

Comparative Adsorption of Pb (II) from Aqueous Solution Using Rice-Husk and Cotton-Straw Biochars and KOH-Activated Cotton-Straw Biochar

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Abstract:

Lead contamination of water is an important environmental concern, creating a need for inexpensive and effective adsorbent materials. In the present study, three agricultural-residue-derived biochars—rice-husk biochar (BC-RH), cotton-straw biochar (BC-CS), and KOH-activated cotton-straw biochar (KBC-CS)—were investigated for the removal of Pb(II) from aqueous solution. Batch adsorption experiments were evaluated with respect to initial Pb(II) concentration (10–400 mg L⁻¹), contact time (5–180 min), initial solution pH (2–7), and adsorbent dose (0.25–2.0 g L⁻¹). Equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models, while adsorption kinetics were evaluated using pseudo-first-order, pseudo-second-order, and intraparticle-diffusion models. Experimental results demonstrated that Pb(II) uptake increased with increasing initial concentration before approaching saturation. KOH activation substantially improved the adsorption performance of cotton-straw biochar. Under the investigated conditions, KBC-CS exhibited the highest maximum adsorption capacity ($q_{\text{max}} = 222.10 \text{ mg g}^{-1}$) compared to BC-CS (151.17 mg g⁻¹) and BC-RH (110.63 mg g⁻¹). Equilibrium data fitted the Langmuir model ($R^2 = 0.9852\text{--}0.9923$) better than the Freundlich model, while kinetic profiles followed the pseudo-second-order equation ($R^2 = 0.9986\text{--}0.9996$). Increasing solution pH from 2 to 6 significantly enhanced Pb(II) uptake due to decreased proton competition for surface sites. Maximum removal reached approximately 98% for KBC-CS at an adsorbent dose of 2.0 g L⁻¹. The findings confirm that KOH-activated cotton-straw biochar is a highly efficient, sustainable material for lead remediation.

Keywords: Biochar; Lead removal; KOH activation; Rice husk; Cotton straw; Adsorption isotherms; Chemical kinetics; Heavy metal remediation.

1. Introduction

Lead (Pb²⁺) is a non-biodegradable, highly toxic heavy metal that poses severe environmental and public health hazards when discharged into aquatic ecosystems. Industrial effluents from battery manufacturing, metal plating, mining, pigment manufacturing, and petrochemical processing serve as major point sources of aqueous lead contamination. Chronic human exposure to elevated lead levels can cause irreversible neurological impairment, renal dysfunction, hypertension, and developmental delays in children.

Consequently, establishing efficient, cost-effective technologies for heavy-metal decontamination is an environmental priority.

Conventional techniques for removing lead from aqueous waste streams include chemical precipitation, ion exchange, electrocoagulation, membrane filtration, and reverse osmosis. Although effective, many of these operational routes are constrained by high capital costs, high energy consumption, toxic sludge generation, and poor efficiency at low contaminant concentrations. Adsorption onto porous carbonaceous materials has emerged as a superior alternative due to its simplicity, cost-effectiveness, high removal efficiency, and potential for adsorbent regeneration.

Biochar—a carbon-rich, porous material produced via thermochemical pyrolysis of biomass under oxygen-limited conditions—has gained substantial attention as a sustainable adsorbent. Agricultural residues such as rice husk and cotton straw are abundant, low-cost biochar precursors. However, raw biochars often exhibit moderate specific surface areas and limited functional group density. Chemical activation using alkaline agents, particularly potassium hydroxide (KOH), can dramatically enhance surface area, induce micropore and mesopore development, and introduce reactive oxygenated functional groups onto the carbon backbone.

Although several studies have investigated heavy metal removal using modified biomass, a systematic comparison of pristine versus KOH-activated agricultural biochars evaluated across identical kinetic and thermodynamic frameworks remains essential. The objective of this study is to evaluate and compare the Pb(II) removal performance of rice-husk biochar (BC-RH), cotton-straw biochar (BC-CS), and KOH-activated cotton-straw biochar (KBC-CS) across varied experimental parameters (concentration, contact time, pH, and dosage) and to model the underlying isotherm and kinetic mechanisms.

