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Adsorption of Lead Ions from Aqueous Solution by Fe-Mn Modified Corn Straw Biochar Composite

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Abstract: Industries such as mining and smelting, electroplating, and lead-acid battery manufacturing discharge large amounts of lead-containing wastewater. Lead, as a highly toxic heavy metal, easily accumulates through the food chain, posing a serious threat to aquatic ecosystems and human health. Adsorption has attracted widespread attention in the field of heavy metal wastewater treatment due to its advantages of simple operation, low cost, and no secondary pollution. Biochar prepared from agricultural straw has a well-developed pore structure and abundant raw material sources, but pristine straw biochar has limited surface active functional groups and poor adsorption capacity for lead ions in aqueous solution. In this study, corn straw biochar was used as the substrate, and Fe-Mn binary modified straw biochar composite adsorbent (Fe-Mn-BC) was prepared by co-precipitation method. The adsorption performance of Fe-Mn-BC for Pb(II) in water was systematically investigated. The effects of Fe/Mn molar ratio, solution pH, and coexisting ions on the adsorption were examined. Adsorption kinetics, adsorption isotherms, and adsorption thermodynamic models were fitted. The results showed that under the conditions of initial Pb(II) concentration of 50 mg/L, adsorbent dosage of 0.1 g, and pH = 6, Fe-Mn-BC exhibited the maximum equilibrium adsorption capacity when the Fe/Mn molar ratio was 1:2. The adsorption kinetics process was better fitted by the pseudo-second-order kinetic model, indicating that chemisorption was the main rate-controlling step. Thermodynamic calculations showed that the adsorption process was spontaneous and exothermic, with decreased entropy. Lower temperature favored the adsorption reaction. This study provides experimental data and theoretical reference for the resource utilization of agricultural straw solid waste and the treatment of actual lead-containing wastewater.

Keywords: Straw biochar; Fe-Mn binary modification; lead ion; adsorption; heavy metal wastewater; FT-IR.

1. Introduction

With the rapid development of non-ferrous metal mining and smelting, electroplating, and lead-acid battery manufacturing industries, large amounts of lead-containing wastewater are discharged into the water environment [1]. Lead is a highly toxic heavy metal that cannot be biodegraded. It easily accumulates in aquatic organisms and human internal organs and bones, and can damage the human nervous system, hematopoietic system, and kidney organs. Even low-concentration lead exposure can cause irreversible damage to children's intellectual development. Lead pollution control in water has become a key research direction in the field of water environment remediation [2,10].

Current treatment technologies for lead-containing wastewater mainly include chemical precipitation, membrane separation, ion exchange, biological treatment, and adsorption [11]. Chemical precipitation consumes large amounts of reagents and produces a large amount of hazardous sludge. Membrane separation equipment is expensive and membranes are prone to fouling. Traditional ion exchange resins are costly. Compared with the above processes, adsorption has outstanding advantages such as simple operation, low operating cost, recoverable heavy metals, and low secondary pollution risk, making it a highly promising wastewater treatment technology [2,4].

Agricultural straw is a huge amount of agricultural waste that is mostly burned in situ, wasting resources and causing air pollution. Pyrolyzing straw to prepare biochar realizes solid waste resource utilization [6,7]. Pristine straw biochar has a porous structure and large specific surface area, but the number of surface negative charge sites and active hydroxyl functional groups is insufficient, resulting in limited adsorption capacity for lead ions in aqueous solution. Metal modification is needed to introduce a large number of active sites to improve adsorption performance [5,6]. Iron oxides and manganese oxides are rich in hydroxyl groups on their surface and have strong affinity for heavy metal cations [8,9]. Binary metal modification can combine the advantages of two metal oxides and produce synergistic effects. Compared with single metal modification, it can further enrich adsorption sites and improve adsorption selectivity and capacity [3].

Existing studies have mostly focused on single iron or single manganese modified biochar for heavy metal treatment [5,9]. Systematic research on Fe-Mn binary modified straw biochar for lead removal from water still needs to be supplemented [3]. In this study, corn straw biochar was used as the substrate, and Fe-Mn binary modified biochar (Fe-Mn-BC) was prepared by co-precipitation method. Batch adsorption experiments were systematically carried out to investigate key influencing factors. Combined with model fitting and FT-IR characterization, the adsorption mechanism was analyzed. This study provides theoretical support for the preparation of adsorbents from agricultural waste for lead-containing wastewater treatment.

