury

Madhu et al. utilized dead mango leaves for the synthesis of spherical nanoparticle-decorated BC that simultaneously detected Pb²⁺, Cd²⁺, Cu²⁺, and Hg²⁺ [107]. The mango leaves were dried, pulverized, and chemically activated using KOH under an N₂ atmosphere by pyrolyzing them at different temperatures (700, 800, and 900 °C) for two hours at a heating rate of 10 °C min^{−1}. The resulting material was then washed with HCl and water, dried, and ground. Subsequent characterization revealed that the BC synthesized at 900 °C possessed a higher surface area and pore volume, which in turn enhanced the electrochemical sensing behavior upon coating over a GCE. A byproduct from the brewing industry, barley dust, was used for BC preparation by Djemmoe et al. [108]. The first step involved chemical activation with sodium carbonate upon continuous stirring for three

hours, followed by washing to a neutral pH and drying at 105 °C. This material was further made into a carbon paste electrode (CPE) for the simultaneous detection of Pb^{2+} , Cd^{2+} , and Hg^{2+} ions. Walnut shells were used for BC synthesis by Hamdouni et al. [109] through cleaning, drying at 105 °C for 24 h, grinding, and pyrolyzing at 600 °C for 2 h under vacuum. The obtained BC was found to have a higher carbon content and was modified into a CPE by mixing with a poly-tyrosine film, which resulted in increased surface functionality and conductivity. This was extended to the simultaneous electrochemical detection of Pb^{2+} , Cd^{2+} , Hg^{2+} , and Cu^{2+} ions.

Oak wood biomass was prepared by Pu et al. [110] by heating the BC, which was soaked in auric chloride solution, at 850 °C for two hours under an N_2 atmosphere at a slow heating rate of 2 °C min^{-1} , followed by treatment with HCl, water, ethanol, and drying at 60 °C. The obtained BC was found to be porous, thermally stable, and to exhibit a lotus-root-like microstructure. Lastly, this BC was modified into a CPE and used for the simultaneous detection of Pb^{2+} , Cd^{2+} , and Hg^{2+} ions. Li et al. used starch as the BC precursor, which was doped with N and S using thiourea as the source. These were subjected to HTC and fast pyrolysis [111]. Starch and thiourea were heated at 180 °C for 5 h, followed by carbonization at 800 °C in an N_2 atmosphere and intermediate pre-carbonization at 300 °C (Figure 7). The obtained BC was used for the simultaneous detection of Pb^{2+} , Cd^{2+} , and Hg^{2+} ions and demonstrated the critical role of HTC doping and high-temperature carbonization in the synthesis of BC. Similar to the previous work, Huang et al. prepared a multi-doped porous BC from *Cinnamomum camphora* branches [112] by HTC using H_3PO_4 as a chemical activator and Pluronic F127 as a porogen. The chemical activator enabled P-doping, and the material was further doped with Fe_3O_4 nanoparticles (by chemical precipitation) and attapulgite clay, which increased its magnetic properties, ion exchange capacity, and surface area. Subsequently, the BC was doped with a bismuth film via electrodeposition, and the resulting sensor was integrated with a smartphone-operated wireless device, exhibiting simultaneous detection of Pb^{2+} , Cd^{2+} , and Hg^{2+} ions with ultra-low detection limits for field deployment.