2. Materials and Methods

2.1 Reagents and Materials

Rice husk and cotton straw were collected from local agricultural processing centers in Maharashtra, India. Analytical-grade lead nitrate, $\text{Pb}(\text{NO}_3)_2$, potassium hydroxide (KOH), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Merck Chemicals. All aqueous solutions were prepared using deionized water. Stock solution of Pb(II) (1000 mg L^{-1}) was prepared by dissolving an exact quantity of $\text{Pb}(\text{NO}_3)_2$ in deionized water and diluted as required.

2.2 Adsorbent Preparation

2.2.1 Rice-Husk Biochar (BC-RH)

Rice husk was repeatedly washed with deionized water to remove adhering dust and dirt, dried in a hot-air oven at 105°C for 24 h, and crushed. Thermochemical carbonization was performed in a muffle furnace under oxygen-limited conditions at 500°C for 120 min (heating rate of $10^\circ\text{C min}^{-1}$). The biochar was cooled inside the furnace, ground, passed through a standard mesh sieve, and stored in an airtight container. The biochar yield was 38.6%.

2.2.2 Cotton-Straw Biochar (BC-CS)

Cotton straw was washed, oven-dried at 105°C for 24 h, chopped, and pyrolyzed under oxygen-limited conditions at 550°C for 120 min. The resulting biochar was cooled, milled, sieved, and designated as BC-CS. The biochar yield was 34.2%.

2.2.3 KOH-Activated Cotton-Straw Biochar (KBC-CS)

Cotton-straw biochar was chemically impregnated with 1.0 mol L⁻¹ KOH solution at a biochar-to-KOH mass ratio of 1:2. The slurry was stirred for 4 h, dried at 105 °C, and then subjected to secondary thermal treatment in a muffle furnace under oxygen-limited conditions at 550 °C for 120 min. After cooling, the activated biochar was thoroughly washed with 0.1 mol L⁻¹ HCl followed by warm deionized water until the filtrate reached neutral pH ($\approx$ 7.0). The dried activated product was designated KBC-CS. The yield was 27.8%.

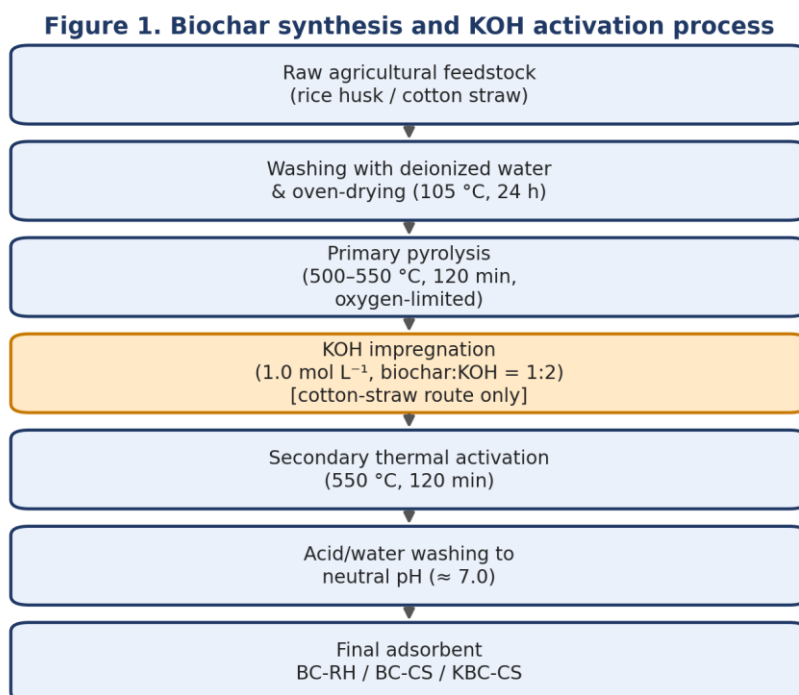


Figure 1. Schematic representation of biochar synthesis and chemical activation process.

Flowchart illustrating raw agricultural feedstock washing → drying → primary pyrolysis at 500–550 °C → KOH impregnation (1:2 ratio) → secondary activation thermal treatment at 550 °C → acid/water washing to neutral pH → final KBC-CS adsorbent.

