



Original Research Article

Equilibrium Sorption Studies of Cobalt (II) Ions Removal from Aqueous Solution

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ABSTRACT

*This study assessed the equilibrium sorption for Co^{2+} uptake from aqueous solutions using modified biochars from palm shells (*Elaeis guineensis* Jacq.) and sugarcane peels (*Saccharum officinarum*). $\text{KMnO}_4/\text{HNO}_3$ oxidation was used for modification due to their high oxidative nature, increasing biochar surface area. Unmodified and modified biochars were characterized for functional groups, morphology, elemental analysis, and surface area using Fourier transform infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), energy-dispersive spectroscopy (EDS), and Single/Multi-Point Brunauer-Emmett-Teller (BET/MBET). Batch equilibrium sorption for Co^{2+} uptake was analyzed using atomic absorption spectroscopy. Results showed that the $\text{KMnO}_4/\text{HNO}_3$ -modified palm shell (AP1) and sugarcane peel (BS2) biochars had higher surface areas (MBET: $450.0 \text{ m}^2/\text{g}$, SBET: $256.0 \text{ m}^2/\text{g}$ for AP1; MBET: $392.5 \text{ m}^2/\text{g}$, SBET: $241.9 \text{ m}^2/\text{g}$ for BS2) compared to unmodified biochars (MBET: $356.76 \text{ m}^2/\text{g}$, SBET: $244.2 \text{ m}^2/\text{g}$ for palm shells; MBET: $418.33 \text{ m}^2/\text{g}$, SBET: $227.2 \text{ m}^2/\text{g}$ for sugarcane peels). Sorption data fit the Freundlich model (R^2 : 0.9976 for AP1, 0.9426 for BS2). AP1 showed the highest Co^{2+} adsorption with maximum adsorption capacities of $1.49 \times 10^{18} \text{ mg/g}$ and reusability of 83.1%. $\text{KMnO}_4/\text{HNO}_3$ -modified palm shell biochar had more and better adsorption sites for Co^{2+} , indicating potential for superior heavy metal adsorption compared to unmodified and modified sugarcane peel biochar.*

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1. INTRODUCTION

Cobalt usage and accidental environmental release have grown dramatically in recent decades, primarily due to the industry's need for the metal for technological growth (Golroudbary et al., 2022). Using chemical additives to clean up contaminated soil reduces the environmental risk that heavy metals provide through adsorption, precipitation, and complexation, among other chemical processes (Beesley,

2011; Chao et al, 2018). Prior studies have demonstrated the effectiveness of inorganic materials such as phosphate, zeolite, and lime in immobilizing heavy metals (Karczewska et al., 2017).

Biochar is the ideal option for the most effective cobalt remediation material due to its highly porous nature (Zhang et al., 2018). The substantial affinity between several functional groups in biochar, such as metal cations, carboxyl, phenolic, and hydroxyl groups, is highlighted by Dai et al. (2018). The sorption capacities of this material are determined by its stability and composition. Important characteristics for heavy metal sorption, such as pH, surface negative charge, cation exchange, and metal surface complexation potential, are mainly influenced by the surface functional groups in organic carbonaceous materials (Mukherjee et al., 2011). Calcite, quartz, sylvite, whitlockite, and periclase are among the organic and mineral components found in biochars (Qi et al., 2017). The mineral components in biochars promote ion exchange and surface complexation, increase the number of metal sorption sites, and aid in the formation of metal precipitates by releasing soluble ions such as phosphates, sulphates, and carbonates (Xia et al., 2019). Compared to carbon-based sorbents, biochar is a more promising and reasonably priced adsorbent for removing metals from water. In recent years, extensive research has been conducted on the effectiveness of biochar in eliminating heavy metals, especially cobalt, from aqueous solutions (Sun et al., 2019). Even though much of the current research has focused on sorption strategies for metals in general, evaluating biochar's potential for heavy metal sorption requires comparing various metal removal mechanisms.

Biochars (BCs) are recognized as environmentally friendly and adaptable materials with significant potential for the remediation of contaminated soils, while modified biochars (MBCs), which have the advantages of a large specific surface area and high porosity, are a commonly used microbial-immobilization carrier (Kim et al., 2018). Biochar offers microorganisms a conducive environment, produced from natural biomass resources like sawdust and agricultural waste. Additionally, biochar can improve the interaction between pollutants and microorganisms due to its great potential for adsorbing petroleum toxins. Biochar, for instance, is a material with significant promise for treating contaminated soil that is both cost-effective and environmentally friendly. It is produced when biomass is pyrolyzed and has been demonstrated to improve soil properties (porosity, water holding capacity, aeration, and aggregate stability), raise soil pH and cation exchange capacity, and increase productivity while adsorbing hydrophobic organics (Sizmur et al., 2016). Biochars' unique physicochemical properties and adsorption capabilities allow for additional functionalization to enhance their attributes and promote environmental and agricultural sustainability. To improve the rate of pollutant removal, the properties of the biochar can be altered using a variety of physical, chemical, and biological methods (Xiao et al., 2018; Wang et al., 2017). Among these treatments are clays, metal oxides, biofilms, alkali or acid alterations, steam activation, and organic compounds. These methods are used to add extra materials for specific purposes, change the surface properties of pure biochar, and expand its surface area.

Since different metals exist in distinct species or valence states under various pH or redox circumstances, they might have variable primary sorption processes (Li et al., 2017). Although cobalt is frequently found in soil as Co^{2+} and Co^{3+} ions, these species' bioavailability varies, and soil may contain environmental risks. The behavior of Co in soils is greatly influenced by Fe and Mn oxides, which are known to have a remarkable affinity for Co. This is due to the fact that the majority of Cobalt (up to 79%) has been shown to be strongly coupled to soil-based Mn and Fe oxyhydroxides.

Leyssens et al. (2017) state that Co (II) is highly soluble in water, bioavailable, and probably very mobile. One important mechanism that reduces soil bioavailability and co-mobility of Co is the surface oxidation of Co^{2+} on oxyhydroxide minerals, which mostly generates Co (III). This is one significant mechanism that reduces the bioavailability and mobility of Co in soils (Ma et al., 2010).

