

Magnetic Biochar-Based Electrocatalytic Sensor for Sensitive Detection of Trace Pb²⁺ in Water

Zhepeng Zhao,^a Hai Bo,^{a,b,*} and Lijun Ding^{a,b,*}

Monitoring Pb²⁺ levels is essential for aquatic environmental safety. Compared to conventional methods, electrochemical sensors offer a low-cost and efficient alternative for trace heavy metal analysis, with electrocatalytic sensing strategies playing a key role in signal amplification. While biochar (BC) is a promising electrode modifier due to its porous structure and surface functionalization, its application is often restricted by low conductivity. Herein, magnetic biochar (MBC) was prepared *via* co-precipitation and utilized to fabricate a modified glassy carbon electrode (MBC/GCE). Characterization of MBC revealed an excellent pore structure and a specific surface area of 120 m²/g, markedly higher than that of BC. This increased surface area offers abundant active sites for the adsorption and preconcentration of Pb²⁺ ions, significantly enhancing the subsequent electrocatalytic reduction process. Electrochemical characterization, including electrocatalytic activity evaluation, showed that the MBC/GCE substantially decreased charge transfer resistance and promotes the redox kinetics of Pb²⁺. Under optimized conditions, the platform exhibited high sensitivity toward Pb²⁺ within a linear range defined by $I = 6.34 + 64.5C$ ($R^2 = 0.996$), achieving a detection limit of 68 nmol/L. These results highlight the potential of MBC/GCE as an effective electrocatalytic sensing platform for Pb²⁺ monitoring in water.

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INTRODUCTION

Lead (Pb²⁺) is a pervasive and highly toxic heavy metal pollutant that poses a formidable threat to human health and ecological integrity. Due to its non-biodegradability and high bioaccumulation factor, Pb²⁺ enters the human body through pathways such as contaminated drinking water, soil, and atmospheric dust (Kumar *et al.* 2020). Once ingested, it accumulates in vital organs—including the skeletal system, liver, and kidneys—with a biological half-life spanning decades. Chronic exposure is clinically linked to neurological impairments, renal dysfunction, hypertension, and cognitive developmental delays (Bellinger 2011). Consequently, developing rapid, sensitive, and cost-effective analytical platforms for Pb²⁺ monitoring is imperative for environmental surveillance and public health protection (Zhang *et al.* 2021).

Conventional analytical techniques, while precise, are often hindered by prohibitive instrumentation costs, complex sample pretreatment, and limited suitability for on-site

monitoring. Among them, electrocatalytic sensing has attracted increasing interest because it can lower the overpotential and accelerate the electrode reaction kinetics, thereby improving the sensitivity and selectivity for heavy metal detection. Specifically, Anodic Stripping Voltammetry (ASV) significantly lowers the limit of detection (LOD) *via* an electrochemical pre-concentration step (Shang *et al.* 2024; Heidari *et al.* 2021). Among ASV techniques, Square Wave Voltammetry (SWV) is preferred for trace analysis, as it effectively suppresses background charging currents, thereby enhancing the signal-to-noise ratio. The performance of electrochemical sensors is fundamentally governed by the electrode modification materials (Yuan *et al.* 2024).

In recent years, researchers have developed a large number of novel electrode modification materials for the construction of highly sensitive and highly selective Pb^{2+} electrochemical sensors. Metal oxide nanomaterials have attracted attention due to their high specific surface area, abundant surface-active sites, and tunable electronic structures. Beyene *et al.* (Madhivanan *et al.* 2025) constructed an electrochemical sensor for the simultaneous detection of Pb^{2+} and Cd^{2+} by modifying a carbon paste electrode with bismuth ferrite nanoparticles, which exhibited good analytical performance. Metal-organic frameworks (MOFs) represent another class of electrode modification materials that have attracted considerable attention.

A breakthrough has been achieved with the PANI@Bi-MOF electrochemical sensor, which is constructed from a composite of bismuth-based MOF (Bi-MOF) and the conductive polymer polyaniline. This sensor utilizes the composite formed by uniformly coating polyaniline onto the Bi-MOF surface. By leveraging the abundant lead ion enrichment sites provided by the high specific surface area of the MOF, in synergy with the excellent electron transport capability of the conductive polymer, efficient signal enhancement and sensitive detection are realized. The results show a detection limit as low as approximately $0.0108 \mu\text{g}\cdot\text{L}^{-1}$, with a linear response range covering 0.025 to $20 \mu\text{g}\cdot\text{L}^{-1}$. The sensor exhibits high selectivity for Pb^{2+} in real water samples, as well as excellent stability, reproducibility, and selectivity (Saleem *et al.* 2025).

In addition to metal oxides and MOF materials, novel two-dimensional materials represented by layered transition metal carbides/nitrides (MXenes) have emerged rapidly due to their unique layered structures, excellent electrical conductivity, and abundant surface chemical properties. Sapna *et al.* (2025) fabricated a modified MXene composite sensor containing sulfur impurities and successfully applied it to the electrochemical detection of lead ions in aqueous systems. Electrode modification strategies for the electrochemical detection of lead ions are increasingly showing a trend towards diversification and hybridization. Among the various functionalization strategies, carbon-based nanomaterials play a key role in electrochemical sensors due to their high electrical conductivity, good chemical stability, and abundant surface functional groups.

Biochar (BC), derived from the oxygen-limited pyrolysis of biomass, has gained prominence due to its hierarchical pore structure and abundant oxygen-containing functional groups (*e.g.*, carboxyl and hydroxyl groups) (Lingamdinne *et al.* 2021; Azim *et al.* 2024). These features facilitate Pb^{2+} capture *via* complexation and electrostatic attraction. However, the application of pristine biochar is often restricted by its poor intrinsic conductivity and limited active site stability. To circumvent these issues, compositing biochar with magnetic nanoparticles can synergistically enhance its physicochemical properties. The combination of biochar with metal oxide nanoparticles can achieve a synergistic enhancement effect in terms of sensitivity, selectivity, and stability (Tshoko *et al.* 2025). For example, Huang *et al.* (2023a) utilized a magnetic Fe_3O_4

nanoparticle-modified phosphorus-doped biochar-attapulgite/bismuth film electrode coupled with a smartphone-operated wireless portable sensor to achieve ultratrace voltammetric detection of Cd^{2+} , Pb^{2+} , and Hg^{2+} . The linear ranges were 0.1 nM to 5 μM , 0.01 nM to 7 μM , and 0.1 nM to 3 μM , with detection limits as low as 0.036 nM, 0.003 nM, and 0.011 nM, respectively, and satisfactory recoveries were obtained in real samples such as tap water and lake water. Furthermore, Ge *et al.* (2025) made an electrochemical sensor with ultrasensitive and selective recognition capability for Pb^{2+} and Cd^{2+} by loading NiCo_2O_4 nanosheets onto nitrogen and sulfur co-doped rice husk biochar *via* an *in-situ* growth method, demonstrating excellent detection performance. Hoa *et al.* (2026) reported a magnetically assisted electrochemical sensor based on an $\text{Fe}_3\text{O}_4@\text{UiO}-66\text{-Py/rGO}$ nanocomposite for the ultratrace detection of Pb^{2+} and Cd^{2+} , achieving detection limits of 0.3 to 0.4 ppb, with a linear range covering 1 to 200 ppb, and obtained recoveries of 92% to 102% in actual seafood samples from Vietnam. These studies collectively demonstrate that magnetic biochar-based composites exhibit broad application prospects in the field of electrochemical sensing of heavy metal ions. Moreover, the incorporation of magnetic nanoparticles not only enhances adsorption but also introduces additional electrocatalytic active sites, which are beneficial for the electrochemical oxidation/reduction of heavy metal ions.