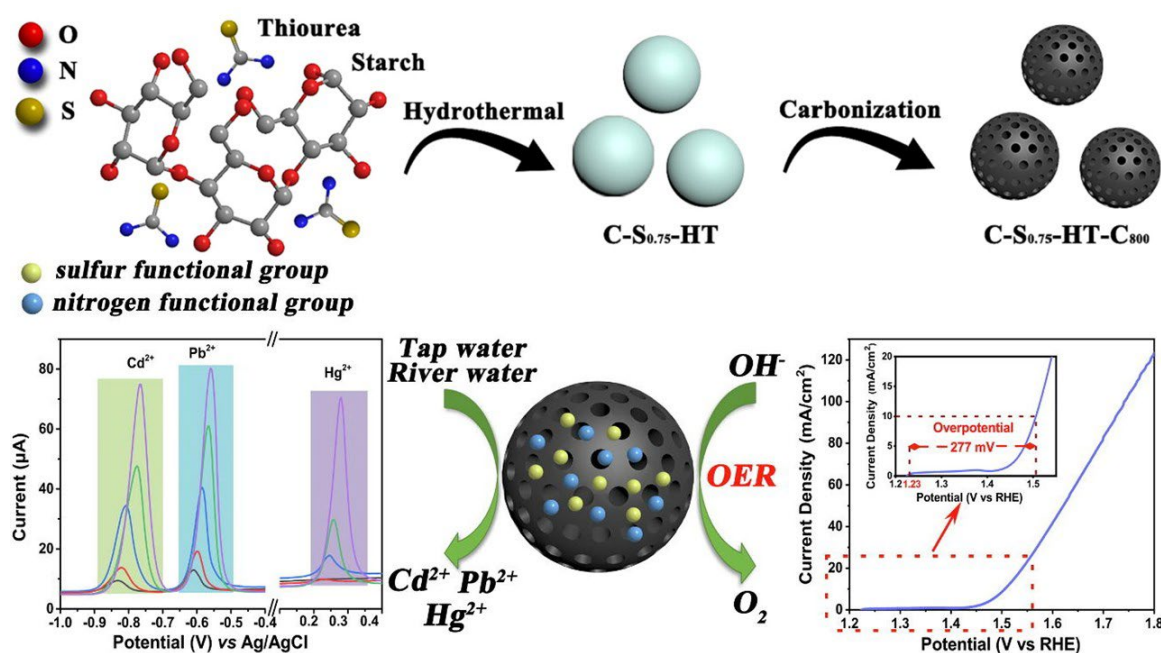


Figure 7. Schematic representation of the synthesis of N, S-co-doped BC derived from starch and its application for the simultaneous detection of Pb(II), Cd(II), and Hg(II) ions. Reproduced with permission from [111]. © 2023 Elsevier Inc.

Overall, this review highlights several research vignettes demonstrating how BC-derived electrochemical sensors detect trace amounts of heavy metals. For instance, the BCs created by Mojica et al. [60], Li et al. [64], and Agustini et al. [61] demonstrate that when BC's surface chemistry and porosity are activated, they improve the sensitivity, selectivity, and strong detection of Pb^{2+} . This often occurs in real, complex mixtures like groundwater, ceramics, and biological fluids. Radotić et al. [68] and Su et al. [72] support the benefits of green synthesis and processing through minimal energy use or direct modification of the electrode surface. This approach promotes sustainability while achieving effective sensing performance. Sharma et al. [73] and Mamatha et al. [71] focus on modification strategies, particularly doping and adding nanoparticles, as essential for adjusting sensor selectivity, sensitivity, and resilience against interference in complex environments. Suguihiro et al. [90], Zeinu et al. [92], and Qin et al. [93] show BC's flexibility in multi-ion sensing platforms. Surface tuning, such as activation, doping, and integrating nanomaterials, enables cost-effective and portable solutions for environmental monitoring. Jangi and Khoobi [78], Rani et al. [79], and Zou et al. [85,86] utilize plant extracts and natural compounds in sensor construction. This method enables the green synthesis of nanomaterials and supports circular economy models, increasing the practical relevance and sustainability of sensor platforms. Su et al. and Huang et al. combine BC's material benefits with improved signal processing and mobile technologies. These examples indicate a shift toward the next generation of intelligent, low-cost, and widely accessible environmental sensors. Through tailored production, functional improvement, and smart technology integration, research shows the significant potential for sensitive, selective, eco-friendly heavy metal detection, supported by practical studies from real-world environmental and biological settings.

A summary of all the works included in this review is given in Table 5. This extensive research highlights the impressive flexibility and importance of biochar (BC) in developing high-performance electrochemical sensors. These sensors can detect multiple heavy metal ions, including Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , and Hg^{2+} . The studies show that by carefully adjusting the synthesis conditions—such as pyrolysis parameters and chemical activation with substances like KOH or citric acid, and by strategically adding different nanomaterials like bismuth, palladium, iron, platinum, copper, silver, nickel-cobalt LDH, MOFs, and carbon nanotubes—biochar's properties can be improved. This optimization enhances porosity, conductivity, surface functionality, and electrocatalytic activity. Using a variety of sustainable biomass sources not only helps create sensitive, selective, and often multi-functional sensors but also points to a clear path for eco-friendly and practical solutions for environmental monitoring and health diagnostics. This includes real-world applications and potential integration with smart technologies.