Metal ore mining and smelting activities (mostly of copper, zinc, lead, and cobalt) as well as cobalt-containing alloys and compounds are the main causes of cobalt pollution in the environment (Gál et al., 2008). Furthermore, the main sources of cobalt pollution have been determined to be sewage effluents, urban runoff, and agricultural runoff (from phosphate fertilizers and pesticides). Since rechargeable lithium-ion batteries absorb half of the world's cobalt supply (Alves Dias et al., 2018), the cobalt

dependence of the electronic device industry should be acknowledged as a growing environmental concern.

However, how much cobalt was released into the environment is still unclear. The problem appears to be limited since elevated levels of cobalt in soil and groundwater are localized and may be caused by local geological factors, air deposition at smelting sites, or metal ore mining. However, cobalt can readily seep into groundwater or infiltrate soil by air deposition, posing a risk to food safety and agricultural quality (Liu et al., 2019). Despite being a necessary component of vitamin B12, excessive cobalt intake has been associated with several adverse health outcomes, such as asthma-like allergies (Leyssens et al., 2017). Future exposure to cobalt may result in asthma attacks, manifesting as shortness of breath, chest tightness, wheezing, and/or coughing.

Additionally, cobalt exposure can harm the thyroid, liver, kidneys, and heart. Long-term or frequent exposure to cobalt dust can result in lung fibrosis or scarring, even without early symptoms. The existence of xenobiotics, which have unknown effects on the environment and human health, is one of the new challenges in reducing the danger of elemental transfer into food systems.

One of the most significant challenges currently facing the treatment of heavy metal pollution in water is the development of adsorption materials with high adsorption capabilities for cobalt (Co). By producing biochar from a variety of two materials (in this study, sugarcane peel and palm shell), researchers and practitioners can improve the sustainability and efficacy of heavy metal removal from water, lower costs, and optimize the qualities of biochar for specific uses (Nan et al., 2018). Adsorption is the primary method of removing heavy metals from water, and it is characterized by its low cost, straightforward processes, and renewal (Foo and Hameed, 2009). Chemical oxidation methods that use H_2O_2 , KMnO_4 , HNO_3 , or an $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture are frequently employed to achieve surface oxidation (Godwin et al., 2019). Since both methods have strong oxidative qualities and won't react, $\text{KMnO}_4/\text{HNO}_3$ oxidation is used after pyrolysis to help further alter the biochar. A prior study found that when yak dung biochar was treated with HNO_3 , the adsorption capacity of Co^{2+} rose from 76.4 to 169.6 mg/g (Wang et al., 2018). The C=C on the surface of the biochar was oxidized to C=O by HNO_3 , which is responsible for eliminating Co^{2+} , according to their FTIR data.

The results of this study address the pressing need for efficient Cobalt adsorption technologies and open the door to a new strategy for the sustainable management of invasive species. This study demonstrates for the first time the highly effective adsorption of Cobalt (Co (ii)) by biochar made from sugarcane peel and palm shell, presenting a novel method for repurposing invasive biomass into useful sorbents.

2. MATERIALS AND METHODS

2.1. Materials

The Palm shells were purchased from Boundary Market Ajegunle, Lagos, Nigeria and the Sugarcane Peels were collected at Park Lane Apapa, Lagos, Nigeria. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was obtained from Ace Chemicals and allied Products Ojota market Lagos, Nigeria. Prior to use, diluted standard Co (II) solutions were made right away. Hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium permanganate (KMnO_4), and nitric acid (HNO_3) were all obtained from the University of Lagos Laboratory's Chemistry Department. They were manufactured by Kernel, Qualikems, and Merck chemicals in Darmstadt, Germany.

The sugarcane peels and palm shells were cleaned with deionized water, dried in an oven at 103°C to a consistent weight, ground into a powder, and then placed in a crucible. After that, the palm shells and sugarcane peels were carbonized for six hours at $500\text{--}550^\circ\text{C}$ and two hours at $600\text{--}650^\circ\text{C}$, respectively, in a muffle furnace (QXL-201, CN). After bringing the products to room temperature, they were taken out and pulverized using a pestle and mortar to create BC, which was then dried and put away.

After being weighed, 60 g of palm shell biochar and 50 g of sugarcane peel biochar were impregnated into 1000 mL of a solution containing a specific concentration of potassium permanganate and nitric acid. The mixture was then kept at 25°C for 24 hours on a constant-temperature shaker.

After impregnation, the product was carefully rinsed with deionized water until the pH reached a neutral level. Then, it was dried in an oven set at 105°C until it reached a consistent weight, producing modified Sugarcane Bagasse BC and modified Palm Shell Biochar (BC). The dry material was then crushed into a fine powder for use in ensuing adsorption tests as shown in Figure 1.

To optimize the unmodified palm shell biochar (OP) modification procedure and unmodified sugarcane peel biochar (OS), several potassium permanganate and nitric acid ratios were developed. AP1, AS2, BP1, BS2, and AP1 were modified palm shell and sugar peel biochars with $\text{KMnO}_4\text{:HNO}_3$ ratios of 0.3:2.0 and 0.8:2.0 mol.L^{-1} , respectively. The optimal conditions for modified biochars were estimated using the Co^{2+} elimination rate as a reference index.



Figure 1: Pictorial view of biochar formation process

2.2. Biochar Characterization

Using the methodology described by Jindo et al. (2014), the biochars were assessed for pH, total ash content, liming potentials, specific surface area, biochar yield, and shape.

pH Determination: The potentiometric method, an instrumental technique that involves measuring potential, was used to determine the pH of the biochar sample. We calibrated the pH meter using standard buffers 4, 7, and 10. Five grams (5 g) of biochar were placed in a 1:2 ratio beaker, and ten millilitres (ml) of deionized water were added. After stirring the sample for 30 minutes, the pH electrode was immediately placed in the slurry, and the pH was measured immediately (Qin H et al., 2023).