Alfalfa (*Medicago sativa*), a perennial flowering plant widely cultivated as a high-protein forage crop, is known for its deep root system and high biomass yield. Due to its abundant lignocellulosic components and natural nitrogen content, alfalfa-derived biochar possesses a well-developed porous structure and intrinsic heteroatom doping (Lakić *et al.* 2021), making it a promising precursor for functional carbon materials. Therefore, in this work, magnetic alfalfa biochar (MBC) was synthesized using renewable alfalfa biomass through a combined pyrolysis and iron-salt co-precipitation strategy. The MBC was utilized to modify a glassy carbon electrode (MBC/GCE) for Pb^{2+} sensing. Systematic characterization of the microstructure, porosity, and surface chemistry confirmed the successful fabrication of the composite. Under optimized conditions (HAc-NaAc buffer, pH 5.5, deposition potential of -1.8 V, and deposition time of 160 s), the MBC/GCE exhibited a robust linear response toward Pb^{2+} in the range of 0.2 to 1.0 μM . The linear regression equation was $I = 6.34 + 64.5C$ ($R^2 = 0.996$), with a limit of detection (LOD) of 68 nM ($S/N = 3$). The integrated benefits of high conductivity, abundant active sites, and hierarchical porosity position the MBC/GCE as a promising material platform for the sensitive detection of heavy metal ions. By integrating the adsorption properties of magnetic nanoparticles and biochar with electrochemical sensing, this study demonstrates a low-cost, easily prepared, and robust heavy metal ion-sensitive interface. Compared with previously reported MOFs, MXenes, or other biochar-based composites, this work highlights the unique advantages of alfalfa-derived magnetic biochar in the integrated design of ‘structure-function’, providing a promising candidate material for electrocatalytic on-site environmental monitoring.

Materials and Methods

Reagents

The alfalfa was purchased from Ningxia Jinsai Grass Industry Co., Ltd. (Ningxia, China); ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, A.R) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, A.R) from Shanghai Adamas Reagent Co., Ltd. (Shanghai, China); sodium hydroxide (NaOH, A.R) and aluminum oxide (1.0, 0.3, and 0.05 μm Al_2O_3 , A.R) from Tianjin Fengchuan

Chemical Reagent Technology Co., Ltd. (Tianjin, China); and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, A.R) from Tianjin New Technology Industrial Park Kemao Chemical Reagent Co., Ltd. (Tianjin, China). Potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, A.R) and Potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$, A.R) were from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China).

Preparation of Alfalfa Biochar

Raw alfalfa was dried at $60\text{ }^\circ\text{C}$ for 12 h, mechanically ground, and passed through a 100-mesh sieve. After sequential washing with deionized water and ethanol, the sample was re-dried and kept in a cool, dry environment. For carbonization, a designated amount of the pretreated alfalfa was loaded into a corundum boat within a tube furnace. The sample was heated to $700\text{ }^\circ\text{C}$ at a ramp rate of $5\text{ }^\circ\text{C}/\text{min}$ and maintained for 2 h under a constant nitrogen flow. Finally, the derived solid was ground and sieved to yield the alfalfa biochar (BC).

Preparation of Magnetic Biochar

8.6 g of $\text{Fe}_2(\text{SO}_4)_3$ and 1.5 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 250 mL of deionized water, followed by the addition of 10 g of the pristine alfalfa biochar. The resulting suspension was magnetically stirred at $60\text{ }^\circ\text{C}$ for 0.5 h to achieve a homogeneous dispersion. Subsequently, a NaOH solution was added dropwise to adjust the pH to 11 to 12, and the mixture was continuously maintained under heating and stirring for an additional 3 h. Upon completion, the synthesized composite was separated *via* centrifugation, washed 2 to 3 times with deionized water and absolute ethanol, and finally dried to yield the magnetic alfalfa biochar (MBC).

Preparation of the Modified Glassy Carbon Electrode

Before modification, the glassy carbon electrode (GCE) was successively polished with 1.0, 0.3, and $0.05\text{ }\mu\text{m}$ Al_2O_3 powder, ultrasonically rinsed with deionized water and absolute ethanol, and finally dried with N_2 . For the preparation of the catalyst ink, 5 mg of BC or MBC was added into 2 mL of a solvent mixture (ethanol/water = 1:1, v/v, containing $5\text{ }\mu\text{L}$ of 5 wt% Nafion). After being ultrasonicated to form a uniform dispersion, $5\text{ }\mu\text{L}$ of the respective suspension was drop-cast onto the GCE surface and dried at ambient temperature, yielding the BC/GCE and MBC/GCE.

Characterization

The X-ray powder diffraction (XRD, TD-3700) was conducted using monochromatic Cu $\text{K}\alpha 1$ radiation ($\lambda = 0.15405\text{ nm}$) operated at power (35 kV, 25 mA). Quantitative diffraction data analysis was conducted using Jade 9 software. The detection range spanned from 5° to 80° , with a scanning speed of $5^\circ/\text{min}$ and a wavelength of 0.15406 nm . The sizes and morphologies of BC and MBC were examined by scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) at an acceleration voltage of 15 kV. Following ultrasonic dispersion in ethanol, the samples were deposited onto the surface of a silicon wafer. Subsequent to the evaporation of the ethanol, the samples were examined, and mapping tests were performed to obtain and analyze their elemental content. X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Scientific Inc., Waltham, MA, USA) of MBC was conducted using a monochromatic X-ray excitation source of Al anode $\text{K}\alpha$ radiation (1486.6 eV). The binding energies were calibrated to the C 1s peak of carbon at 284.6 eV prior to the actual measurements. N_2 adsorption-desorption

measurements of BC and MBC were conducted using BSD-PS2. The Brunauer–Emmett–Teller (BET) method was used to estimate the specific surface areas. Raman spectroscopy (Thermo Fisher Scientific DXR laser Raman microscope) was used to characterize the graphitization degree of carbon materials, employing a 532 nm wavelength laser.

Electrochemical Measurement

Electrochemical measurements were performed in a standard three-electrode configuration using a CHI 660E electrochemical analyzer (Shanghai Chenhua Instrument Co., Ltd. Shanghai, China). The electrochemical cell comprised a catalytic electrode as the working electrode, a Pt sheet counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. All SWV measurements were performed under the following experimental conditions: amplitude, 50 mV; step voltage, 4 mV; frequency, 15 Hz.

RESULTS

Characterization of the Materials

The surface morphologies of the two materials were investigated using SEM. As depicted in Fig. 1a, the pristine alfalfa biochar exhibits an irregular, block-like structure with a relatively smooth surface and distinct edges.