Table 5. Summary of the works reported in this review.

Biomass Feed	Target Ions	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
<i>Pennisetum setosum</i>	Pb^{2+}	-	0.048	Groundwater, canal water	[59]
Banana tissue	Pb^{2+}	4.8–96.5	0.483	Water	[60]
Castor oil cake	Pb^{2+}	0.005–1.0	0.001	Ceramic dishes	[61]
<i>Cladophora rupestris</i>	Pb^{2+}	0.96–4.83	0.35	-	[62]
Oil palm empty fruit bunches	Pb^{2+}	0.048–0.29	0.001	Blood serum	[63]
Bayberry kernel	Pb^{2+}	48.3–3861	~0.0002	-	[64]
Almond shells	Pb^{2+}	9.65–579.15	3.4	Tap water	[65]
<i>Acacia senegal</i>	Pb^{2+}	4.826–48.26	2.442	Plastic toys	[66]

Table 5. Cont.

Biomass Feed	Target Ions	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
<i>Benincasa hispida</i> + <i>Holstein Friesian</i>	Pb ²⁺	2.4–482.6	0.965	Tap water, lake water	[67]
<i>Zea mays</i> L.	Pb ²⁺	0.1–5.0	0.02	Tap water	[68]
Spent coffee grounds	Pb ²⁺	0.128–2.44	0.004	Gunshot residues Hair dye	[69]
<i>Litsea cubeba</i>	Pb ²⁺	14.5–4.8	0.000005	Paddy water	[70]
<i>Centella Asiatica</i>	Pb ²⁺	-	-	-	[71]
Tea residue	Pb ²⁺	0.386–5.791	0.002365	River water, farmland water	[72]
Coconut husk	Pb ²⁺	0.06–0.14	0.022	Tap water	[73]
Yerba-mate tea extracts	Pb ²⁺	0.027–0.034	0.012	-	[74]
Green tea extract	Cd ²⁺	0.05–6.0	0.00101	River water, drinking water	[77]
Sour tea extract	Cd ²⁺	0.02–20	0.00110	Milk, chocolate	[78]
Orange peel	Cd ²⁺	10–1000	0.00047	-	[79]
<i>Plumeria alba</i>	Cd ²⁺	0.00996–149.45	8.9×10^{-6}	River water, tap water, rice	[80]
<i>Plumeria alba</i>	Cd ²⁺	0.0747–9.96	4.98×10^{-5}	-	[81]
<i>Litsea cubeba</i>	Hg ²⁺	0.000448–4.487	0.00015	Paddy water, apple	[85]
<i>Litsea cubeba</i>	Hg ²⁺	4.99×10^{-6} –4.987	1.50×10^{-6}	Lettuce	[86]
Honeycomb polypore	Hg ²⁺	0.05–2	0.002309	Lake water, tap water, sewage water	[87]
<i>Magnolia soulangeana</i> leaves	Hg ²⁺	0.0005 to 3.49	0.00015 μM	Lake water	[88]
Castor oil cake	Pb ²⁺	0.05–10	0.0098	Water	[90]
	Cd ²⁺	0.25–50	0.069		
Castor oil cake	Pb ²⁺ Cd ²⁺ Cu ²⁺	-	-	-	[91]
Corn flour	Pb ²⁺	0.5×10^{-6} –	1.72×10^{-6} 1.58×10^{-6}	Lake water	[92]
	Cd ²⁺	10×10^{-6} – 10×10^{-6} – 100×10^{-6}			
Bacterial cellulose	Pb ²⁺	0.0096–0.4825	0.001592	Tap water	[93]
	Cd ²⁺	0.0178–0.8896	0.003380	Waste water	
<i>Trichoderma asperellum</i>	Pb ²⁺	-	0.01	Water	[94]
	Cd ²⁺		0.1		
OPEFB	Pb ²⁺	0.0483–0.2413	0.00053	Tap water Blood serum Palm oil mill effluent	[95]
	Cd ²⁺	0.0889–0.4448	0.00098		
	Cu ²⁺	0.157–0.787	0.00173		
	Zn ²⁺	0.153–0.765	0.00168		
Pomelo peels	Pb ²⁺	0.025–0.500	0.00919	Water	[96]
	Cd ²⁺	0.025–0.500	0.0209		
	Cu ²⁺	0.025–0.500	0.01478		
Kelp	Pb ²⁺	0.01–0.5	0.01138	-	[97]
	Cd ²⁺	0.00445–0.4448	0.0233		
Spent coffee grounds	Pb ²⁺	30–189	90	-	[98]
	Cd ²⁺	30–269	89		