2. Materials and Methods

2.1. Instruments and Reagents

Instruments: SHA-B thermostatic water bath shaker (Changzhou Guohua Electric Co., Ltd.); pHS-3C precision pH meter (Shanghai Leici Instrument Factory); AA-6300 atomic absorption spectrophotometer (Shimadzu, Japan); TENSOR27 Fourier transform infrared spectrometer (Bruker, Germany); electronic analytical balance; blast drying oven; magnetic stirrer; vacuum filtration device.

Reagents: Corn straw biochar (pyrolyzed at 500 °C, passed through 100-mesh sieve); lead nitrate, ferrous sulfate heptahydrate, manganese sulfate monohydrate; sodium hydroxide; dilute nitric acid; absolute ethanol; calcium chloride, magnesium chloride, sodium chloride, potassium chloride, sodium sulfate (all analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd.); all experimental water was deionized water.

2.2. Experimental Methods

2.2.1. Preparation of Fe-Mn-BC Composite

Pretreatment of corn straw biochar: The biochar was repeatedly washed with deionized water to remove soluble ash impurities, dried in an oven at 60 °C, passed through a 100-mesh standard sieve, and sealed for later use.

Preparation of Fe-Mn mixed salt solution: Ferrous sulfate heptahydrate and manganese sulfate monohydrate were weighed separately, and mixed aqueous solutions were prepared according to different Fe/Mn molar ratios. Pretreated straw biochar was added to the salt solution with a solid-liquid ratio of 1 g:50 mL, and magnetically stirred for 30 min to fully disperse the biochar particles in the metal salt solution [3].

A 2 mol/L NaOH solution was slowly added dropwise to the mixed suspension to adjust the system pH to 10. The mixed system was transferred to a thermostatic water bath and continuously magnetically stirred at 65 °C for 2.5 h, so that iron and manganese ions co-precipitated on the biochar surface to form iron-manganese oxyhydroxides. After the reaction, the mixture was cooled to room temperature, and the solid product was separated by vacuum filtration. The filter cake was repeatedly washed with deionized water until the filtrate pH was close to neutral. The solid material was dried in a blast drying oven at 60 °C for 12 h, taken out, ground, and passed through a 100-mesh sieve to obtain Fe-Mn binary modified straw biochar, designated as Fe-Mn-BC. Pristine biochar (BC), single iron modified biochar (Fe-BC), and single manganese modified biochar (Mn-BC) were also prepared as controls.

2.2.2. Batch Adsorption Experiments

50 mL of lead solution with a certain initial concentration was placed in a 250 mL conical flask, and a certain amount of Fe-Mn-BC adsorbent was added. The conical flask was placed in a thermostatic water bath shaker at an oscillation speed of 180 r/min. After reaching the set adsorption time, the sample was taken and filtered through a 0.45 μm aqueous filter membrane. The residual concentration in the filtrate was determined by atomic absorption spectrophotometry.

The adsorption capacity was calculated by the following equation:

$q_t = (C_0 - C_t) \times V / m$

where q_t is the adsorption capacity at time t (mg/g); q_e is the equilibrium adsorption capacity (mg/g); C_0 is the initial concentration (mg/L); C_t is the residual concentration at time t (mg/L); C_e is the residual concentration at equilibrium (mg/L); V is the volume of lead ion solution (L); m is the mass of adsorbent added (g).

2.2.3. Adsorption Kinetics Experiments

A Pb(II) solution with an initial concentration of 50 mg/L was prepared, and the pH was adjusted to 6 with dilute nitric acid/sodium hydroxide. 0.1 g of Fe-Mn-BC was added to 50 mL of lead solution and shaken at 25 °C and 180 r/min. Samples were taken and filtered at 0, 0.5, 1, 1.5, 2, 3, 4, 5, and 6 h to determine the residual lead ion concentration.

The pseudo-first-order kinetic model, pseudo-second-order kinetic model, intraparticle diffusion (IPD) model, and Elovich model were used to fit the kinetic data to analyze the adsorption rate and rate-controlling steps.