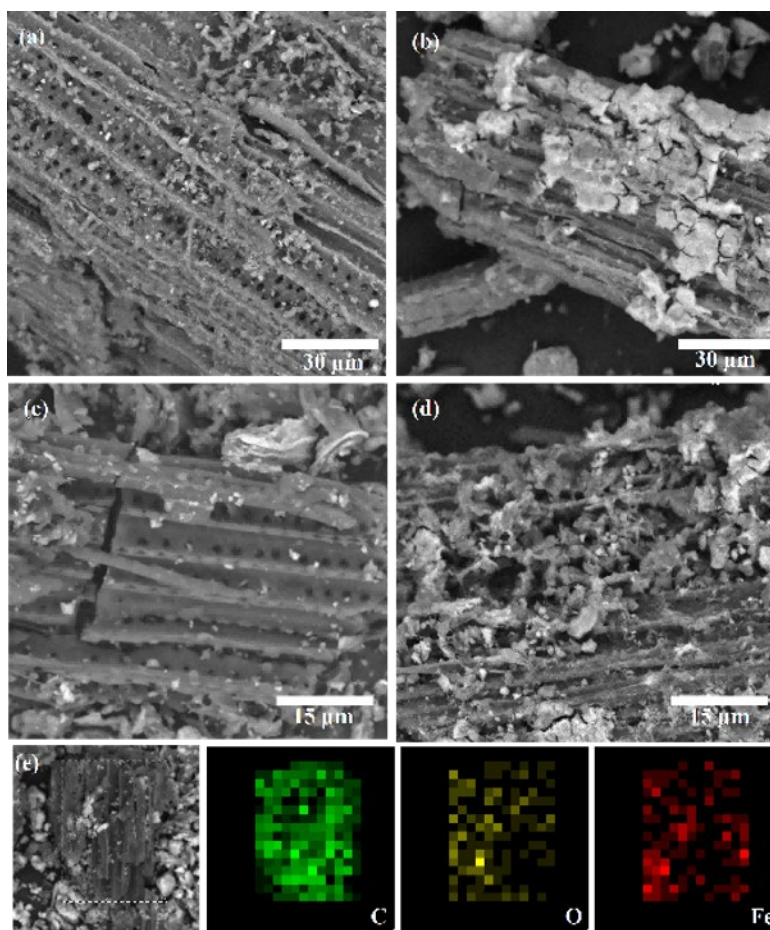


Fig. 1. SEM images of alfalfa biochar (a, c) and Magnetic Biochar (b, d). (e) Elemental mapping of C, O, and Fe for the magnetic biochar

While a few primary pores are visible, their connectivity is poor. High-magnification observation (Fig. 1c) further reveals that the surface is dominated by micron-scale fissures and isolated pores, devoid of hierarchical stacking structures. This unmodified biochar relies heavily on the residual pores derived from the pyrolyzed plant skeleton, leading to a limited specific surface area and inadequate exposure of active sites. Conversely, following magnetic modification (Fig. 1b), the particle surface is markedly roughened. An abundance of nano- to submicron-scale particles are anchored onto the surface, forming “grape-like” or “island-like” clusters. As observed at higher magnification (Fig. 1d), these particles are either uniformly dispersed or locally agglomerated across the carbon matrix. Moreover, the modification process induces the generation of secondary pores, yielding an uneven and porous texture that effectively enhances both the specific surface area and interfacial roughness. Figure 1e shows the elemental mapping of the magnetic biochar, where the existence of C, O, and Fe can be observed in the sample.

To further elucidate the textural properties of BC and MBC, N₂ adsorption-desorption isotherms and pore size distributions were systematically evaluated. As illustrated in Figs. 2a and 2c, both BC and MBC exhibit typical Type IV isotherms with distinct hysteresis loops in the relative pressure range of $P/P_0 \approx 0.4$ to 1.0. The Type IV profile is characteristic of mesoporous materials, and the presence of the hysteresis loop indicates capillary condensation, confirming the predominance of mesopores. Concurrently, a slight nitrogen uptake at low relative pressures ($P/P_0 < 0.1$) suggests the existence of micropores, whereas the lack of an adsorption plateau at high relative pressures (P/P_0 approaching 1.0) implies the coexistence of macropores. Consequently, both BC and MBC feature a hierarchical porous architecture predominantly composed of mesopores, complemented by micro- and macropores. This hierarchical structure is highly advantageous for providing abundant diffusion pathways and active sites, rendering it an ideal configuration for electrode modification.

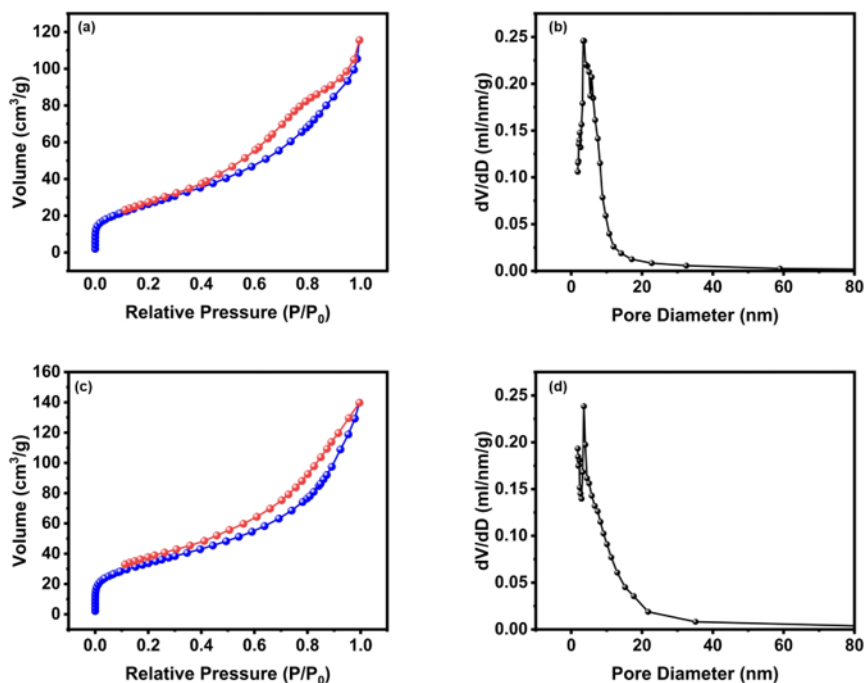


Fig. 2. (a, b) N₂ adsorption-desorption curves and pore size distribution of alfalfa biochar; (c, d) N₂ adsorption-desorption curves and pore size distribution of magnetic biochar

According to Table 1, the specific surface area (SSA) of BC is 97.2 m²/g, which is elevated to 120 m²/g for MBC. This enhanced SSA can be ascribed to the magnetic modification, which generates additional micro/mesopores and thereby maximizes the exposed surface area per unit mass. Pore size distribution curves (Figs. 2b and 2d) reveal that the pores were primarily distributed within 0 to 7 nm, dominated by 2 to 7 nm mesopores along with a minor fraction of micropores (< 2 nm). For the electrochemical detection of Pb(II), the enlarged SSA offers numerous active sites for the adsorption and enrichment of lead ions, substantially boosting the pre-concentration efficiency. Furthermore, the hierarchical porous network—where micropores afford high adsorption energy and meso/macropores serve as rapid transport channels—effectively shortens the ion diffusion pathways and accelerates internal mass transfer, ultimately enhancing the sensitivity and stability of the electrochemical response. In conclusion, the exceptional SSA and rationally engineered hierarchical pore structures of BC and MBC provide a robust foundation for their superior electrochemical sensing capabilities.