2.3 Batch Adsorption Experiments

Batch adsorption studies were conducted in 250 mL Erlenmeyer flasks containing 50 mL of Pb(II) solution at an initial dosage of 1.0 g L⁻¹ (0.050 g adsorbent) unless otherwise specified. Flasks were agitated in a temperature-controlled orbital shaker at 150 rpm and 298 K.

- Initial Concentration Effect & Equilibrium Isotherms: $C_0 = 10\text{--}400$ mg L⁻¹ at pH 5.0 ± 0.1 for 180 min.
- Contact Time & Kinetics: $C_0 = 100$ mg L⁻¹ with sampling intervals at $t = 5, 10, 20, 30, 45, 60, 90, 120,$ and 180 min.
- pH Influence: Solution pH was adjusted from 2.0 to 7.0 using 0.1 M HCl or 0.1 M NaOH.
- Adsorbent Dosage: Dosages ranged from 0.25 to 2.00 g L⁻¹ (0.0125–0.100 g per 50 mL) at $C_0 = 100$ mg L⁻¹.

At predefined intervals, solutions were filtered through 0.45 μ m membrane filters, and residual Pb(II) concentrations were determined via Flame Atomic Absorption Spectrometry (FAAS).

2.4 Data Analysis and Mathematical Formulations

The equilibrium adsorption capacity q_e (mg g^{-1}) and percentage removal were calculated using Equations 1 and 2:

$$q_e = (C_0 - C_e)V / m \quad (1)$$

$$\text{Removal (\%)} = [(C_0 - C_e) / C_0] \times 100 \quad (2)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium Pb(II) concentrations, V (L) is the solution volume, and m (g) is the dry mass of adsorbent.

2.4.1 Adsorption Isotherm Models

Equilibrium data were evaluated using the Langmuir (Equation 3) and Freundlich (Equation 4) isotherms:

$$q_e = q_{\text{max}} \cdot KL \cdot C_e / (1 + KL \cdot C_e) \Rightarrow C_e / q_e = 1 / (q_{\text{max}} \cdot KL) + C_e / q_{\text{max}} \quad (3)$$

$$q_e = KF \cdot C_e^{1/n} \Rightarrow \ln q_e = \ln KF + (1/n) \ln C_e \quad (4)$$

where q_{max} (mg g^{-1}) is the theoretical maximum adsorption capacity, KL (L mg^{-1}) is the Langmuir equilibrium constant, KF [$(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$] is the Freundlich capacity factor, and n is the heterogeneity index.

2.4.2 Adsorption Kinetic Models

Time-dependent adsorption profiles were fitted using Pseudo-First-Order (Equation 5), Pseudo-Second-Order (Equation 6), and Intraparticle-Diffusion (Equation 7) kinetic models:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$q_t = k_2 \cdot q_e^2 \cdot t / (1 + k_2 \cdot q_e \cdot t) \Rightarrow t / q_t = 1 / (k_2 \cdot q_e^2) + t / q_e \quad (6)$$

$$q_t = k_{id} \cdot t^{1/2} + C \quad (7)$$

where q_t (mg g^{-1}) is the adsorption capacity at time t (min), k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the first- and second-order rate constants, k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant, and C (mg g^{-1}) represents boundary layer thickness.

3. Results and Discussion

3.1 Preparation Yields and Adsorbent Characteristics

The yields obtained for the biochars were 38.6% for BC-RH, 34.2% for BC-CS, and 27.8% for KBC-CS (Table 1). The lower yield observed for KBC-CS is attributed to chemical etching and mass loss during KOH activation, where alkaline degradation promotes pore evacuation and structural ablation, sacrificing total yield to yield higher effective porosity and active site density.

Table 1. Biochar preparation conditions and gravimetric yields

Adsorbent Code	Precursor	Pyrolysis Temp. ($^{\circ}\text{C}$)	Hold Time (min)	Chemical Activation	Yield (%)
BC-RH	Rice husk	500	120	None	38.6
BC-CS	Cotton straw	550	120	None	34.2
KBC-CS	Cotton straw	550	120	1.0 M KOH (1:2 ratio)	27.8

3.2 Effect of Initial Pb(II) Concentration

The effect of initial concentration on equilibrium uptake capacity was evaluated over $C_0 = 10\text{--}400\text{ mg L}^{-1}$ (Tables 2–4). Across all three biochars, adsorption capacity q_e increased progressively with C_0 . For BC-RH, q_e rose from 8.2 to 102.0 mg g^{-1} ; for BC-CS, from 8.8 to 138.0 mg g^{-1} ; and for KBC-CS, from 9.4 to 203.0 mg g^{-1} .