Pseudo-first-order kinetic model: $\log(q_e - q_t) = \log q_e - k_1 t / 2.303$

Pseudo-second-order kinetic model: $t/q_t = 1/(k_2 q_e^2) + t/q_e$

Intraparticle diffusion model: $q_t = k_p t^{0.5} + C$

Elovich model: $q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$

where k_1 is the pseudo-first-order rate constant (h^{-1}); k_2 is the pseudo-second-order rate constant ($g \cdot (mg \cdot h)^{-1}$); k_p is the intraparticle diffusion rate constant ($mg \cdot (g \cdot h^{0.5})^{-1}$); C is the boundary layer constant; α is the initial adsorption rate ($mg \cdot (g \cdot h)^{-1}$); β is a constant related to surface coverage ($g \cdot mg^{-1}$).

2.2.4. Adsorption Isotherm Experiments

Water bath temperatures were set at 298 K (25 °C), 308 K (35 °C), and 318 K (45 °C). The pH was fixed at 6, adsorbent dosage was 0.1 g, and initial lead ion concentration gradients were set at 20, 40, 60, 80, 100, and 120 mg/L. The shaker was oscillated for 8 h to ensure adsorption equilibrium. Samples were taken to determine the equilibrium concentration. Langmuir and Freundlich isotherm models were used to fit the experimental data.

Langmuir model (monolayer adsorption): $C_e/q_e = 1/(q_m K_L) + C_e/q_m$

Freundlich model (heterogeneous multilayer adsorption): $\ln q_e = \ln K_F + (1/n) \ln C_e$

where q_m is the theoretical saturated adsorption capacity (mg/g); K_L is the Langmuir adsorption equilibrium constant; K_F and n are empirical constants of the Freundlich model.

2.2.5. Adsorption Thermodynamics Experiments

Using the equilibrium data obtained from isotherm experiments at different temperatures, the distribution coefficient K_d was calculated, and then Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were further calculated.

$\Delta G = -RT \ln K_d$

$\ln K_d = \Delta S/R - \Delta H/(RT)$

where R is the gas constant ($8.314 J \cdot (mol \cdot K)^{-1}$); T is the thermodynamic temperature (K).

2.2.6. Coexisting Ions Interference Experiments

Common anions and cations in actual water bodies were simulated. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and NO_3^- were selected. The molar ratio of interfering ions to lead was 1:1. The initial lead concentration was 50 mg/L, pH was 6, and 0.1 g of adsorbent was added. The mixture was shaken at 25 °C until equilibrium. The equilibrium adsorption capacity was determined to analyze the inhibitory or promoting effects of coexisting ions on adsorption.

3. Results and Discussion

3.1. Effect of Fe/Mn Molar Ratio on Adsorption Performance

With the initial lead concentration fixed at 50 mg/L, pH = 6, and adsorbent dosage of 0.1 g, a series of Fe-Mn-BC adsorbents were prepared with different Fe/Mn molar ratios (2:1, 1:1, 1:2, 1:3) for adsorption experiments. The results showed that as the proportion of manganese increased, the equilibrium adsorption capacity first increased and then decreased. When Fe:Mn = 1:2, the equilibrium adsorption

capacity reached the maximum value.

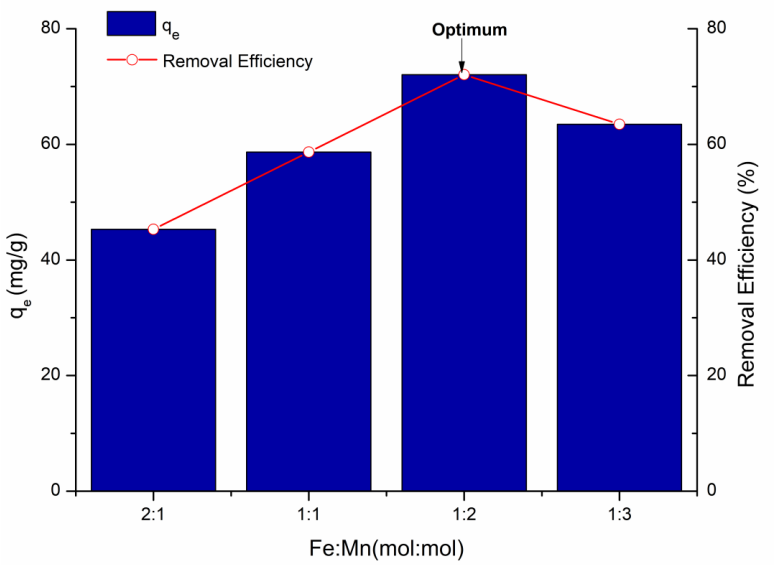


Figure 1. Optimization of Fe/Mn molar ratio

The optimal Fe-Mn-BC was compared with pristine straw biochar (BC), single iron modified (Fe-BC), and single manganese modified (Mn-BC) for adsorption performance.