Table 1. Specific Surface Area, Porosity, and Pore Size of Alfalfa Biochar and Magnetic Biochar

Samples	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	R _{Avg} (nm)
BC	97.2	0.168	6.93
MBC	120	0.211	7.01

To gain deeper insights into the crystallographic structures and phase compositions of BC and MBC, XRD characterization was conducted (Fig. 3a). The XRD pattern of BC displays sharp and distinct diffraction peaks near $2\theta \approx 30^\circ$ and 40° , corresponding to mineral impurities. Matching with the standard database (PDF 04-007-8561) confirmed these peaks originate exclusively from the KCl crystalline phase, implying the presence of residual potassium salts in the pristine biochar. Aside from these impurities, the pattern exhibited a broad and diffuse halo without sharp graphitic or crystalline carbon peaks, revealing the predominantly amorphous nature of the biochar, which is highly favorable for exposing abundant defect sites. Conversely, the XRD pattern of MBC demonstrated striking alterations. Initially, the complete disappearance of the KCl peaks suggests that soluble impurities were effectively eliminated or phase-transformed during the magnetic modification (e.g., iron salt loading and subsequent co-precipitation/pyrolysis). Furthermore, newly emerged peaks at $2\theta = 30.02^\circ$, 53.57° , and 62.59° correspond to the (220), (422), and (440) planes of Fe₃O₄ (magnetite), respectively. Concurrently, diffractions at $2\theta = 35.46^\circ$, 43.16° , and 56.91° are indexed to the (311), (400), and (511) planes of γ -Fe₂O₃ (maghemite) (Gupta and Nayak 2012). These findings verify the successful anchorage of Fe₃O₄ and γ -Fe₂O₃ magnetic nanoparticles onto the BC matrix, which not only facilitates magnetic separation but also potentially participates in electron transfer and target adsorption during electrochemical processes.

Raman spectroscopy was further employed to assess the structural integrity and defect nature of the carbon matrix (Fig. 3b). Both samples displayed two prominent bands at approximately 1350 cm⁻¹ and 1580 cm⁻¹, designated as the D band and G band, respectively (Aziz *et al.* 2022; Yang *et al.* 2025a). The D band originates from structural defects, edge states, and disordered sp³ carbon atoms, reflecting the abundance of amorphous structures. The G band arises from the in-plane stretching vibration of sp²-hybridized carbon atoms, representing the graphitic ordering. Consequently, the intensity

ratio of the D to G band (I_D/I_G) serves as a vital indicator of the graphitization degree and structural ordering in carbonaceous materials (Yang *et al.* 2025b). The calculated I_D/I_G ratio for MBC was notably lower than that of BC. This reduction signifies that the magnetic modification enhanced the graphitization degree and increased the ordered carbon fraction, thereby significantly boosting the electrical conductivity of the material. Nevertheless, MBC still exhibited a robust D band, indicating that the modification process did not eradicate defects but rather engineered a unique composite architecture featuring a “highly graphitized core and a defect-rich surface”. This enhanced graphitization expedited the interfacial electron transfer kinetics, thereby amplifying the sensing sensitivity. Simultaneously, the preserved defect sites acted as active centers for the preferential adsorption and enrichment of heavy metal ions. Overall, the synergistic XRD and Raman results confirm that the magnetic modification not only successfully introduced magnetic components but also tailored the carbon skeleton, endowing the material with superior conductivity and abundant active sites—ideal prerequisites for heavy metal adsorption and electrocatalytic processes.

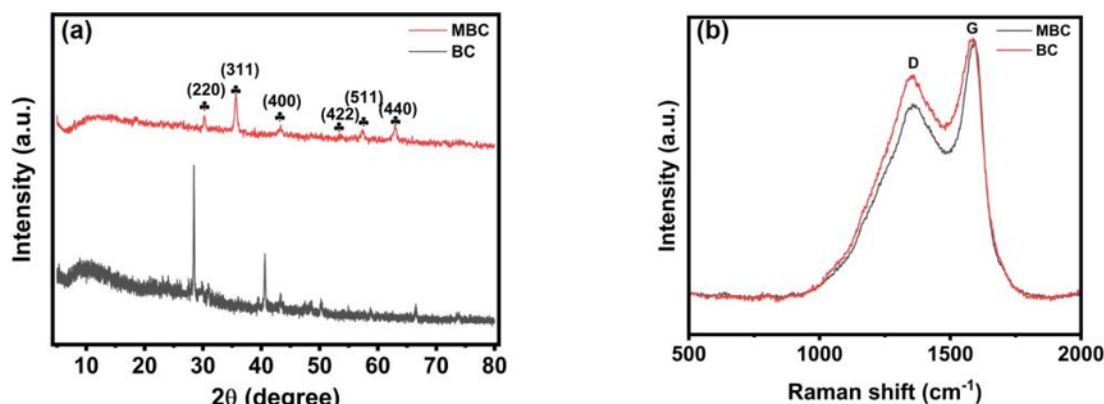


Fig. 3. (a) XRD spectra of alfalfa biochar and magnetic biochar, (b) Raman spectra of alfalfa biochar and magnetic biochar

X-ray photoelectron spectroscopy (XPS) was utilized to further elucidate the surface chemical composition, elemental states, and valence distribution of the MBC composite. The XPS survey spectrum (Fig. 4d) exhibits three prominent photoelectron peaks at binding energies of ~284.8 eV, 546.8 eV, and 710.7 eV, corresponding to C 1s, O 1s, and Fe 2p, respectively. This explicitly verifies the coexistence of C, O, and Fe, corroborating the XRD and Raman analyses and affirming the successful incorporation of magnetic iron oxides into the biochar matrix.

To gain deeper insight into the chemical states of carbon, the high-resolution C 1s spectrum was deconvoluted (Fig. 4a). The spectrum can be resolved into three distinct sub-peaks: the dominant peak at 284.85 eV is assigned to the sp^2 -hybridized C–C bonds, representing the graphitic carbon framework; the peak at 286.2 eV corresponds to C–N bonds, signifying successful nitrogen doping into the carbon lattice during preparation or modification; and the peak at 287.35 eV is ascribed to C=O bonds, indicating the presence of carbonyl-like oxygen-containing functional groups. These polar functionalities (C–N and C=O) not only augment the complexation affinity of MBC toward heavy metal ions (e.g., Pb^{2+}) but also boost the hydrophilicity of the material, thereby ensuring intimate contact between the electrolyte and the electrode surface.

The peak fitting of the high-resolution Fe 2p spectrum is shown in Fig. 4b, which displays two principal characteristic peaks at 712.7 eV and 725.5 eV, arising from the spin-orbit splitting of Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Manyatshe and Sibali 2025; Zaharani *et al.* 2025). The binding energies and peak profiles suggest that iron in the MBC predominantly exists as Fe³⁺. In conjunction with the XRD findings (identifying Fe₃O₄ and γ -Fe₂O₃), it can be deduced that iron predominantly occupies the lattice sites in a trivalent state. This configuration favors the atmospheric chemical stability of the magnetic nanoparticles and potentially facilitates electron transfer during electrocatalytic processes.

Deconvolution of the high-resolution O 1s spectrum (Fig. 4c) yields three distinct oxygen species: the peak at 529.9 eV is attributed to the Fe–O lattice oxygen of the iron oxides; the peak at 531.2 eV corresponds to C=O bonds, matching the carbonyl groups identified in the C 1s spectrum; and the peak at 533.3 eV represents the –OH groups, originating from surface hydroxyls or chemisorbed water. Such abundant oxygenated functionalities (particularly –OH and C=O) drastically enrich the active site density, enabling efficient capture of Pb(II) *via* coordination or electrostatic attraction. Concurrently, the Fe–O networks impart robust magnetic responsiveness to the composite.

Consequently, XPS analysis not only corroborates the ternary elemental composition (C, O, Fe) of MBC but also unravels a carbon skeleton enriched with heteroatomic functionalities (C–N, C=O), an iron oxide phase dominated by Fe³⁺, and a surface abundant in hydroxyl/carbonyl active sites. Together, these compositional and structural attributes forge a highly favorable microenvironment for rapid electron transport and efficient target enrichment in the electrochemical sensing of Pb(II).