Table 5. Cont.

Biomass Feed	Target Ions	Linear Range (μM)	LOD (μM)	Real Sample	Ref.
<i>Platanus</i>	Pb ²⁺	0.0024–0.2413	0.000627	Tap water	[99]
	Cd ²⁺	0.0178–0.4448	0.000712	Lake water	
<i>Posidonia oceanica</i>	Pb ²⁺	0.0096–0.2413	0.001005	Drinking water	[100]
	Cd ²⁺	0.01–0.45	0.001713		
Peanut shell	Pb ²⁺	0.1–8	0.008250	Domestic sewage	[101]
	Cd ²⁺	0.06–9	0.016		
Peanut shell	Pb ²⁺	0.2413–2.413	0.063	Seawater	[102]
	Cd ²⁺	0.4448–4.448	0.182		
<i>Magnolia grandiflora</i>	Pb ²⁺	0.000014–4.826	0.00000483	River water	[103]
	Hg ²⁺	0.000015–4.985	0.00000499	Paddy water	
Gum arabic	Pb ²⁺	24.13–1448.55	20.26	Farm water	[104]
	Hg ²⁺	4.99–997.0	4.48		
	Cu ²⁺	157.4–4723.0	151.15		
	Zn ²⁺	30.58–2293.5	29.06		
Orange peel Lemon peel	Cd ²⁺	2.2–12	0.0270	-	[105]
	Hg ²⁺	2.95–11.8	0.0253		
	Cd ²⁺	0.17–1.5	0.0096		
	Hg ²⁺	0.12–1.2	0.0135		
Banana root bulb	Cd ²⁺	0.01–2	0.008	Lake water	[106]
	Hg ²⁺	0.06–1.5	0.003		
<i>Mangifera indica</i>	Cd ²⁺	0.09–4.8	24.4	-	[107]
	Pb ²⁺	0.09–5.7	0.0057		
	Cu ²⁺	0.09–4.8	23.2		
	Hg ²⁺	0.09–0.99	0.0246		
<i>Hordeum vulgare</i> L.	Pb ²⁺	0.0002–0.014	0.000069	River water Tap water	[108]
	Cd ²⁺	0.01–0.085	0.001820		
	Hg ²⁺	0.001–0.0115	0.000237		
Walnut shell	Pb ²⁺	0.001–0.075	0.000175	River water Soil	[109]
	Cd ²⁺	0.001–0.075	0.000086		
	Cu ²⁺	0.005–0.075	0.000246		
	Hg ²⁺	0.005–0.075	0.000383		
Oak, pine, and peach wood	Pb ²⁺	0.5–6.0	0.366	Lake water Cucumber	[110]
	Cd ²⁺	0.5–6.0	0.09		
	Hg ²⁺	0.5–6.0	0.489		
Starch	Pb ²⁺	0.25–2	0.00191	Tap water River water	[111]
	Cd ²⁺	0.25–2	0.00138		
	Hg ²⁺	0.25–2	-		
<i>Cinnamomum camphoras</i> (L.)	Pb ²⁺	0.00001–7	0.000003	Tap water Lake water	[112]
	Cd ²⁺	0.0001–5	0.000036		
	Hg ²⁺	0.0001–3	0.000011		