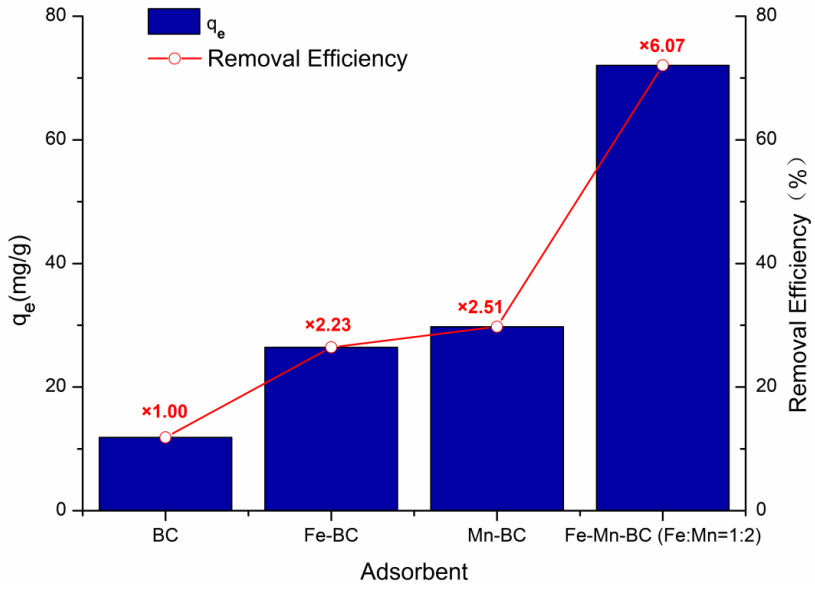


Figure 2. Comparison of adsorption performance of different adsorbents

Pristine straw biochar (BC) relied only on its own pore structure and a small number of functional groups to adsorb lead ions, resulting in very low adsorption capacity. The adsorption capacity of single iron modified Fe-BC and single manganese modified Mn-BC was improved compared with pristine biochar, but the improvement was limited. After Fe-Mn binary modification, iron oxyhydroxide and manganese oxyhydroxide were simultaneously generated on the biochar surface. The synergistic effect of the two metal oxides greatly increased the number of surface hydroxyl active sites, significantly enhancing the Pb2+ capture ability. When the manganese ratio was too high, the proportion of active iron components was too low, reducing the total number of adsorption sites and causing the adsorption capacity to decline. Therefore, the Fe/Mn molar ratio of 1:2 was selected for all subsequent batch adsorption experiments.

3.2. Effect of Initial Solution pH on Adsorption Performance

pH is an extremely critical influencing factor in heavy metal adsorption systems. It not only changes the surface charge state of the adsorbent, but also changes the existing form of lead ions in aqueous solution. In this experiment, the pH range was set at 2.0-6.0. When pH > 6, lead hydroxide precipitate forms in the aqueous solution, making it impossible to distinguish between precipitation and adsorption [11]. Therefore, experiments at pH > 6 were not conducted.