Table 2. Equilibrium adsorption data for BC-RH (T = 298 K, pH 5.0, dose = 1.0 g L^{-1})

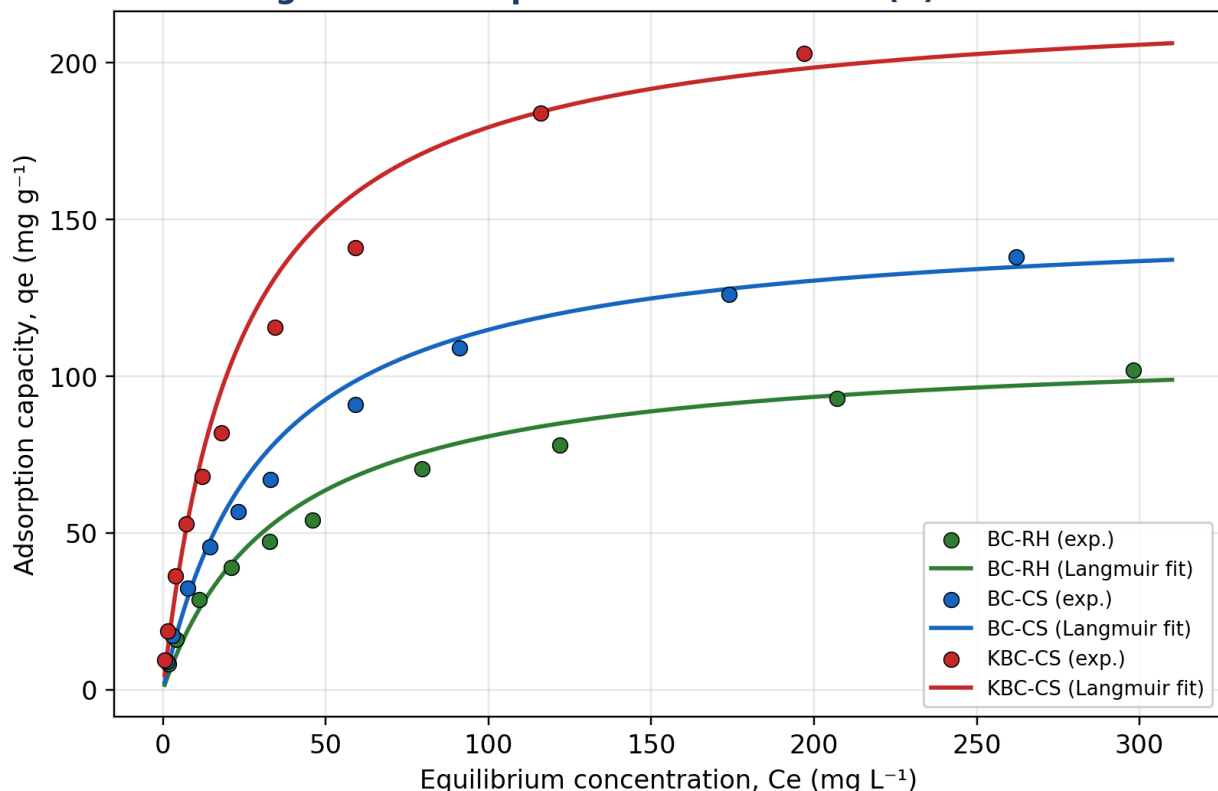
C_0 (mg L^{-1})	C_e (mg L^{-1})	q_e (mg g^{-1})	Removal (%)
10	1.8	8.2	82.0
20	4.0	16.0	80.0
40	11.2	28.8	72.0
60	21.0	39.0	65.0
80	32.8	47.2	59.0
100	46.0	54.0	54.0
150	79.5	70.5	47.0
200	122.0	78.0	39.0
300	207.0	93.0	31.0
400	298.0	102.0	25.5

Table 3. Equilibrium adsorption data for BC-CS (T = 298 K, pH 5.0, dose = 1.0 g L^{-1})