Total Ash: Dry combustions at 720 °C for three hours in a muffle furnace were used to determine the total ash content. Jindo et al. (2014) were followed in calculating the mineral element content.

Biochar liming potential: Depending on the feedstock and procedure, the ash component of biochar, which contains carbonates and alkaline oxides, can considerably raise alkalinity (Vassilev et al. 2013a) (Xie et al. 2015). As a result of this, biochars can be utilized as liming agents in acidic soils and acquire liming capabilities (Novak et al. 2009). It is not possible to propose lime until the soil's pH-buffering capacity (pH-BC) and the biochar's liming potential have been established.

The carbonate content of soil was determined by modifying the Rayment and Higginson (1992) method. Liming equivalent, or calcium carbonate equivalent, was calculated. This is accomplished by combining 0.5 g of ground biochar with 10.0 mL of a standardized 1 M HCl solution, stirring the combination for two hours. After that, it is left on an end-over-end shaker for sixteen hours. The slurry is then titrated without the need for a separate process using an auto titrator that vigorously swirls a standardized 0.5 M NaOH solution until a neutral pH (~7.0) is reached.

It is stated how many milliliters of NaOH solution were used. After performing a blank titration (i.e., without biochar) using 10.0 mL of standardized 1 M HCl, the volume of NaOH solution utilized is measured (b mL).

The batch also includes a reference sample of CaCO₃ powder that was dried for an hour at 105°C. The limiting equivalence (% CaCO₃-equivalent) is then obtained using the following formulas:

Chemical reaction and calculations:



In equation (1) the reaction above, one mole of CaCO₃ (about 100.09 g of CaCO₃) is dissolved using two moles of HCl. Titration is utilized to find unreacted H⁺. The amount of H⁺ neutralized by the biochar is then calculated using the difference between the biochar sample and the blank. Thus, the % CaCO₃ -eq is calculated in Equation (2):

$$\% \text{CaCO}_3 \text{ equivalent} = \frac{(M \times (b-a) \times 10^{-3} \times 100.09 \times 100)}{(2 \times W)} \quad (2)$$

Where:

M = mol L⁻¹, the standardized molarity of NaOH

b = the blank's NaOH consumption volume (mL)

a = amount of NaOH that the biochar sample consumed (mL)

To convert volume from mL to L 100, use the conversion factor 10⁻³. 09 = CaCO₃ molar mass 100 = multiplier to represent the outcome as a percentage

W = biochar mass (g)

Since 1 mole of CaCO₃ reacts with 2 moles of H⁺, 2 = factor accounted for the stoichiometry

Biochar Yield: The biochar yield was calculated using the weight ratio of the pyrolysis product to the original ingredients as described in Equation (3). % Yield (dry weight basis) of processed material based on weight differential before and after pyrolysis.

$$\% \text{Yield} = \frac{\text{Actual yield}}{\text{initial weight of feedstock}} \times 100 \quad (3)$$

The morphologies and structural composition of the biochars were examined using scanning electron microscopy (SEM). A Phenom-World scanning electron microscope was used to conduct energy-dispersive spectroscopy (EDX). The Brunauer-Emmett-Teller (BET) method (Quantachrome NovaWin – Data collection and Reduction for NOVA instrument version 11.03, Ahmadu Bello University, Zaria) was used to measure the biochars' specific surface area before and after the alteration. The adsorbent's functional groups' surface was verified using Agilent's Fourier transform infrared (FT-IR) spectroscopy. The collected spectra ranged from 4000 to 650 cm⁻¹.

2.3. Adsorption Experiment

The pollutant used in the experiment was a stock solution of Co (II). In order to do adsorption investigations, 1g of adsorbent was added to the appropriate concentration of various components. An atomic absorption spectrophotometer was used to quantify the concentration of Co (II) in the suspensions following a 12-hour shake period. Equations (4) and (5) were used to determine the amount of Co (II) adsorbed on the biochars when the system was in equilibrium (Hou et al. 2016). The Langmuir and Freundlich isothermal adsorption models were examined in Equations (6) and (7).

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (4)$$

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \% \quad (5)$$

$$\ln q_e = \ln K_T + \frac{1}{n} \ln C_e \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (7)$$

q_e ($\text{mg}\cdot\text{g}^{-1}$) in the equations represents the adsorbent's equilibrium adsorption capability on cobalt. C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the cobalt concentration in the initial solution, whereas C_e ($\text{mg}\cdot\text{L}^{-1}$) is the cobalt concentration in the solution when adsorption reaches equilibrium. The adsorbent's mass is denoted by M (mg), the aqueous solution's volume by V (mL), and the theoretical maximum adsorption capacity for cobalt is q_m ($\text{mg}\cdot\text{g}^{-1}$). KL is the Langmuir model constant ($\text{L}\cdot\text{mg}^{-1}$).

Impact of dosage on sorption: To generate the sorption dosage data, the following requirements have to be fulfilled: 0.1 to 1.0 g of the adsorbent per 100 mL of solution; 2 ppm for metal ion concentrations; 7.85 pH for all sorption investigations; and 12 hours of shaking time.

Impact of pH on sorption: To provide sorption pH data, the following parameters are used: dose of the adsorbent, 0.5 g/100 mL of solution; metal ion concentrations for Co^{2+} range from 2 ppm, and all sorption tests have a pH of 2; 4, 6, 8, and 10; The sorption test would be carried out at 27.5 °C for a duration of 12 hours of shaking.

Impact of Cd (II) ions concentration on sorption: When producing data, the following standards are used: All sorption tests use a sorbent dose of 0.5 g per 100 mL of metal ion solution, a metal ion concentration ranging from 5 to 7 ppm, a pH of 7.85 for Co^{2+} , and a 12-hour shaking duration. The sorption tests were conducted at a temperature of 27.5°C.

Impact of contact time on sorption: The impact of contact time on sorption was studied using 0.5 g of adsorbent per 100 mL of solution, a starting metal concentration of 2 ppm for Co^{2+} , and contact times ranging from 2 to 12 h under continuous shaking. The pH was 7.85. The temperature of the mixtures was maintained at 27.5°C.