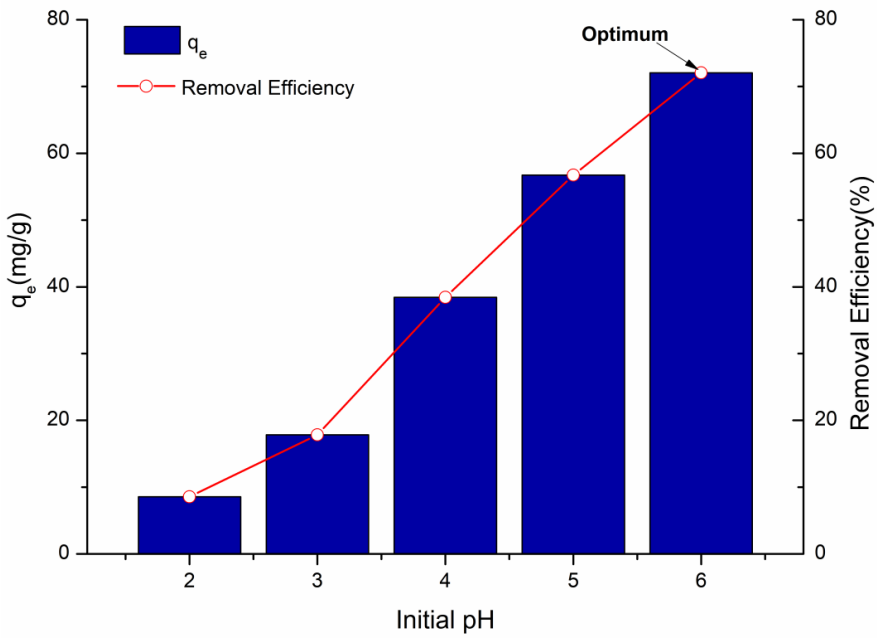


Figure 3. Effect of initial solution pH on adsorption performance

The experimental results showed that as pH increased from 2 to 6, the equilibrium adsorption capacity of Fe-Mn-BC for Pb2+ continuously increased.

At low pH (pH = 2-3), a large number of H+ ions existed in the solution system. Hydrogen ions competed with Pb2+ for limited active sites on the adsorbent surface. Meanwhile, the hydroxyl functional groups on the adsorbent surface were protonated, and the surface carried a large amount of positive charge, producing electrostatic repulsion with Pb2+ cations, resulting in poor adsorption.

When pH increased to 4-6, the H+ concentration in the solution decreased, and the competition effect of hydrogen ions weakened. The hydroxyl groups (-OH) on the adsorbent surface were deprotonated, and the surface carried negative charge, capturing Pb2+ in the solution through electrostatic attraction. A large number of hydroxyl sites were exposed on the surface of iron-manganese oxides, which could undergo complexation reactions with lead ions, and the adsorption capacity continued to rise. The adsorption capacity reached its peak at pH = 6. Considering all factors, the optimal pH for this study was determined to be 6. This material is suitable for weakly acidic lead-containing wastewater treatment. For strongly acidic lead-containing wastewater, the wastewater pH needs to be pre-adjusted before practical application.

3.3. Adsorption Kinetics Analysis

The adsorption experimental data at different times were fitted with four kinetic models to obtain the kinetic model parameters.