C_0 (mg L^{-1})	C_e (mg L^{-1})	q_e (mg g^{-1})	Removal (%)
10	1.2	8.8	88.0
20	2.8	17.2	86.0
40	7.6	32.4	81.0
60	14.4	45.6	76.0
80	23.2	56.8	71.0
100	33.0	67.0	67.0
150	59.0	91.0	60.7
200	91.0	109.0	54.5
300	174.0	126.0	42.0
400	262.0	138.0	34.5

Table 4. Equilibrium adsorption data for KBC-CS (T = 298 K, pH 5.0, dose = 1.0 g L⁻¹)

C ₀ (mg L ⁻¹)	C _e (mg L ⁻¹)	q _e (mg g ⁻¹)	Removal (%)
10	0.6	9.4	94.0
20	1.4	18.6	93.0
40	3.8	36.2	90.5
60	7.2	52.8	88.0
80	12.0	68.0	85.0
100	18.0	82.0	82.0
150	34.5	115.5	77.0
200	59.0	141.0	70.5
300	116.0	184.0	61.3
400	197.0	203.0	50.8

Figure 2. Adsorption isotherms of Pb(II) at 298 K

Figure 2. Adsorption Isotherm Curves for Pb(II) removal onto BC-RH, BC-CS, and KBC-CS at 298 K.

Plot showing equilibrium concentration C_e (mg L⁻¹) on the x-axis versus equilibrium adsorption capacity q_e (mg g⁻¹) on the y-axis, comparing experimental data points with solid lines representing the non-linear Langmuir fit.

3.3 Adsorption Kinetics

Kinetic profiles ($C_0 = 100 \text{ mg L}^{-1}$, dosage = 1.0 g L^{-1}) demonstrated rapid initial lead uptake during the first 20–30 min, reaching equilibrium near 180 min (Tables 5–7).

Table 5. Kinetic adsorption data for BC-RH ($C_0 = 100 \text{ mg L}^{-1}$, pH 5.0)

Time (min)	$C_t \text{ (mg L}^{-1}\text{)}$	$q_t \text{ (mg g}^{-1}\text{)}$
0	100.0	0.0
5	78.0	22.0
10	67.0	33.0
20	57.0	43.0
30	51.0	49.0
45	47.0	53.0
60	45.0	55.0
90	43.0	57.0
120	42.0	58.0
180	41.0	59.0

Table 6. Kinetic adsorption data for BC-CS ($C_0 = 100 \text{ mg L}^{-1}$, pH 5.0)

Time (min)	$C_t \text{ (mg L}^{-1}\text{)}$	$q_t \text{ (mg g}^{-1}\text{)}$
0	100.0	0.0
5	70.0	30.0
10	54.0	46.0
20	40.0	60.0
30	32.0	68.0
45	27.0	73.0
60	24.0	76.0
90	21.0	79.0
120	19.5	80.5
180	18.0	82.0

Table 7. Kinetic adsorption data for KBC-CS ($C_0 = 100 \text{ mg L}^{-1}$, pH 5.0)

Time (min)	$C_t \text{ (mg L}^{-1}\text{)}$	$q_t \text{ (mg g}^{-1}\text{)}$
0	100.0	0.0

Time (min)	Ct (mg L ⁻¹)	qt (mg g ⁻¹)
5	52.0	48.0
10	35.0	65.0
20	23.0	77.0
30	17.0	83.0
45	13.0	87.0
60	11.0	89.0
90	9.5	90.5
120	8.5	91.5
180	8.0	92.0

Figure 3. Adsorption kinetics of Pb(II) ($C_0 = 100 \text{ mg L}^{-1}$)