Effect of temperature on sorption: The following settings were applied in order to produce sorption thermodynamic data: The sorption tests would be conducted using an adsorbent dosage of 0.5 g/100 mL of solution, metal ion concentration ranges of 2 ppm Co^{2+} , pH 7.85, and a 12-hour shaking period. Temperatures of 10, 20, 30, 40, and 50 degrees would be used for the sorption tests.

The pseudo-first-order (8) and pseudo-second-order (9) models were employed to match the sorption kinetics.

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad (8)$$

Where k_1 is the pseudo-first-order rate constant (1/min), Q_t (mg/g) is the sorption amount at time t , and Q_e (mg/g) is the sorption amount at equilibrium.

$$Q_t = \frac{k_2 Q_e^2 t}{(k_2 Q_e t + 1)} \quad (9)$$

The sorption amount at equilibrium is Q_e (mg/g), the sorption amount at time t is Q_t (mg/g), and the pseudo-second-order rate constant is k_2 ($\text{g}/(\text{mg}\cdot\text{min})$).

Equations (6) and (7) were used to calculate the Co ion sorption capacity and the ion adsorption efficiency (η), respectively. By averaging the three times the same processes were performed, the adsorbent's ultimate capacity was ascertained. The ions concentration at the adsorption equilibrium and the initial concentration are denoted by C_e (mg/L) and C_0 (mg/L), respectively; the volume of the ions solution used in the experiment is denoted by V (L); and the dry weight of the biochar added to the ions solution is denoted by m (mg). The sorption capacity of modified adsorbent ions is denoted by Q_e (mg/g).

3. RESULT AND DISCUSSION

3.1. Surface Characteristics Analysis of the Biochar

The adsorbent's surface chemistry and morphology significantly impact adsorption processes (Ghanim et al., 2020). Table 1 lists the volume, DR micropore width, and BET N₂ surface area of the modified (AP1, AS2, BP1, and BS2) and unmodified (OP and OS) biochars. Compared to AS2, which has values of 229.8m²/g and 371.390m²/g, respectively, the modified biochar AP1 has a superior single and multi-point

BET surface area of 256.0m²/g and 450.023m²/g. Both Chars were altered using a ratio of 0.3:2 KMnO₄:HNO₃. In comparison to BP1, this also had 0.8:2 KMnO₄:HNO₃ changed; BS2 has a better single and multi-point BET surface area of 241.9m²/g and 392.508m²/g, with values of 220.2m²/g and 345.364m²/g. In contrast to OS, which has single and multi-point BET surface areas of 227.2m²/g and 418.333m²/g, respectively, OP has single and multi-point BET surface areas of 244.4m²/g and 356.276m²/g. Following treatment with KMnO₄ and HNO₃, the surface area of the modified biochars rose. The higher BET may accelerate the adsorption capacity (Tang et al., 2018). Following characterizations and batch adsorption tests, AP1 and BS2 of the modified biochar were utilized, and they were subsequently contrasted with the unmodified biochar.

Table 1: BET surface area and DR micro pore values of the modified and unmodified biochar

Samples	SBET(m ² /g)	MBET(m ² /g)	DR micro pore width (nm)	DR micro pore volume (cc/g)
AP1	256.0	450.023	6.381	0.1626
AS2	229.8	371.390	6.195	0.1418
BP1	220.2	345.364	6.083	0.1350
BS2	241.9	392.508	6.214	0.1502
OP	244.4	356.276	5.839	0.1454
OS	227.2	418.333	6.538	0.1475

When combined with energy dispersive X-ray spectroscopy (EDS or EDX), scanning electron microscopy (SEM) offers a comprehensive view of the biochar's morphological features and elemental makeup. The SEM results for the modified and unmodified biochar with large surface areas (AP1, BS2, OP, and OS) at 500x, 1000x, and 2000x are displayed in Figure 2. The cellulose structure of sugarcane peel, which may be divided into fibrous, prismatic, and spherical forms, is likely the source of the noticeable longitudinal fibrous structures seen in the biochar OS and BS2 (Joseph et al, 2010). Due to the raw material's dehydration, a small number of pores of varying sizes developed in the biochar. Additionally, AP1 and BS2 are clean in the SEM image, indicating that the KMnO₄/HNO₃ oxidant has largely or completely removed the ashes from the unmodified biochar. One characteristic of biochar is that its surface is flat and moderately porous. The largest pore distribution was found on the surface of biochar AP1 and BS2, which may provide more adsorption sites and increase the biochar's adsorption capacity.

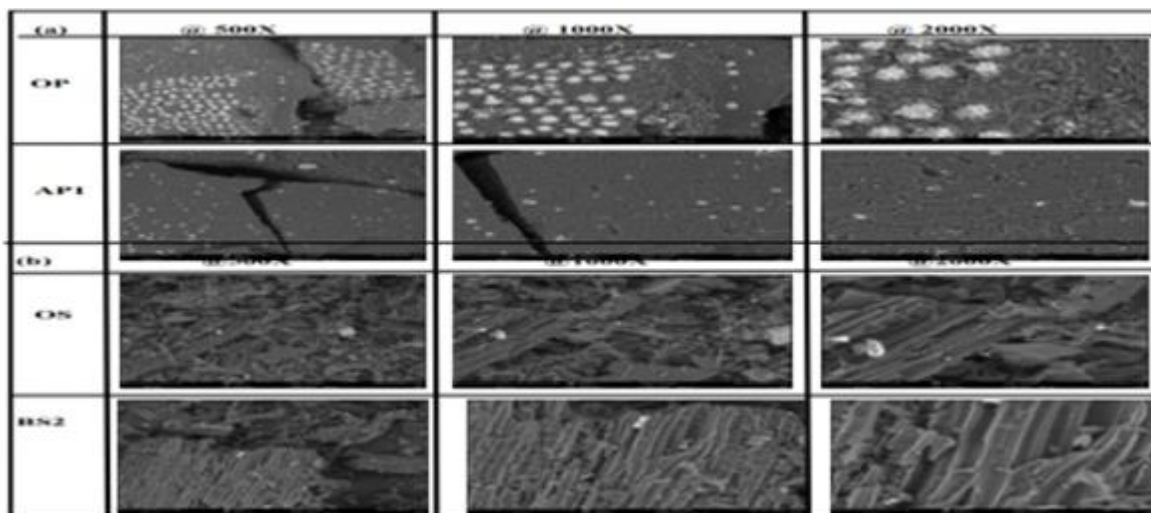


Figure 2: SEM images comparing (a) OP with AP1 and (b) OS with BS

3.2. Elemental Analysis of Biochar

According to Table 2, the non-metallic elements with the highest amounts were C, N, and Si. In contrast to the modified biochar (AP1 and BS2), the unmodified biochar (OP and OS) had higher C and Si