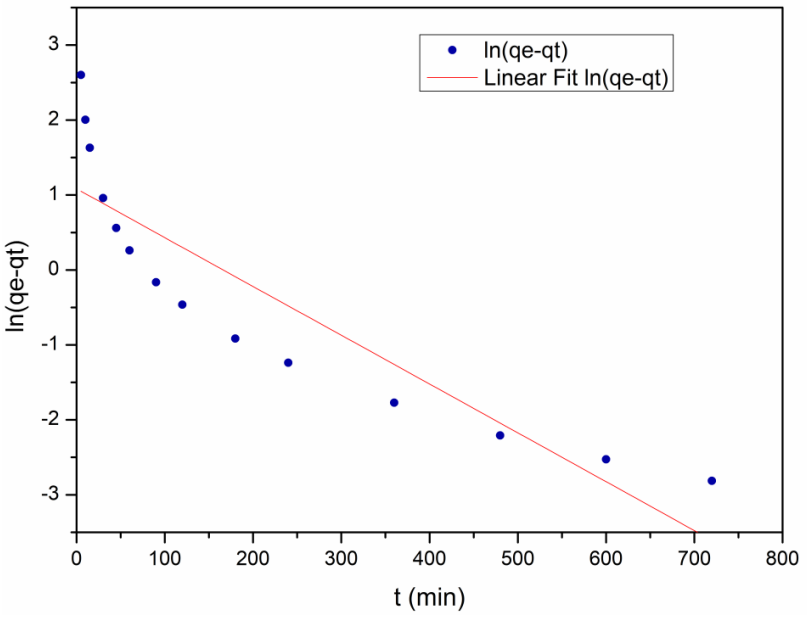


Figure 4. Pseudo-first-order kinetic model

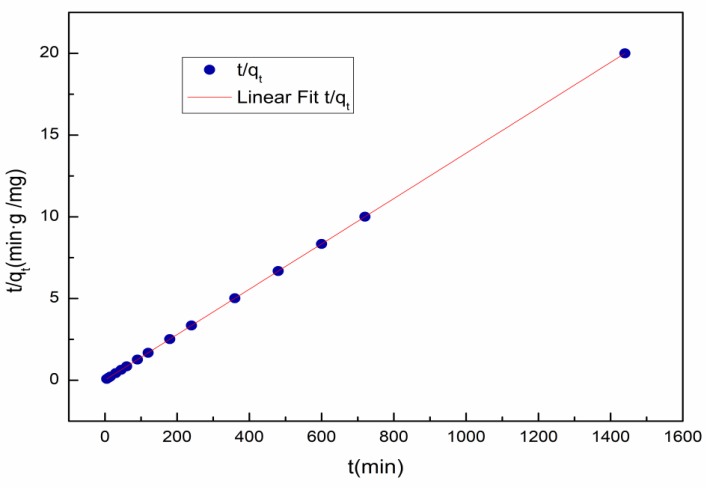


Figure 5. Pseudo-second-order kinetic model

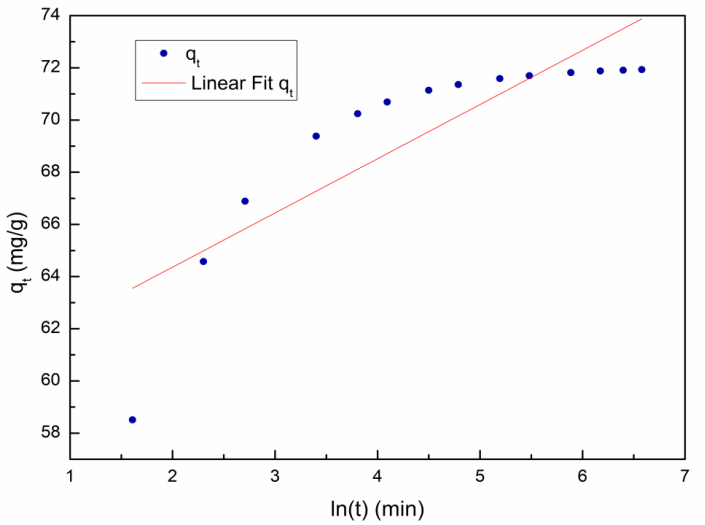


Figure 6. Elovich model

The correlation coefficient of the pseudo-second-order kinetic model was higher than those of the pseudo-first-order kinetic and Elovich models [2,6]. Moreover, the theoretical equilibrium adsorption capacity calculated by the pseudo-second-order kinetic model was close to the experimentally measured equilibrium adsorption capacity. This indicates that the adsorption process of Pb2+ onto Fe-Mn-BC from aqueous solution is mainly controlled by chemisorption, and chemical reactions such as surface complexation and ion exchange are important rate-limiting steps [3,5].

The intraparticle diffusion model fitting showed a multi-segment line, and the fitted lines did not pass through the coordinate origin, indicating that intraparticle diffusion was not the sole rate-controlling step.

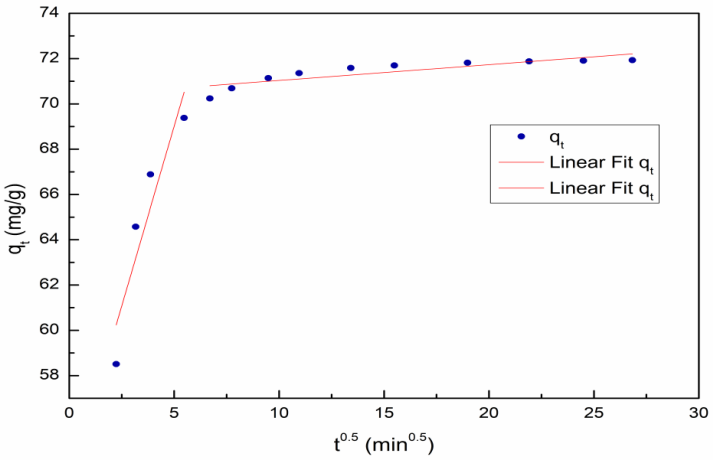


Figure 7. Intraparticle diffusion model

The entire adsorption process was divided into two stages. The first stage was the liquid film diffusion stage, where lead ions rapidly diffused from the solution to the outer surface of the adsorbent, with a fast adsorption rate. The second stage

was intraparticle diffusion, where lead ions slowly entered the internal pores of the adsorbent, and the adsorption rate slowed down. Liquid film diffusion and intraparticle diffusion jointly controlled the entire adsorption process.

3.4. Adsorption Isotherm Analysis

The Langmuir model assumes that adsorption occurs on a uniform surface as monolayer adsorption. The Freundlich model is suitable for multilayer adsorption on heterogeneous surfaces.