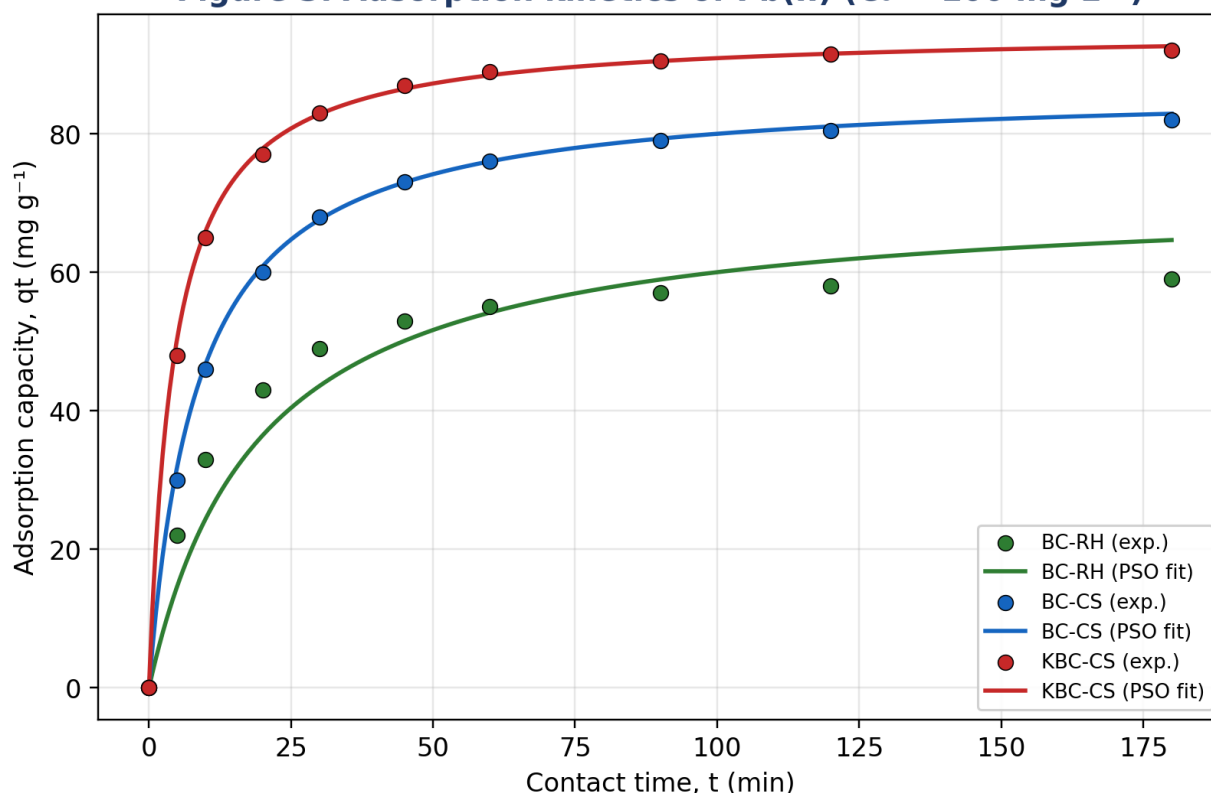


Figure 3. Kinetic adsorption profiles (qt vs. time t) for Pb(II) uptake onto BC-RH, BC-CS, and KBC-CS.

Graph showing contact time t (min) from 0 to 180 min on the x-axis versus adsorption capacity qt (mg g⁻¹) on the y-axis, highlighting the superior uptake kinetics of KBC-CS fitted with pseudo-second-order curves.

3.4 Influence of Solution pH and Adsorbent Dose

Solution pH governs both lead speciation and biochar surface charge. Between pH 2 and 6, Pb(II) removal increased markedly for all adsorbents (Table 8). Increasing adsorbent dosage from 0.25 to 2.00 g L⁻¹

increased percentage removal across all materials (Table 8), with KBC-CS reaching 98% removal at 2.0 g L⁻¹.

Table 8. Effect of initial solution pH and adsorbent dosage on Pb(II) removal efficiency (%)

Parameter	Range / Value	BC-RH Removal (%)	BC-CS Removal (%)	KBC-CS Removal (%)
Solution pH	2	31	38	52
Solution pH	3	48	57	72
Solution pH	4	63	72	84
Solution pH	5	72	82	92
Solution pH	6	76	87	95
Solution pH	7	78	89	96
Adsorbent Dose (g L ⁻¹)	0.25	42	49	61
Adsorbent Dose (g L ⁻¹)	0.50	58	68	79
Adsorbent Dose (g L ⁻¹)	1.00	72	82	92
Adsorbent Dose (g L ⁻¹)	1.50	80	89	96
Adsorbent Dose (g L ⁻¹)	2.00	85	93	98