elemental concentrations. In contrast to OP and OS, AP1 and BS2 have a very high N elemental concentration. This is because of the $\text{KMnO}_4/\text{HNO}_3$ alteration, which demonstrates the reduction in ash brought on by the loss of silicon and carbon (Fan et al., 2018). Except Na, which is nearly equal in OP (0.25%) and AP1 (0.27%) and decreases from OS to BS2, the unmodified biochar (OP and OS) has a significant amount of the metallic elements Mg and K.

Table 2: EDS elemental composition of the modified and unmodified biochar's

Samples	Non-metallic elements (%)						Metallic elements (%)					
	C	N	Si	Cl	S	P	Mg	Na	K	Ca	Fe	Ti
OP	88.32	5.18	4.24	0.12	0.15	0.17	0.30	0.25	4.24	0.38	0	0
OS	89.48	4.24	0.99	0.37	0.26	0.58	0.46	0.37	2.57	0.28	0	0.08
AP1	88.13	8.62	1.42	0.31	0.16	0.14	0.27	0.27	0.19	0	0.12	0.04
BS2	86.78	7.24	0.75	2.51	0.31	0.43	0.37	0.20	0.34	0.23	0.31	0

The FTIR spectra of the modified and unmodified biochars are displayed in Figure 3. Carboxyl, esters, and anhydride groups are among the several active functional groups found in biochar (Ma et al., 2010). It is clear that the oxygen-containing functional groups on the surface of AP1 and BS2 are significantly impacted by the alteration process. The stretching vibration of OH is responsible for the absorption peak at wavenumber 3380cm^{-1} for AP1 and 3570cm^{-1} for BS2 (Chen et al., 2008). The findings imply that the biochar treated with $\text{KMnO}_4/\text{HNO}_3$ has more oxygen-containing functional groups, such as hydroxyl groups. The existence of the aldehyde terminal C-H functional group, which also suggests the presence of oxygen-containing functional groups, is shown by the stretching seen at 2922.2cm^{-1} in AP1. The stretching vibrations of different aromatic ethers, or O-H and C-O, are represented by the absorption peak in the biochars between wave numbers 1039.9cm^{-1} and 11107.7cm^{-1} , suggesting that the biochars have a good aromatic structure (Li B et al., 2017).

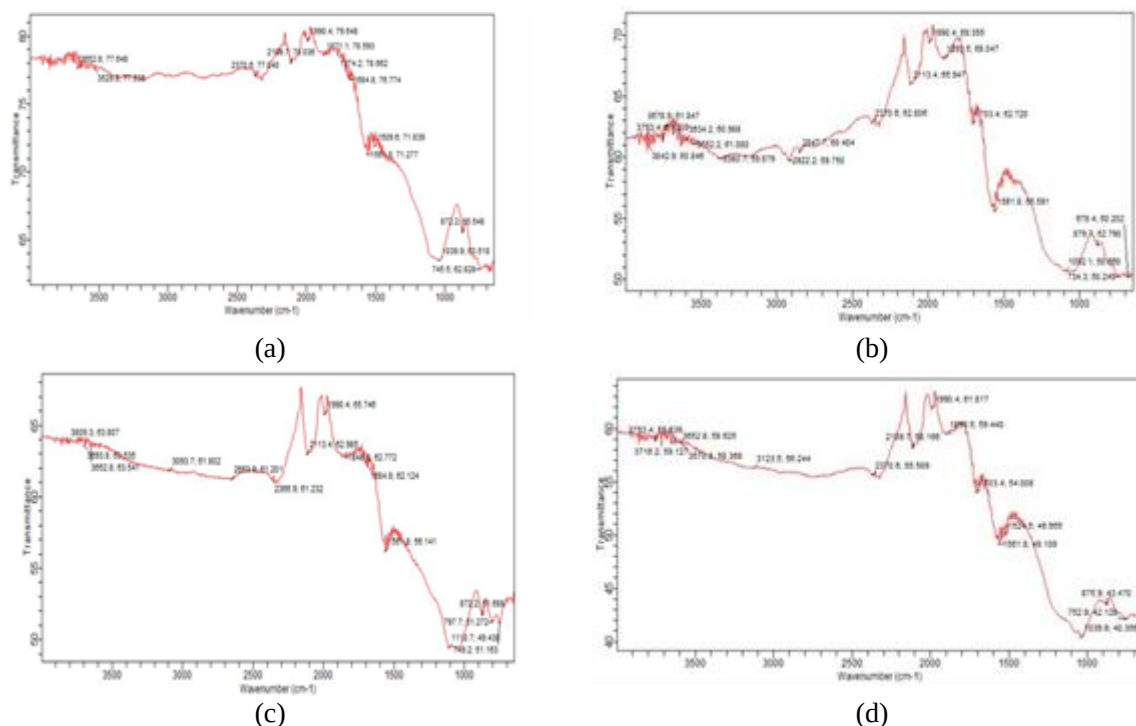


Figure 3: FTIR spectrum of (a) OP, (b) AP1, (c) OS and (d) BS2

3.3. Properties Analysis

Table 3 displays the proximate analysis for the unmodified biochars (OS and OP). The alkaline biochars had pH values of 10.7 and 9.1, CaCO₃ equivalents of 48.04% and 26.98%, and total ash contents of 4.5% and 1.8%. The yields for OS and OP were 26.8% and 33.2%, respectively.