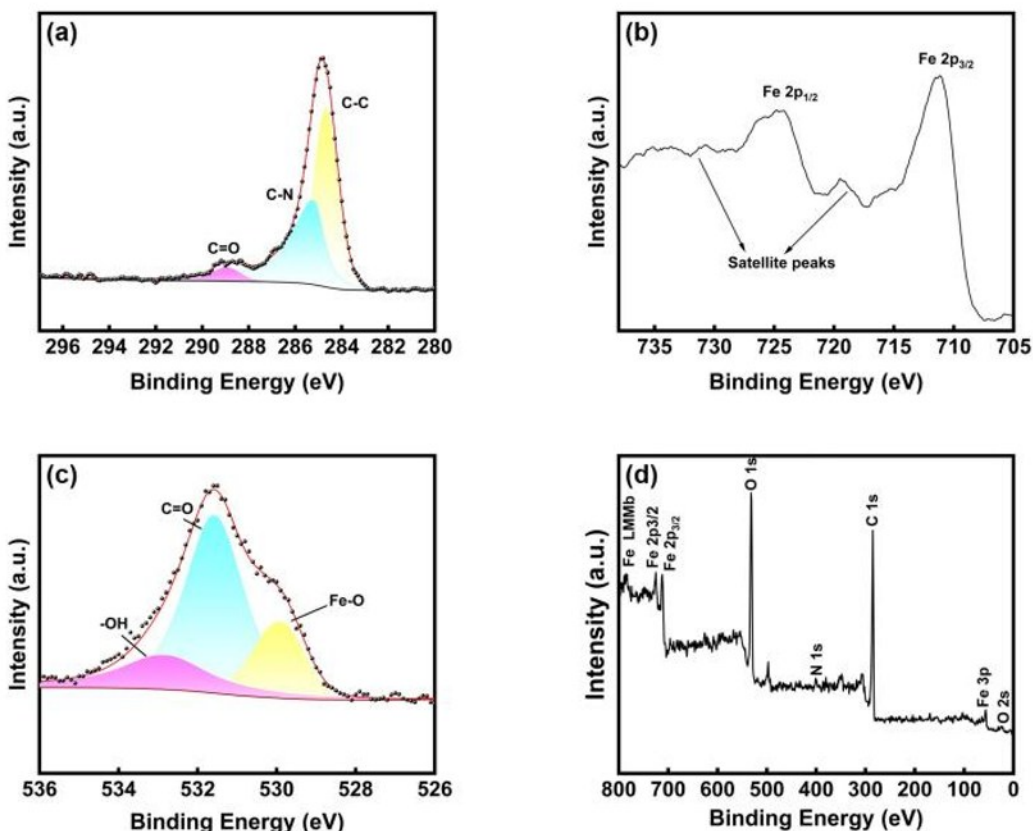


Fig. 4. XPS spectra of magnetic biochar: (a) C 1s, (b) Fe 2p, (c) O 1s, (d) full spectrum

To investigate the effect of strong cathodic polarization on the phase and surface valence state of iron oxides in MBC, the MBC/GCE was subjected to potentiostatic polarization at -1.8 V (vs. Ag/AgCl) for 160 s, followed by ex-situ XPS characterization. As shown in Fig. 5, after polarization, the binding energy of the Fe $2p_{3/2}$ main peak shifted to a lower binding energy by 0.39 eV. Meanwhile, the intensity of the characteristic Fe³⁺ satellite peak (*ca.* 718.5 eV) decreased significantly. These changes indicate that γ -Fe₂O₃ underwent electrochemical reduction under a strong cathodic potential, with partial reduction of Fe³⁺ to Fe²⁺, leading to a marked change in the phase and surface valence state of the electrode modification material. This reduction process facilitates the formation of an Fe²⁺-rich active layer on the electrode surface (possibly transforming into Fe₃O₄ or non-stoichiometric iron oxides), providing a favorable interfacial environment for the adsorption and electrochemical enrichment of Pb²⁺.

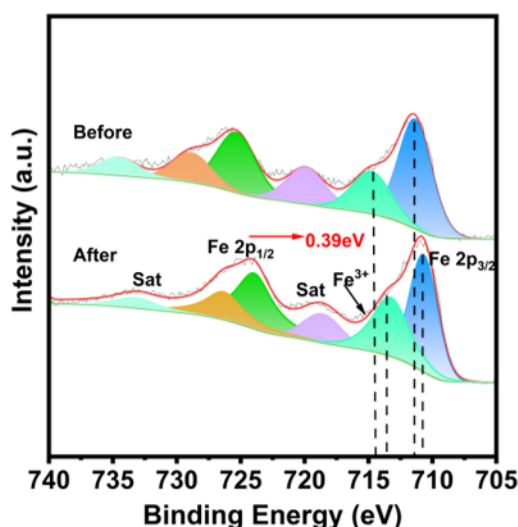


Fig. 5. Comparison of Fe 2p XPS spectra before and after testing

Pb(II) Detection Performance

The electrochemical activities of bare GCE, BC/GCE, and MBC/GCE were initially probed using cyclic voltammetry (CV) in [Fe(CN)₆]^{3-/4-} (Fig. 6a). All electrodes displayed a well-defined pair of redox peaks within the potential range of -0.5 to $+1.5$ V. While BC/GCE exhibited a similar peak profile to the bare GCE, MBC/GCE showed a marked enhancement in peak current, signifying superior reversibility and improved sensitivity. Specifically, the anodic peak current of MBC/GCE (448.65 μ A) was substantially higher than those of bare GCE (270.14 μ A) and BC/GCE (287.37 μ A) (Fig. 6b), confirming that magnetic modification effectively boosted the electrical conductivity and facilitates electron transport.

To further elucidate the interfacial charge transfer kinetics, electrochemical impedance spectroscopy (EIS) was performed. A Nyquist plot consists of a semicircle and a straight line. The intercept of the high-frequency region with the real axis represents the resistance of the electrolyte. The semicircle in the high-frequency region corresponds to the charge transfer resistance (R_{ct}), which indicates a charge-transfer-controlled process. The straight line in the low-frequency region represents the Warburg impedance, *i.e.*, the diffusion resistance, which corresponds to a diffusion-controlled process. Therefore, the magnitude of the charge transfer resistance can be determined from the radius of the

semicircle in the Nyquist plot: a larger radius indicates a higher charge transfer resistance, implying a lower charge transfer efficiency (Kong *et al.* 2015; Wang *et al.* 2015). As shown in the Nyquist plots (Fig. 6c), the bare GCE exhibited a characteristic semicircle corresponding to its charge transfer resistance (R_{ct}). A marginal increase in R_{ct} was observed for BC/GCE, which can be likely ascribed to surface oxygen-containing groups or residues that slightly impede ion diffusion. In contrast, MBC/GCE displayed the smallest semicircle diameter, indicating the lowest R_{ct} and most efficient charge transfer, in excellent agreement with the CV observations.

The sensing efficacy for Pb(II) was examined *via* square wave voltammetry (SWV) in 0.1 M acetate buffer (pH 4.0). Upon addition of 0.5 μM Pb^{2+} , all electrodes yield a distinct stripping peak at -0.5 V, which can be attributed to the typical reduction-stripping process of lead (Figure 6d). Notably, MBC/GCE achieves the highest stripping current and exceptional sensitivity, highlighting its robust potential for the trace detection of heavy metal ions.