3.5. Comparative Evaluation of Electrochemical Techniques in Biochar-Based Heavy Metal Detection

Various electrochemical techniques, including DPASV, SWASV, SWV, DPV, DPSV, and CV, have been extensively used in BC-modified sensor platforms to analyze trace metal ions. Each method offers specific advantages suited to different sensing conditions. Among these techniques, SWASV and DPASV are the most-used electroanalytical methods for detecting trace heavy metals with BC-based sensors. They are recognized for their high sensitivity, selectivity, and ease of operation. Both involve a pre-concentration step combined with sensitive voltammetric detection, enabling detection limits from sub-micromolar to nanomolar levels. This is shown in several studies summarized in Table 3. For example,

BC made from OPEFB reached a limit of detection (LOD) of 0.001 μM for Cd^{2+} ions using SWASV [95]. Similarly, BC from castor oil cake demonstrated comparable sensitivity for Pb^{2+} with an LOD of 0.001 μM using DPASV [90]. These low detection limits, along with wide linear ranges (e.g., 0.088–0.44 μM and 0.05–10 μM), underscore the effectiveness of these voltammetric methods for analyzing environmental and biological samples, including blood serum, groundwater, and ceramic surfaces. SWASV offers several benefits, such as a fast scan rate, low capacitive background currents, and enhanced selectivity. These features make it particularly suitable for real-time and on-site measurements. It is especially effective for detecting multiple ions at once, as shown by BC platforms that identify Pb^{2+} , Cd^{2+} , and Cu^{2+} in complex samples like lake water and palm oil mill effluent [109]. Conversely, DPASV provides excellent resolution and peak separation for redox processes that are closely spaced. This allows for high precision even in samples containing interfering substances. DPASV is also more tolerant of small variations in experimental conditions and is often preferred for preparing modified electrodes through green and reproducible methods, such as using HTC-derived BC from almond shells [65] or *Litsea cubeba* [85,86].

However, both techniques have their limitations. The pre-concentration step relies on the surface, making the reproducibility of fabrication and electrode fouling major challenges—particularly when used repeatedly in complex samples like farm water and domestic sewage. Additionally, both SWASV and DPASV require careful adjustment of parameters such as pulse amplitude, frequency, and accumulation time, which can vary depending on different BC matrices and target ions. Another issue is the overlap of peak potentials among some metal ions, such as Pb^{2+} and Cd^{2+} , which can compromise the accuracy of multi-ion detection unless advanced deconvolution or masking techniques are applied. Furthermore, while many studies utilize non-toxic carbon-based electrodes, some still employ mercury-based film electrodes, raising concerns about sustainability and safety. In contrast, SWV and DPV offer moderate to high sensitivity and are generally easier to implement. They are often used when the simultaneous detection of multiple ions is not necessary. Their shorter acquisition times and simple waveform generation make them suitable for low-resource sensing platforms. DPASV, though less frequently reported, has shown promising results with complex BC matrices in detecting heavy metals at ultra-trace levels. Studies using *Plumeria alba* [80,81] and walnut shell [109] biomass support this finding. CV is not ideal for detailed quantitative analysis but remains valuable for initial explorations of redox behavior and surface interactions between the BC electrode and metal ions. Researchers often use CV to characterize the electrochemical active surface area and to verify the presence of redox-active functional groups or pathways involved in metal ion interactions on BC-modified electrodes. Although CV helps study mechanisms, it lacks the sensitivity needed to detect ions at environmentally relevant levels. Peak overlap also presents a significant challenge during multi-metal analysis, often requiring complexing agents or advanced deconvolution algorithms. In conclusion, selecting and optimizing these voltammetric techniques, along with tailored biochar synthesis methods like pyrolysis or HTC, allows for the development of versatile and sustainable electrochemical sensors. Each technique contributes differently to sensitivity, selectivity, speed, and practicality, making their combined use crucial in metal ion sensor research.