Table 3: Proximate analysis of unmodified biochar (OS and OP)

Samples	pH	Total ash	CaCO ₃ equi. (%)	Yield (%)
OS	10.7	4.5	48.04	26.8
OP	9.1	1.8	26.98	33.2

3.4. Adsorption Isotherms of Co(II)

According to Wang et al. (2023), Table 4 shows the unmodified (OP and OS) and modified (AP1 and BS2) plots, respectively, contain the linear constant (n), the Langmuir model constant KL(L/mg), the Freundlich model constant Kf(mg/g), and the predicted maximum adsorption capacity for Cobalt qm(mg/g). The interaction between the adsorbent (biochars) and the adsorbate (Co²⁺) could be examined using the Langmuir and Freundlich isotherm models, which provided valuable insights into the adsorption process. Table 4 also shows the experimental parameters of the Langmuir and Freundlich adsorption, while figure 4 and 5 shows the statistical plot Co²⁺ uptake by AP1, OP, BS2, OS and their fit to the Langmuir model and Freundlich. The adsorption constant of the Langmuir model of AP1 and BS2 is higher compared to OP and OS, showing the affinity of AP1 and BS2 adsorbent with CO²⁺ in solution, and it is easier to immobilize free CO²⁺ by the adsorption reaction. AP1 and BS2 are also higher sequentially when compared to OP and OS. The 1/n values (from 0.0257 - 0.847) shows the intensity of the adsorption reaction, and values is less than one, showing that the adsorption of Co²⁺ is an ideal adsorption process that easily occur (Faust and Scipenbush, 2014). The Freundlich plot for AP1 (R² = 0.9976) is superior to the Langmuir plot (g) (R² = 0.9659), while the Freundlich plot for BS2 (R² = 0.9426) is superior to the Langmuir plot (e) (R² = 0.914), which indicates that the Freundlich isotherm can better describe the adsorption of Co²⁺, surfaces having heterogeneous adsorption sites or multi-layer adsorption are better described by the Freundlich model (Liu et al., 2019).

Table 4: Shows the Langmuir and Freundlich isotherm parameters for AP1, OP, BS2, OS

Samples	q _e (mg.g ⁻¹)	Langmuir K _L (L.Mg ⁻¹)	R ²	Freundlich K _F (Mg.g ⁻¹)	1/n	R ²
AP1	84.74	0.177	0.9659	1.49x10 ¹⁸	0.0518	0.9976
OP	41.15	0.117	0.9334	1.12x10 ⁴⁰	0.0257	0.8734
BS2	714.28	60.75	0.914	9.6x10 ²	0.8473	0.9426
OS	74.07	1.687	0.877	4.3x10 ⁻²	0.0436	0.8011

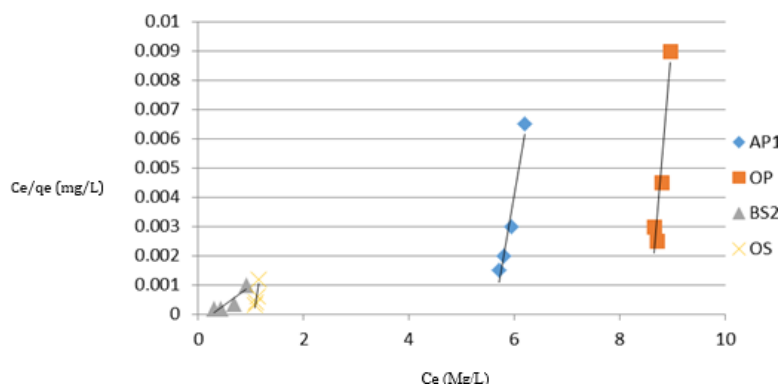


Figure 4: Experimental isotherm data of Co²⁺ uptake by AP1, OP, BS2, OS and their fit to the Langmuir model

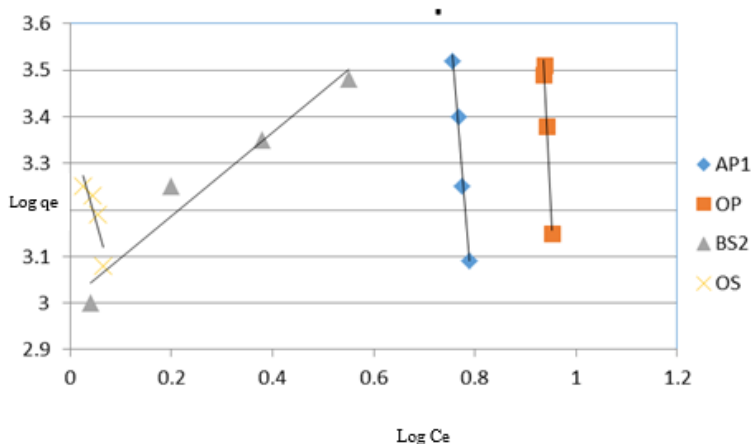


Figure 5: Experimental isotherm data of Co^{2+} uptake by AP1, OP, BS2, OS and their fit to the Freundlich model

3.5. Kinetic Analysis of Co^{2+} Sorption

The sorption kinetics of Co^{2+} ions were analyzed using the pseudo-first-order and pseudo-second-order Lagergren models. Linear regression of the experimental data yielded strong correlations for both models, as evidenced by high coefficients of determination ($R^2 > 0.89$), indicating close agreement between theoretical predictions and experimental results (Table 5).

Pseudo-second-order dominance: The higher R^2 values for the pseudo-second-order model ($R^2 > 0.99$ for most adsorbents) suggest it better describes the sorption kinetics, implying a chemisorption-dominated process involving valence forces or chemical bonding.

Kinetic parameters: The pseudo-first-order model parameters ($q_{e,calc}$, K_1) and pseudo-second-order parameters ($q_{e,calc}$, rate constant K_2) were derived from linear plots of:

- $\log(q_e - q_i)$ vs. t (pseudo-first-order)
- t/q_t vs. t (pseudo-second-order).