Figure 4. Effects of solution pH and adsorbent dosage on Pb(II) removal

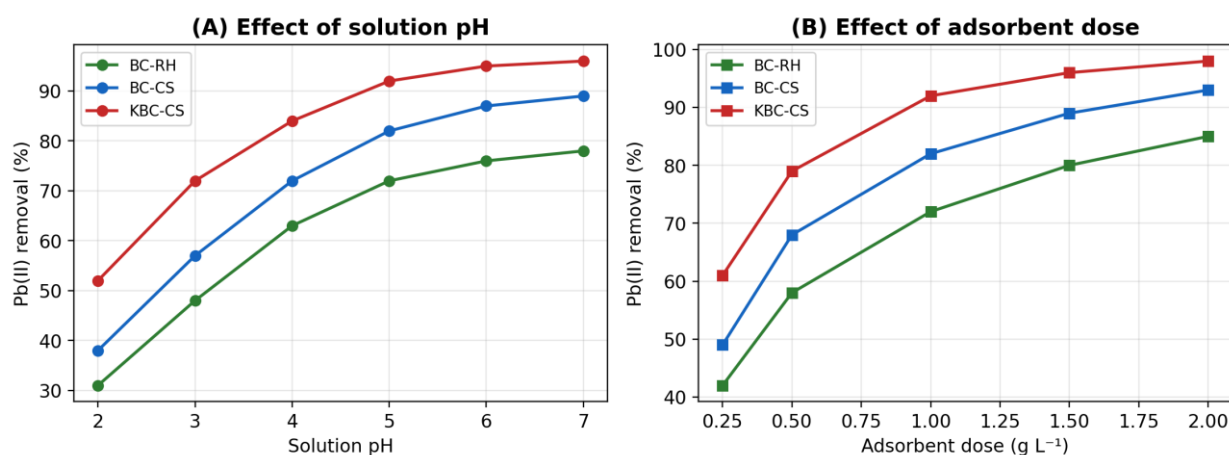


Figure 4. Effects of (A) Initial Solution pH and (B) Adsorbent Dosage on Pb(II) removal percentage.

Dual panel plot showing pH dependence from pH 2 to 7 in Panel A, and dosage dependence from 0.25 to 2.0 g/L in Panel B across all three biochar materials.

3.5 Consolidated Isotherm and Kinetic Parameter Modeling

Table 9 summarizes all derived modeling parameters for the three biochars.

Table 9. Consolidated isotherm and kinetic parameters for Pb(II) adsorption onto BC-RH, BC-CS, and KBC-CS

Model / Parameter	Unit	BC-RH	BC-CS	KBC-CS
Langmuir q _{max}	mg g ⁻¹	110.63	151.17	222.10
Langmuir KL	L mg ⁻¹	0.0271	0.0316	0.0421
Langmuir R ²	—	0.9852	0.9923	0.9881
Freundlich KF	(mg g ⁻¹)(L mg ⁻¹) ^(1/n)	8.01	10.33	16.08
Freundlich n	—	2.09	1.97	1.90
Freundlich 1/n	—	0.478	0.508	0.527
Freundlich R ²	—	0.9720	0.9726	0.9760
q _{e,exp}	mg g ⁻¹	59.00	82.00	92.00
PFO q _{e,cal}	mg g ⁻¹	31.84	42.15	45.60
PFO k ₁	min ⁻¹	0.0304	0.0328	0.0381
PFO R ²	—	0.9821	0.9845	0.9792
PSO q _{e,cal}	mg g ⁻¹	71.57	86.81	94.88
PSO k ₂	g mg ⁻¹ min ⁻¹	7.25×10 ⁻⁴	1.35×10 ⁻³	2.41×10 ⁻³
PSO R ²	—	0.9986	0.9991	0.9996
Intraparticle k _{id}	mg g ⁻¹ min ^{-1/2}	3.12	4.05	3.75
Intraparticle C	mg g ⁻¹	19.80	26.50	47.10
Intraparticle R ²	—	0.8640	0.8520	0.7810

3.6 Proposed Mechanism of Pb(II) Removal

The adsorption of Pb²⁺ onto biochar surfaces occurs through a combination of physical and chemical interactions, including electrostatic attraction between positively charged Pb²⁺ ions and negatively charged functional groups on the biochar surface, together with surface complexation, ion exchange with mobile cations, and micropore diffusion into the activated carbon matrix. The markedly greater performance of KBC-CS is consistent with its enhanced surface area, higher density of oxygenated surface functional groups, and expanded micro/mesoporosity introduced by KOH activation.