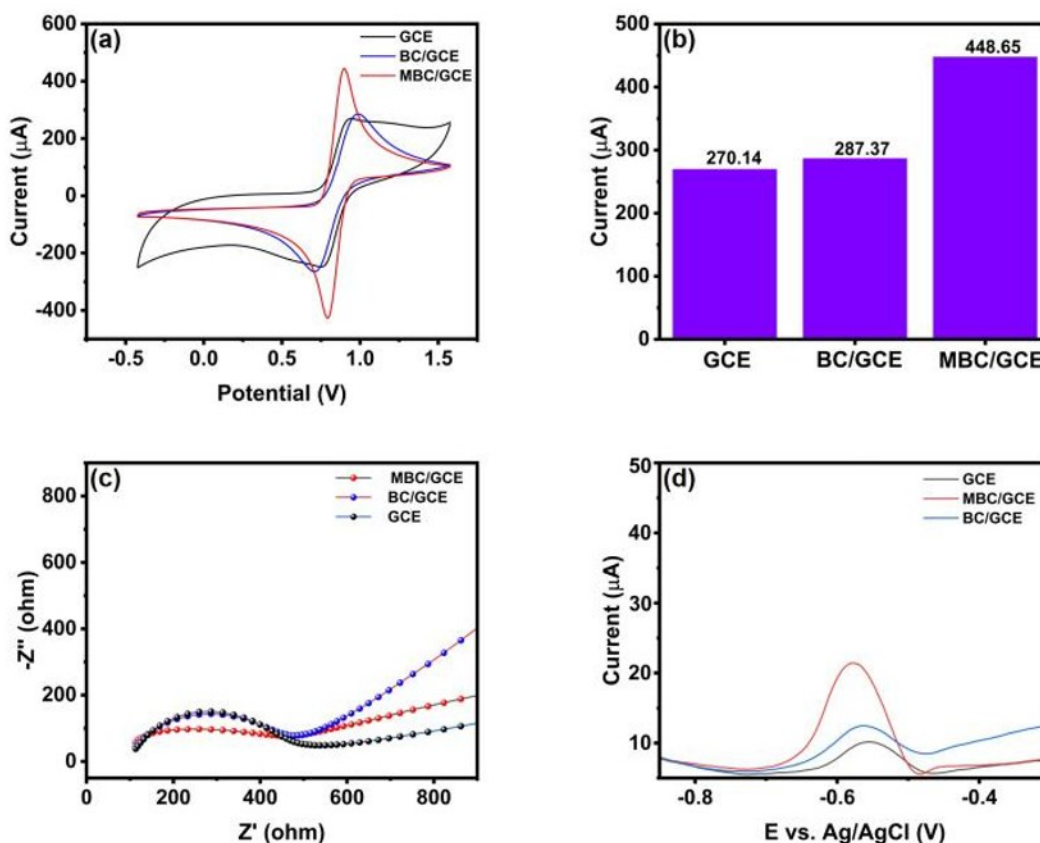


Fig. 6. (a) Cyclic voltammetric curve of GCE, BC / GCE, MBC / GCE; (b) Anode peak current; (c) Nyquist plots (d) Square wave voltammetry curves of different electrodes in 0.1 M acetate buffer (pH 4.0) containing 0.5 μM Pb^{2+}

To achieve optimal electrochemical sensing performance for Pb(II), the critical experimental parameters governing the electrochemical response—namely the buffer type, buffer pH, deposition potential, and deposition time—were systematically optimized. Initially, the effects of various buffer systems on the stripping peak current and peak profile of Pb^{2+} were evaluated to identify the ideal detection medium. Subsequently, the buffer pH (4.0 to 6.0) was fine-tuned, as it directly dictates the speciation of heavy metal ions, the

protonation degree of the electrode surface, and the complexation equilibrium, which collectively exert a profound impact on the pre-concentration efficiency and the ensuing stripping signal intensity. Furthermore, the deposition potential is a pivotal parameter regulating the reductive accumulation of Pb^{2+} onto the modified electrode. An excessively negative potential may trigger hydrogen evolution and other interferences, whereas an insufficiently negative potential leads to poor accumulation efficiency. Similarly, the deposition time dictates the total quantity of Pb^{2+} enriched at the electrode interface; a short duration yields weak responses, while prolonged accumulation may result in surface saturation or amplified background noise. By individually examining these parameters *via* square wave voltammetry (SWV), the optimal experimental conditions were established to maximize the overall sensitivity of the proposed sensor.

The electrochemical response of the MBC/GCE toward Pb(II) was evaluated *via* square wave voltammetry (SWV) across three distinct buffer systems: HAc-NaAc (acetate buffer), PBS (phosphate buffer saline), and $\text{NH}_4\text{Cl-HCl}$. As depicted in the SWV profiles (Figure 7), the maximum stripping peak current is achieved when the HAc-NaAc buffer is utilized. Consequently, the HAc-NaAc buffer was adopted as the optimal supporting electrolyte for subsequent analytical measurements.

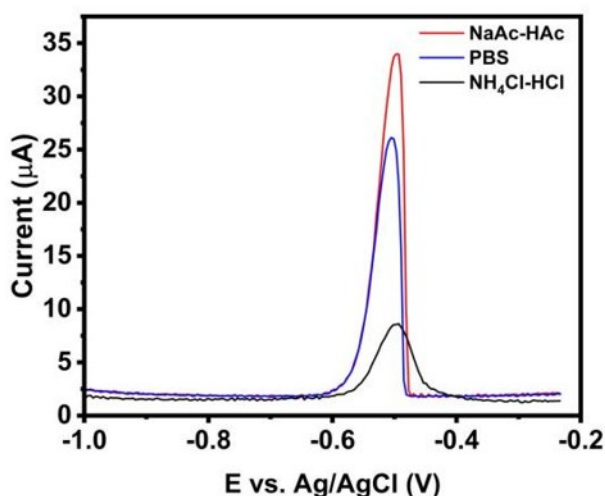


Fig. 7. Square wave voltammograms of different electrolyte solutions

The effect of pH (4.0 to 6.0) on the SWV response of MBC/GCE toward Pb^{2+} was investigated (Fig. 8). The stripping peak current gradually increased from pH 4.0 to 5.5, reaching a maximum at pH 5.5, and then decreased to pH 6.0. This volcano-shaped trend is consistent with previous literature (Berslin *et al.* 2022; Huang *et al.* 2023b). At low pH (< 5.0), H^+ competes with Pb^{2+} for active sites and promotes hydrogen evolution, reducing the pre-concentration efficiency. At pH 5.5, deprotonation of the electrode surface enhances Pb^{2+} adsorption and reduction. When the pH exceeds 5.5, Pb^{2+} hydrolysis generates $\text{Pb(OH)}^+/\text{Pb(OH)}_2$, which lowers the concentration of free Pb^{2+} and passivates the electrode surface. Therefore, pH 5.5 was selected as the optimal condition for all subsequent measurements.