4. Conclusions

Biochar-based electrochemical sensors have emerged as a promising and sustainable alternative for the determination of trace heavy metal ions owing to their low cost, high sensitivity, rapid response, and portable nature. Biochar has a high surface area and porosity, providing many active sites that are important for effectively adsorbing heavy metal ions and facilitating electrochemical reactions. Additionally, its properties can be

modified through controlled pyrolysis, and it generally has good conductivity, especially after carbonization. This makes it a flexible platform. However, specific modifications come with their limitations. For instance, the surface functionalization methods like crosslink-xanthate or nitric acid activation improve the adsorption and binding of metal ions by adding specific functional groups such as hydroxyl, carboxyl, nitrogen, and oxygen but also include increased complexity in synthesis, the risk of leaching active components over time, and difficulties with large-scale production. Similarly, the integration of nanomaterials, like bismuth, palladium, iron oxides, or carbon nanotubes, has synergistic effects, merging biochar's base properties with the unique catalytic activities and high surface areas of nanoparticles; however, these methods typically require complex, multi-step, and sometimes energy-consuming synthesis processes. Costs can rise, especially with noble metal nanoparticles, and there are concerns about the long-term stability and potential clumping of the added nanoparticles. Heteroatom doping, which involves adding elements like nitrogen or sulfur into the biochar matrix, improves the material's electronic structure, enhances conductivity, improves wettability, and can even provide selectivity for specific ions. While some doping methods can be relatively simple, precisely controlling the type and level of doping remains challenging, and the stability of some heteroatom features at high temperatures must be considered. Optimizing pyrolysis conditions—such as temperature, heating rate, atmosphere, and pre-treatment—is crucial because it directly affects important biochar properties like surface area, porosity, and carbon content. This method is cost-effective and straightforward for creating the base material. However, pyrolysis alone may not provide the extreme sensitivity or selectivity that more complex modifications can achieve, and high-temperature processes consume a lot of energy. On the other hand, non-pyrolyzed or green extraction methods, such as using maize stems or tea leaves, are notable for their low energy usage and eco-friendliness. They also retain natural bioactive compounds with useful functional groups. The trade-offs include potentially lower carbon content and conductivity compared to carbonized biochar, reduced chemical and thermal stability, and generally higher detection limits. Finally, electrochemical reshaping, like in situ reshaped nano-biochar, offers an innovative approach. Its main benefits are on-site modifications on the electrode surface, which simplify fabrication, and major improvements in properties such as smaller particle size, better conductivity, and increased hydrophilicity. This method also shows potential for integration with machine learning. The key limitations are its potential specificity to certain biochar types and current challenges in scaling up direct electrode reshaping compared to bulk material synthesis. Ultimately, choosing how to modify biochar requires balancing cost with performance, balancing simplicity in synthesis against the achievable sensitivity and selectivity, and maintaining overall sustainability without sacrificing efficiency. The ultimate goal is to use biochar's potential to create effective and eco-friendly solutions for heavy metal sensing.

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Abbreviations

The following abbreviations are used in this manuscript:

AAS	Atomic Absorption Spectroscopy
DPA _{AdSV}	Adsorptive Stripping Differential Pulse Voltammetry
As ³⁺	Arsenic
BC	Biochar
B	Boron
Cd ²⁺ /Cd(II)	Cadmium
CPE	Carbon Paste Electrode
Cu ₂ O	Copper Oxide
CV	Cyclic Voltammetry
DPSV	Differential Pulse Stripping Voltammetry
DPV	Differential Pulse Voltammetry
ErNBC	Electrochemically reshaped nano-BC
GCE	Glassy Carbon Electrode
GHG	Greenhouse Gas
Au	Gold
HCl	Hydrochloric Acid
HTC	Hydrothermal Carbonization
Hap	Hydroxyapatite
ICP-MS	Induction-Coupled Plasma-Mass Spectrometry
Pb ²⁺ /Pb(II)	Lead
LCA	Life Cycle Assessment
LOD	Limit of Detection
Fe ₃ O ₄	Magnetic Iron Oxide
Hg ²⁺ /Hg(II)	Mercury
MOF	Metal Organic Framework
CeO ₂ nanoparticles	Nanoceria
N/N ₂	Nitrogen
OPEFB	Oil Palm Empty Fruit Bunches
H ₃ PO ₄	Phosphoric Acid
P	Phosphorus
PAFE	Plumeria alba Flower Extract
PANI	Polyaniline
KOH	Potassium Hydroxide
rGO	Reduced Graphene Oxide
NaOH	Sodium Hydroxide
SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
S	Sulfur
H ₂ SO ₄	Sulfuric acid
TiO ₂	Titanium Oxide
XRF	X-Ray Fluorescence
UiO-66-NH ₂ /BC	Zirconium MOF Incorporated BC

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