At 298 K, the Langmuir model had a higher correlation coefficient, indicating that adsorption was dominated by monolayer chemisorption at low temperatures. As the temperature increased to 308 K and 318 K, the Freundlich model fitting correlation coefficient gradually increased, and adsorption shifted toward heterogeneous multilayer adsorption at high temperatures.

The Freundlich model parameter n was all greater than 1, with n in the range of 1-10, indicating that Pb2+ adsorption by Fe-Mn-BC was an easy adsorption process. As the system temperature increased, the theoretical saturated adsorption capacity given by the Langmuir model gradually decreased, indicating that increasing temperature was unfavorable for the adsorption reaction. Low temperature was more favorable for Fe-Mn-BC to remove lead ions from aqueous solution.

3.5. Adsorption Thermodynamics Analysis

Thermodynamic calculations at different temperatures showed that ΔG was negative at 298 K, 308 K, and 318 K, proving that the Pb2+ adsorption reaction by Fe-Mn-BC was spontaneous within the experimental temperature range.

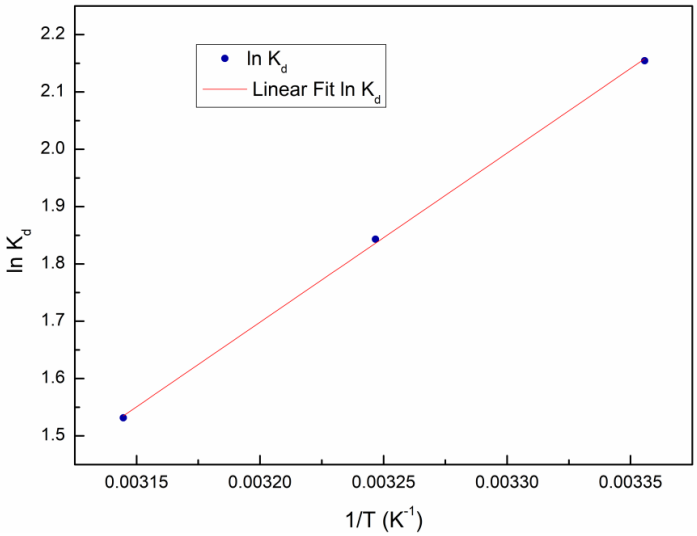


Figure 8. Adsorption thermodynamics

The enthalpy change ΔH was negative, confirming that the adsorption reaction was exothermic. Increasing temperature would inhibit adsorption, which was mutually consistent with the conclusion from isotherm experiments that low temperature was more favorable for adsorption.

The entropy change ΔS was negative. During the adsorption process, freely moving lead ions in the solution were fixed onto the solid surface of the adsorbent, and the disorder of the solution system decreased, manifested as entropy reduction.

As the temperature increased, the absolute value of ΔG continuously decreased, indicating that the higher the temperature, the weaker the spontaneous degree of adsorption.

3.6. Effect of Coexisting Ions on Adsorption

Various anions and cations commonly exist in actual industrial wastewater and surface water bodies, which can interfere with the removal of target heavy metals by adsorption materials.