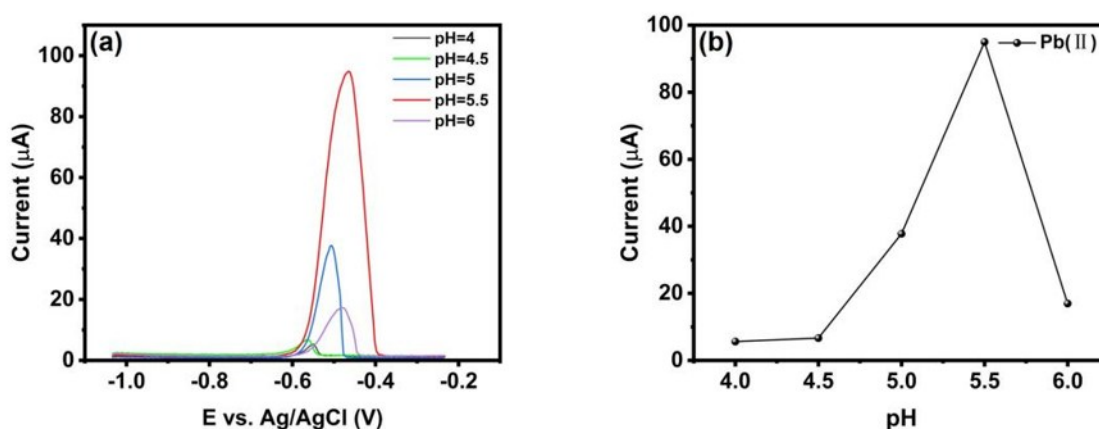


Fig. 8. (a) SWV curves under different pH acetic acid buffer solutions, (b) Effect of pH on response current

The influence of deposition potential on the electrochemical response was investigated by recording the SWV stripping peak currents of Pb(II) at various potentials (ranging from -1.2 to -2.0 V) in the HAc-NaAc buffer (pH 5.5). As depicted in Fig. 9, when the applied potential was shifted negatively from -1.2 V, the stripping current initially escalated and then diminished, exhibiting a distinct maximum at -1.8 V. At less negative potentials (-1.2 V and -1.4 V), the thermodynamic driving force was insufficient for the efficient reductive accumulation of Pb(II) at the electrode interface, yielding a relatively weak stripping signal. As the potential is stepped to -1.8 V, the adequately negative potential facilitates the comprehensive reduction of Pb^{2+} to Pb^0 , driving a substantial deposition of solid lead onto the MBC modifier layer and thereby sharply amplifying the stripping current. However, a further negative shift to -2.0 V triggered a competitive hydrogen evolution reaction (reduction of protons). This side reaction generates gas bubbles that disrupt the electrode surface and ultimately attenuate the stripping response. Consequently, balancing the pre-concentration efficiency and sensing sensitivity, -1.8 V was adopted as the optimal deposition potential for all subsequent measurements.

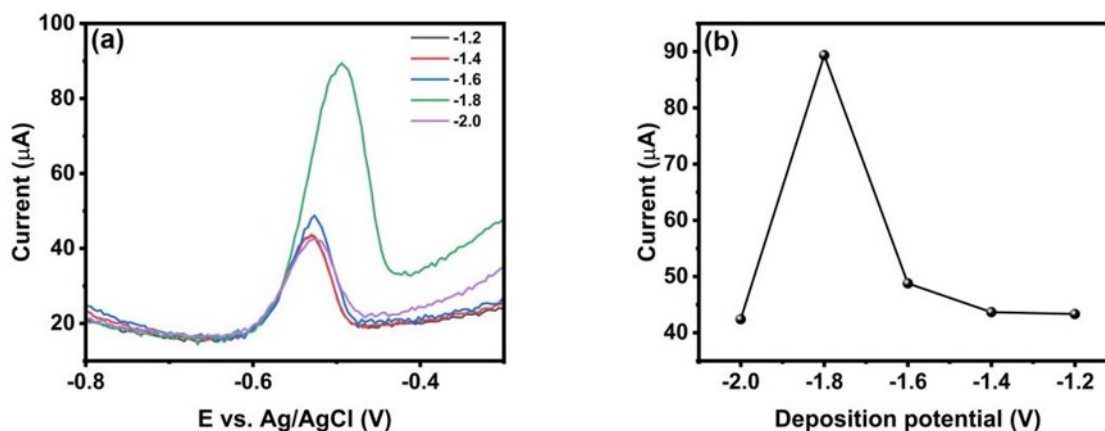


Fig. 9. (a) SWV curves at different deposition voltages, (b) Effect of deposition voltage on response current

To maximize the pre-concentration efficiency, the deposition time was optimized within the range of 100 to 180 s (Fig. 10). The stripping peak current of Pb(II) exhibited a progressive upward trend as the deposition time increases from 100 to 160 s, peaking at 160 s. This enhancement is attributed to the increased electrodeposition of Pb^0 onto the MBC-modified surface, which provides more electroactive species for the subsequent stripping step. Nevertheless, a further extension of the deposition time beyond 160 s resulted in a diminished response or a plateau. This phenomenon suggests that the available active sites on the MBC/GCE surface had reached a state of quasi-saturation. Moreover, an excessively long accumulation period may amplify the background noise, potentially compromising the signal-to-noise ratio. Therefore, considering both sensitivity and analytical efficiency, an optimal deposition time of 160 s was adopted for all further measurements.

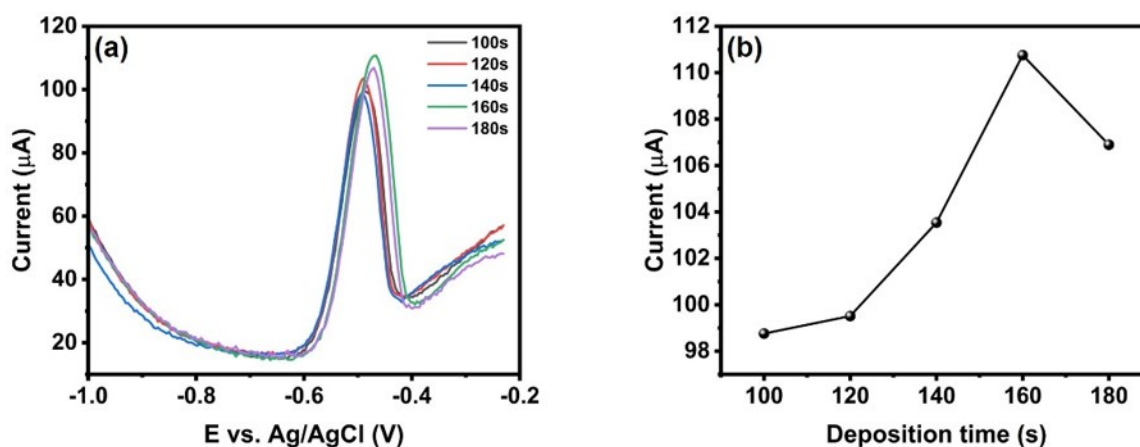


Fig. 10. (a) SWV curves at different deposition times, (b) Effect of deposition time on response current

The SWV responses of MBC/GCE toward Pb(II) at different concentrations (0.2 to 1.0 μM) under optimized conditions are illustrated in Fig. 11a.

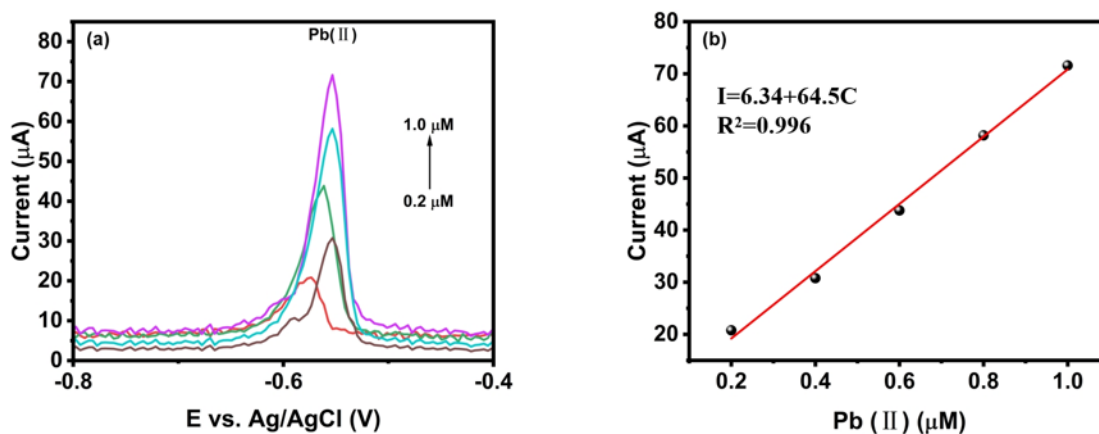


Fig. 11. (a) SWV curves of MBC/GCE in standard Pb^{2+} solutions at different concentrations, (b) corresponding linear equations

The stripping peak current (I) exhibited a proportional increase with the Pb(II) concentration (C) demonstrating a robust linear relationship. The fitted linear equation is $I = 6.34 + 64.5C$ ($R^2 = 0.996$). According to the 3σ criterion, the limit of detection (LOD) for Pb(II) was determined to be 68 nM. The high sensitivity (represented by the steep slope of the calibration curve), combined with the excellent linearity and low LOD, underscores the potential of MBC/GCE as a high-performance electrochemical sensing platform for trace lead detection.