These parameters are critical for predicting sorption rates and optimizing large-scale batch systems (Gupta, 1998).

Table 5. Kinetic Parameters for Co^{2+} Sorption

Model	Parameter	AP1	OP	BS2	OS
Pseudo-first-order	$q_{e,calc}$ (mg/g)	0.7306 (0.8251)	0.9047 (0.8574)	1.1888 (0.8375)	0.8391 (0.8377)
	K_1 (h^{-1})	0.4376 (0.4284)	0.05159 (0.2437)	0.9207 (0.5700)	0.4060 (0.2411)
	R^2	0.9936 (0.8962)	0.9122 (0.9517)	0.9701 (0.9177)	0.9825 (0.9878)
Pseudo-second-order	$q_{e,calc}$ (mg/g)	7.2622 (3.1795)	1.5936 (2.1847)	6.0459 (4.5310)	2.6737 (2.0521)
	K_2 (g/mg·h)	0.0106 (0.0575)	0.3387 (0.1000)	0.0159 (0.0295)	0.0839 (0.1436)
	R^2	0.9988 (0.9941)	0.9911 (0.9817)	0.9986 (0.9962)	0.9925 (0.9877)

Note: Values in parentheses represent replicate or uncertainty estimates.

Practical Implications:

The pseudo-second-order model's superior fit highlights its utility in designing adsorption systems, as it accounts for both surface binding and solute affinity. Kinetic data are indispensable for scaling laboratory results to industrial applications, ensuring efficient contaminant removal.

3.6. Thermodynamic Analysis

The influence of temperature on the sorption of metal ions onto the adsorbents was evaluated using three key thermodynamic parameters: Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The Gibbs free energy (ΔG , kJ mol^{-1}) was calculated using Equation 10:

$$\Delta G = -RT \ln K \quad (10)$$

Equation (10) is Gibbs free energy change, where K is the equilibrium constant derived from the Langmuir constant (Kl mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (K). The van't Hoff equation ($\Delta G = \Delta H - T\Delta S$) was applied by plotting ΔG against T , allowing ΔH (slope) and ΔS (intercept) to be determined (Blázquez et al., 2011).

The negative ΔH values confirmed the exothermic nature of the sorption process. For spontaneity, the Gibbs free energy (ΔG°) must also be negative; Table 6 demonstrates that adsorption was thermodynamically favorable and spontaneous at temperatures below 323 K. At higher temperatures, increased molecular mobility enhanced the affinity between adsorbate and adsorbent.

Table 6: Thermodynamic parameters for Co^{2+} Sorption

Parameter	AP1	OP	BS2	OS
ΔG (kJ/mol)	1.079 (1.026)	0.911 (1.556)	1.545 (1.859)	1.828 (1.859)
ΔH (kJ/mol)	-0.0041 (-0.0033)	-0.0234 (-0.0118)	-0.0155 (-0.0242)	-0.0246 (-0.0246)
ΔS (J/mol·K)	2.365 (2.043)	8.243 (5.099)	6.190 (9.099)	9.196 (9.232)

Note: ΔH = Enthalpy; ΔS = Entropy; ΔG = Gibbs free energy. Values in parentheses represent uncertainties or replicates.

The magnitude of ΔH° further elucidates the sorption mechanism. Physical adsorption (physisorption) typically involves ΔH° values of $2.1\text{--}20.9 \text{ kJ mol}^{-1}$, akin to condensation energies, whereas chemisorption requires higher energies ($80\text{--}200 \text{ kJ mol}^{-1}$). The intermediate ΔH° values in Table 6 suggest a combined physicochemical adsorption mechanism rather than purely physisorption or chemisorption (Ho et al., 2002). A positive ΔS° reflects a strong adsorbent-adsorbate affinity, while high ΔS° values imply structural rearrangements at the solid-solution interface, indicating potential instability (McKay, 1988).

3.7. Impact of dosage and pH on the sorption process

Figure 4 illustrates the pronounced influence of pH on Co(II) removal from aqueous solution. The adsorption capacity exhibited strong pH-dependence, with a 95.95% enhancement in Co(II) uptake as pH increased from 3 to 10. However, adsorption efficiency peaked at pH 7.5, beyond which a gradual decline in cobalt ion removal was observed.

Key mechanisms governing pH-dependent adsorption:

- Metal Solubility:
 - At low pH (<7), high H^+ concentration promotes protonation of functional groups and competes with Co^{2+} for binding sites.
 - Above pH 7.5, Co(II) may precipitate as Co(OH)_2 , reducing soluble ion availability.
- Surface Charge Modulation:
 - The adsorbent's functional groups (e.g., $-\text{COOH}$, $-\text{OH}$) become deprotonated at higher pH, enhancing their affinity for cationic Co^{2+} .
 - The point of zero charge of the adsorbent critically determines its pH-dependent behavior.

The maximum adsorption observed at pH 7.5 aligns with the natural pH range of freshwater ecosystems, as reported by Aditya and Hossain (2018). This pH represents a balance between the solubility of Co(II) ions and the surface charge of the adsorbent. Optimizing this pH is therefore essential for achieving efficient adsorption in both laboratory studies and practical water treatment applications.