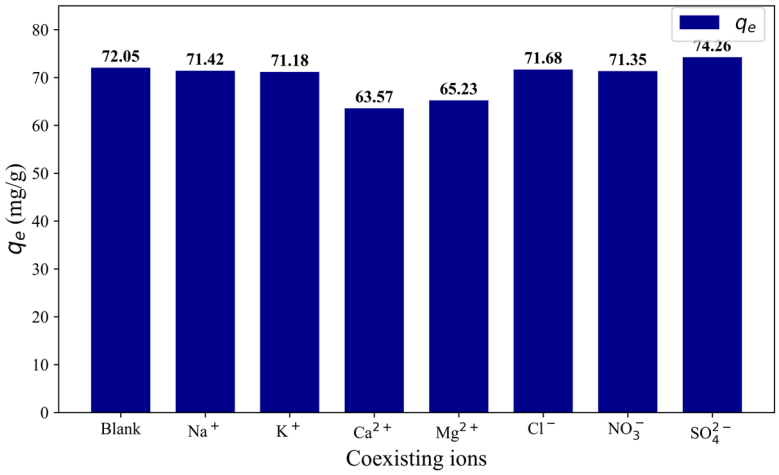


Figure 9. Effect of coexisting ions on adsorption

The experimental results showed that monovalent cations Na+ and K+ had almost no inhibitory effect on Fe-Mn-BC adsorption. Monovalent cations had low charge and weak ability to compete for adsorption sites with Pb2+. Divalent cations Ca2+ and Mg2+ caused a certain decrease in adsorption capacity. Ca2+ and Mg2+, as divalent cations, competed with Pb2+ for negatively charged adsorption sites on the material surface, producing competitive adsorption and inhibiting the removal effect. In terms of anions, Cl- had little effect on adsorption. SO4^2- could form lead sulfate precipitate with some Pb2+, slightly improving the overall lead removal effect. Overall, common coexisting ions in water bodies had limited interference with Fe-Mn-BC lead removal, indicating that this adsorption material has potential application value for treating actual wastewater.

4. Conclusions

Fe-Mn binary modified straw biochar (Fe-Mn-BC) was prepared by co-precipitation. The adsorption performance was optimal when the Fe/Mn molar ratio was 1:2. Under the conditions of initial lead concentration of 50 mg/L and pH = 6, the adsorption performance of the composite material was significantly better than that of pristine straw biochar, single iron modified, and single manganese modified biochar. There was a synergistic adsorption effect between iron and manganese components.

The adsorption process of Pb2+ onto Fe-Mn-BC from aqueous solution conformed to the pseudo-second-order kinetic model, with chemisorption as the main rate-controlling step. Liquid film diffusion and intraparticle diffusion jointly controlled the adsorption rate. The Langmuir model fitted well at low temperature, dominated by monolayer adsorption. The adsorption was a spontaneous, exothermic, and entropy-decreasing reaction. Lower temperature was favorable for lead ion adsorption.

Common monovalent ions in water bodies had almost no interference with adsorption. Divalent cations produced competitive adsorption and slightly inhibited the adsorption effect. Sulfate could form precipitate with lead ions and slightly improve the removal effect. This material has certain application potential for weakly acidic lead-containing wastewater.

References

[1] Chen, S. Q. (2024). Research on biochar and plants for heavy metal removal [Master's thesis]. Chinese Research Academy of Environmental Sciences.

[2] Ji, M. Y., Hu, Y. W., Liang, C., Sang, W. J., & Li, D. X. (2020). Adsorption of lead and cadmium on biochars produced from agroforestry wastes. Journal of Ecology and Rural Environment, 36(1), 106–114. https://doi.org/10.19741/j.issn.1673-4831.2018.0853

[3] Li, Y. Y., Li, Y. J., Wang, J. X., et al. (2026). Study on adsorption of Pb from water by iron-manganese oxide modified straw biochar. China Resources Comprehensive Utilization, 44(7), 4–10+23.

[4] Zhang, H., & Gong, X. (2025). Research progress on the effects of biochar and modified substances on heavy metals in soil. Acta Agriculturae Jiangxi, 37(1), 18–27.

[5] Guo, M., Li, B. B., Xu, L. Y., et al. (2024). Adsorption mechanism of Pb and Cd by NaOH-modified biochar/attapulgite composite. Journal of Ecology and Rural Environment, 40(1), 119–129. https://doi.org/10.19741/j.issn.1673-4831.2022.0851

[6] Zhao, J. B., Zhu, J. B., Zhuang, C. F., et al. (2022). Removal performance and mechanism of Pb and Cd by corn straw biochar in water. Biomass Chemical Engineering, 56(4), 15–24.

[7] Yang, Y. Z., Gao, B. L., Huang, Y., et al. (2023). Adsorption characteristics of straw-based biochar for Pb and Cd at medium-high pyrolysis temperatures. Geology in China, 50(1), 52–60.

[8] Li, G., Li, H. B., Li, Y. H., et al. (2022). Stabilization of arsenic in soil by biochar-supported Fe-Mn double oxides. Environmental Engineering, 40(3), 118–125.

[9] Chen, T. L., Liao, C. J., Li, Q. J., et al. (2023). Adsorption characteristics of Cd and As on potassium permanganate modified iron sludge biochar. Environmental Science & Technology, 46(5), 192–200.

[10] Hu, J., & Zhang, M. (2012). Research progress on remediation technology of heavy metal polluted water. Light Industry Science and Technology, 28(2), 78–79.

[11] Gu, X. C., Mei, P. W., Zhang, Z., Jiang, W., & Li, X. R. (2020). Research progress on treatment technology of lead-containing wastewater. Industrial Water Treatment, 40(12), 14–19.