Figure 5. Proposed mechanisms of Pb^{2+} removal onto biochar surfaces

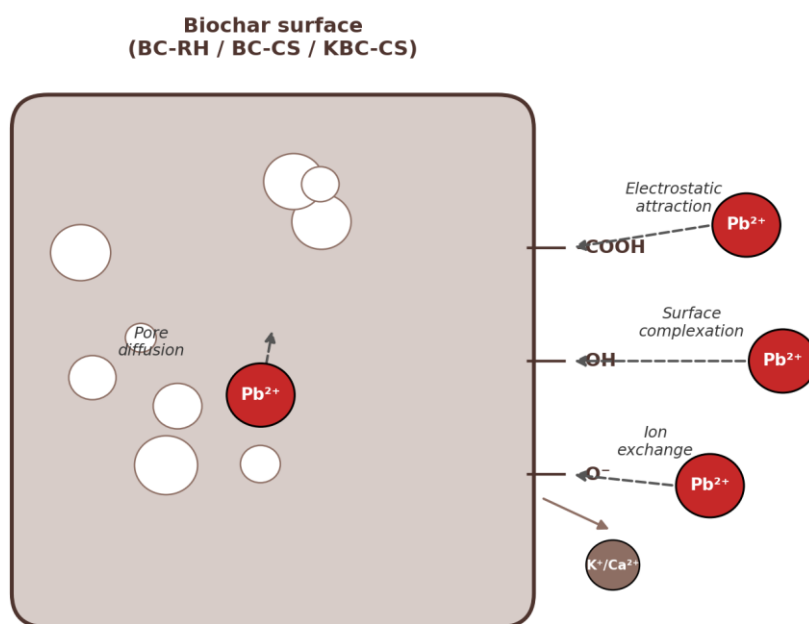


Figure 5. Proposed mechanisms of Pb^{2+} removal onto biochar surfaces.

Schematic showing electrostatic attraction to carboxyl/hydroxyl groups, surface complexation, ion exchange with mobile K^+/Ca^{2+} cations, and diffusion of Pb^{2+} into the biochar's internal pore network.

4. Conclusion

This study compared the Pb(II) removal performance of rice-husk biochar (BC-RH), cotton-straw biochar (BC-CS), and KOH-activated cotton-straw biochar (KBC-CS) under varying initial concentration, contact time, solution pH, and adsorbent dosage. Equilibrium uptake increased with initial Pb(II) concentration for all three materials, and KOH activation produced a substantial improvement in performance: KBC-CS achieved the highest maximum adsorption capacity ($q_{max} = 222.10 \text{ mg g}^{-1}$), exceeding BC-CS (151.17 mg g^{-1}) and BC-RH (110.63 mg g^{-1}) by approximately 47% and 101%, respectively. Equilibrium data were best described by the Langmuir isotherm ($R^2 = 0.9852\text{--}0.9923$) rather than the Freundlich model, indicating predominantly monolayer adsorption onto energetically homogeneous sites. Kinetic data for all three adsorbents conformed closely to the pseudo-second-order model ($R^2 = 0.9986\text{--}0.9996$), consistent with chemisorption as the rate-limiting mechanism, while intraparticle diffusion contributed to, but did not solely control, the overall uptake rate.

Solution pH strongly influenced removal efficiency, with uptake rising sharply between pH 2 and 6 as proton competition for surface sites diminished and electrostatic attraction between Pb^{2+} and negatively charged surface functional groups increased. Increasing adsorbent dosage similarly improved percentage removal by providing a greater density of available binding sites, with KBC-CS reaching approximately 98% Pb(II) removal at a dosage of 2.0 g L^{-1} . Taken together, these results demonstrate that KOH activation meaningfully enhances the surface area, porosity, and functional group density of cotton-straw-derived biochar, making KBC-CS a highly efficient, low-cost, and sustainable adsorbent for the remediation of lead-contaminated aqueous systems. Future work should include surface characterization (e.g., BET

surface area, FTIR, SEM-EDX), desorption and regeneration studies, competitive multi-metal adsorption trials, and evaluation using real industrial wastewater to confirm the practical applicability of these materials.

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