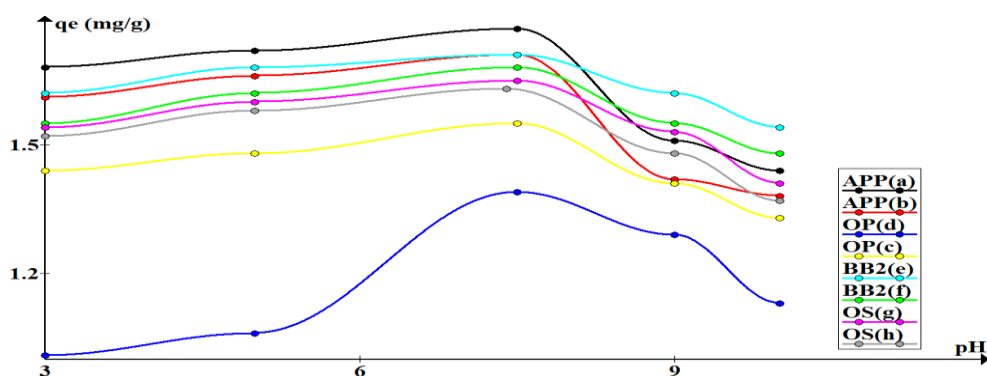


Figure 4: Impact of pH on the sorption of Co (II) ions by adsorbents

The impact of adsorbent dosage on the ability to adsorb Co (II) from aqueous solutions is shown in Figure 5. Higher adsorbent concentrations in the metal solution resulted in a proportionate rise in cobalt biosorption. The uptake of cobalt from the solution was probably promoted by the increased availability of free binding sites or the easier exchange of functional groups, which could be the cause of this improvement in adsorption (Hossain et al., 2015).

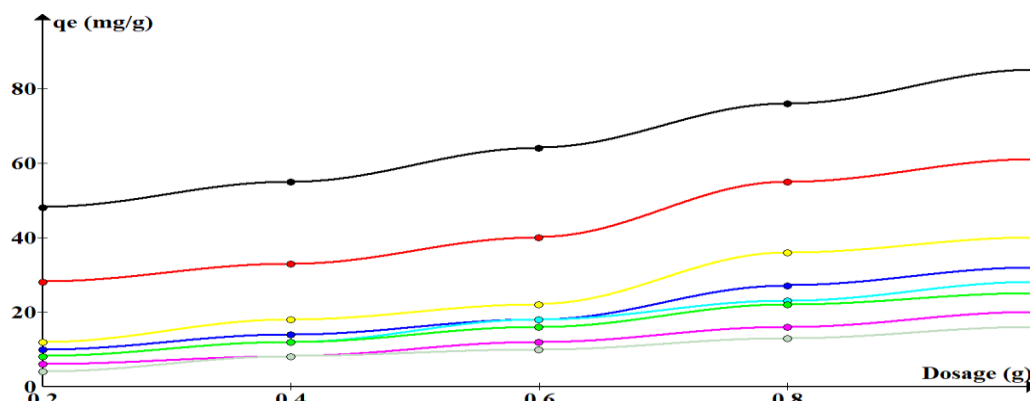


Figure 5: Impact of dosage on the sorption of Co (II) ions by adsorbents

3.8. Reusability

The cycling performance of an adsorbent is a critical factor in determining its practical applicability. To assess the reusability of the modified biochars (AP1 and BS2) for Co²⁺ adsorption, five consecutive adsorption-desorption cycles were conducted. As shown in Figure 6, the adsorption capacity of both AP1 and BS2 gradually declined with each cycle, likely due to structural degradation and the loss of surface-active minerals (Zhang et al., 2017). Despite this, the adsorbents retained 83.1% (AP1) and 78.5% (BS2) of their initial capacities by the fifth cycle, demonstrating their strong potential for repeated use in Co²⁺ removal.

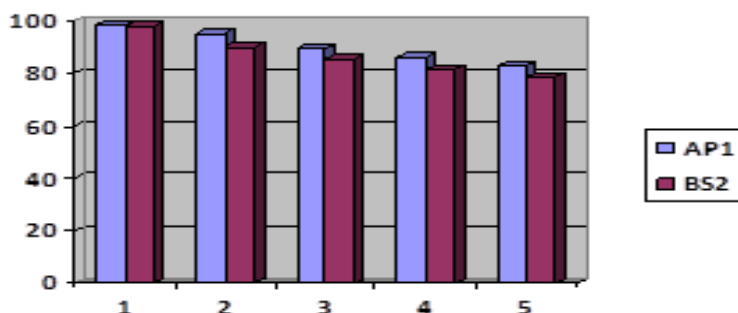


Figure 6: AP1 and BS2 adsorption – desorption recycle performance of Co^{2+}

4. CONCLUSION

In this study, modified biochars (AP1, AS2, BP1, and BS2) were prepared using potassium permanganate and nitric acid at ratios of 0.3:2.0 and 0.8:2.0 $\text{mol}\cdot\text{L}^{-1}$ to assess their Co^{2+} removal capacity in aqueous environments through batch experiments. Characterization revealed that the modified biochars exhibited increased specific surface area, enhanced polarity, and a higher concentration of oxygen-containing functional groups compared to unmodified biochars (OP and OS). These properties provided more adsorption sites, significantly improving their adsorption capacity. Specifically, the SBET surface areas of AP1 and BS2 were $256.0\text{m}^2/\text{g}$ and $241.0\text{m}^2/\text{g}$ higher than those of OP and OS, respectively. Adsorption kinetics demonstrated that Co^{2+} was rapidly adsorbed by the modified biochars within 1 hour, with equilibrium reached after 2–4 hours. Isotherm adsorption experiments showed that the equilibrium data for AP1, BS2, and OS fit well with the Freundlich model, indicating heterogeneous adsorption sites, while OP followed the Langmuir model, suggesting a more homogeneous surface with a maximum adsorption capacity (q_m) of 41.15226 mg/g . The maximum adsorption capacities for heterogeneous sites were $1.49\times 10^{18}\text{ mg/g}$ (AP1), 961.833 mg/g (BS2), and 25603.54 mg/g (OS). Reusability tests revealed a gradual decline in the adsorption capacity of AP1 and BS2 over multiple cycles, likely due to structural degradation and the loss of surface-active minerals. However, after five cycles, AP1 and BS2 retained 83.1% and 78.5% of their initial adsorption capacities, respectively, demonstrating their stability and potential for repeated use. The modified biochars (AP1, AS2, BP1, and BS2) are cost-effective, environmentally friendly, and recyclable adsorbents, making them promising materials for water and soil pollution treatment. Their enhanced adsorption properties and reusability highlight their potential for practical applications in environmental remediation. This study underscores the viability of modified biochars as sustainable solutions for heavy metal removal.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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