To verify the repeatability of MBC/GCE, six consecutive SWV measurements were performed using the same working electrode under optimal detection conditions. As shown in Fig. 12(a), the peak current values of Pb^{2+} exhibited good repeatability throughout the measurements. The relative standard deviation (RSD) for Pb^{2+} over the six repeated measurements was 4.36%. This indicates that MBC/GCE can stably provide nearly consistent current responses across multiple measurements, demonstrating high reliability and repeatability. Furthermore, to evaluate the stability of MBC/GCE, the fabricated working electrode was stored in a refrigerator at 6 °C for 7 days, and SWV tests were performed every 3 days. The stability assessment results of MBC/GCE under long-term storage conditions are shown in Fig. 12(b).

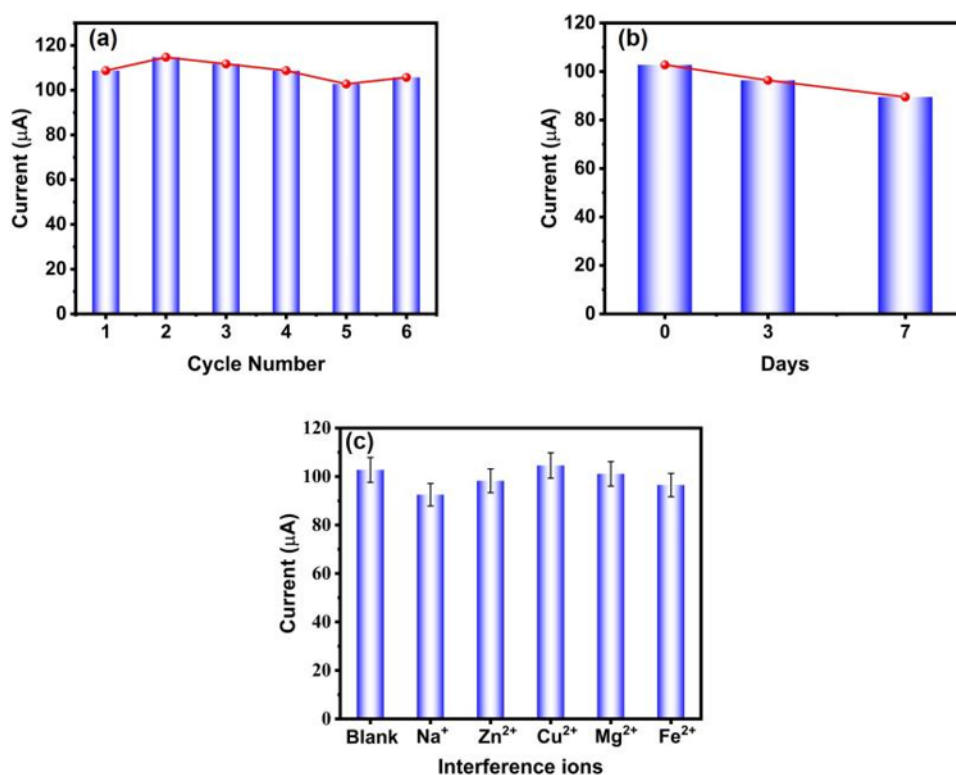


Fig. 12. (a) Repeatability, (b) stability, and (c) anti-interference performance of MBC/GCE

After 7 days of storage, the peak current of Pb^{2+} decreased but remained above 80% of the initial current value. On day 3 and day 7, the peak currents of Pb^{2+} were 93.8% and 87.1% of the initial value, respectively. These results indicate that MBC/GCE not only exhibited excellent electrochemical response stability but also maintained good performance after long-term storage. To evaluate the anti-interference capability of MBC/GCE, interfering ions (Na^+ , Zn^{2+} , Cu^{2+} , Mg^{2+} , Fe^{2+}) were added to a solution

containing Pb^{2+} . The concentration of the interfering ions was set to five times that of Pb^{2+} , and Pb^{2+} was detected under optimal detection conditions. By comparing the peak currents in the SWV before and after the addition of interfering ions (Fig. 12c), it was found that the change in the Pb^{2+} current was less than 10%, indicating that MBC/GCE exhibits good anti-interference performance. Nevertheless, the possibility of poisoning MBC/GCE by other species in complex real water samples cannot be ruled out. In particular, sulfur-containing species can strongly bind to catalytically active sites and irreversibly inhibit the catalytic cycle, while certain heavy-metal ions may irreversibly displace active ions, resulting in decreased sensitivity and selectivity. Potential mitigation strategies include the introduction of protective or antifouling membranes, and these aspects will be addressed in future work.

To further highlight the advantages of the sensor constructed in this study for Pb^{2+} detection, its analytical performance was compared with that of other existing electrochemical sensors for Pb^{2+} . As shown in Table 2, MBC/GCE exhibited superior detection performance for Pb^{2+} compared to the other electrochemical sensing electrodes listed, indicating that the constructed electrochemical sensor holds great potential for Pb^{2+} detection.

Table 2. Electrochemical Sensing Performance of Target Analytes Influenced by Diverse Active Surface Components

Electrode Material	Methods	LOD (nm)	References
MBC/GCE	SWV	68	This work
$\text{GP}_{75}\text{Bc-CS}_{25}$	SWASV	68.9	Mosquera-Ortega <i>et al.</i> 2025
MIL-88B(Fe)- NH_2 /GCE	DPV	192	Tran <i>et al.</i> 2023
SPE/ Fe_3O_4 -MWCNT	SWASV	318.7	Dinu <i>et al.</i> 2024
Fe-MIL-101@PANI/GCE	DPV	340	Abdelghany <i>et al.</i> 2025
NiSe/ZIF/GCE	DPV	470	Nataraj <i>et al.</i> 2024

CONCLUSIONS

1. A novel electrochemical sensor based on magnetic alfalfa-derived biochar (MBC) was successfully developed for the sensitive detection of Pb^{2+} in water. Under optimized conditions (pH 5.5, deposition at -1.8 V for 160 s), the MBC/GCE sensor exhibited a detection limit of 68 nM and a linear response range of 0.2 to 1.0 μM , demonstrating high sensitivity and reproducibility for trace Pb^{2+} analysis.
2. The MBC material, synthesized *via* oxygen-limited pyrolysis and iron salt co-precipitation, possessed a hierarchical pore structure, abundant oxygen-containing functional groups, and improved electrical conductivity. Electrochemical characterization confirmed that the MBC/GCE significantly reduced charge-transfer resistance and provided numerous active sites for Pb^{2+} enrichment. Furthermore, the use of low-cost renewable alfalfa as a precursor, together with magnetic modification, offers a sustainable and easily separable material platform for heavy-metal monitoring.

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Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Use of Generative AI

During the preparation of this work, the authors used Chat GPT to polish the English.

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