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Research Article

Keywords: Adsorption, Biochar, Chemical modification, Ni(II), Pb(II)

Posted Date: June 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-487894/v1>

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Comparative study of biochar modified with different functional groups for efficient removal of Pb(II) and Ni(II)

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Abstract

The potential application of biochar in water treatment is attracting interest due to its sustainability and low production cost. In the present study, H_3PO_4 -modified biochar (H-PBC), ethylenediaminetetraacetic acid-modified biochar (E-PBC), and NaOH-modified biochar (O-PBC) were prepared for Ni(II) and Pb(II) adsorption in an aqueous solution. Scanning electron microscopy (SEM), X-ray diffraction analysis, Brunauer–Emmett–Teller analysis, and Fourier transform infrared (FT-IR) spectroscopy were employed to characterize the as-obtained samples, and their capacities for Ni(II) and Pb(II) adsorption were determined. SEM showed that H-PBC retained the hierarchical porous structure of pristine biochar, and projections were observed on its surface. FT-IR showed that H-PBC possessed abundant oxygen-containing and phosphorus-containing functional groups on the surface. H-PBC, E-PBC, and O-PBC all exhibited excellent performance at Ni(II) and Pb(II) adsorption with q_{max} values of 64.94 mg/g, 47.17 mg/g, and 60.24 mg/g, and 243.90 mg/g, 156.25 mg/g, and 192.31 mg/g, respectively, which were significantly higher than the adsorption capacity (19.80 mg/g and 38.31 mg/g) of pristine biochar. Pseudo-second order models suggested that the adsorption process was controlled by chemical adsorption. Regeneration analysis showed that H-PBC had superior reusability characteristics. H-PBC had a greater adsorption capacity than other adsorbents due to its large specific surface area, and abundant oxygen-containing and phosphorus-containing functional groups. The results obtained in this study suggest that H-PBC is a promising adsorbent for the removal of heavy metals from aqueous solutions.

Keywords Adsorption, Biochar, Chemical modification, Ni(II), Pb(II)

Introduction

The pollution of aquatic environments with heavy metals due to anthropogenic activity may seriously threaten human health. The problem of heavy metal pollution has become increasingly severe due to the rapid development of industrialization in recent decades, (Guo et al., 2012). Among the polluting heavy metals, Ni is highly toxic and potentially carcinogenic, where it can damage the brain, spine, and internal organs of aquatic organisms and humans. Due to the adverse effects of Ni on human health, it is classified as a human carcinogen by institutions around the world (McGuire, 2016). Pb is also extremely harmful to the human body, where it can cause liver and kidney damage, or nervous system disorders by interacting with the sulfhydryl groups of proteins (Needleman, 2004). Combined pollution of water bodies with Ni and Pb can negatively impact the environment and human health. Therefore, there is an urgent need to develop effective methods for removing both Ni and Pb from the environment.

Various techniques have been developed for heavy metal removal, such as adsorption, ion exchange, electro-coagulation, and chemical precipitation (Li and Zhou, 2018; Ma et al., 2019; Tsai et al., 2020; Wang et al., 2021). Among these methods, adsorption using carbon materials has received increasing attention (He and Chen, 2014). For instance, Mohammadi et al. (2014) prepared activated carbon with a high surface area using ZnCl_2 as a porogen, and the maximum adsorption capacities for Pb(II) and Ni(II) were 200 and 166.7 mg/g, respectively. Terracciano et al. (2017) used graphene oxide for Ca(II) adsorption and found that graphene oxide had a high capacity for Ca(II) adsorption when the pH was greater than 7. However, these materials have relatively high costs and they involve complicated fabrication procedures. For instance, the preparation of graphene requires concentrated H_2SO_4 and HNO_3 for exfoliation. Recent studies have shown that biochars obtained from waste biomass, such as rice husk (Yu et al., 2018) and peanut shells (An et al., 2019), have great potential as cost-effective adsorbents for Ni and Pb remediation in soil and water. Biochar has a high capacity for adsorbing heavy metals because of its porous structure and inhomogeneous surface chemistry (Martin et al., 2012).

However, biochar is normally produced by pyrolysis at high temperature, which inevitably reduces the number of functional groups on the biochar's surface, thereby greatly decreasing the amount of active binding sites available for heavy metal adsorption. Thus, various methods have been applied to modify biochar by introducing different functional groups to enhance the capacity for adsorption. For example, Jiang et al. (2019) synthesized H_3PO_4 modified biochar using a solvothermal method and the maximum Pb(II) adsorption capacity was 353 mg/g, thereby demonstrating its potential use in Pb-contaminated soil remediation. Choudhary et al. (2020) modified biochar with NaOH to load more oxygen-containing functional groups on its surface and the capacity for Ni(II) removal was enhanced. In addition, ethylenediaminetetraacetic acid (EDTA) was used to modify biochar and the maximum Pb(II) adsorption capacity of the EDTA-functionalized biochar was 129.31 mg/g (Li et al., 2019). These previous studies demonstrated that modifying biochar with H_3PO_4 , NaOH, and EDTA can improve the adsorption of Pb(II) and Ni(II), but the biochars used in these studies were derived from different raw materials under different synthesis conditions. The adsorption capacity of biochar is highly dependent on its physicochemical properties, which are determined by the different raw materials and synthesis conditions employed (Sun et al., 2011). The most suitable biochar modification method to enhance the removal of both Pb and Ni is still not clear. The effects on the heavy metal adsorption performance of the presence of different functional groups on modified biochar also require further exploration.

In this study, three representative modification methods were applied to synthesize biochar modified with H_3PO_4 , NaOH, and EDTA using the same raw materials. The capacities of the newly synthesized biochars for adsorbing both Pb(II) and Ni(II) were systematically investigated in terms of

their adsorption kinetics and thermodynamics. The results obtained in this study provide insights into the effects of different functional groups on biochar on the adsorption of Pb(II) and Ni(II), thereby facilitating the development of cost-effective modification strategies for synthesizing biochar for highly efficient heavy metal removal.

Experimental

Synthesis of biochars with different functional groups

All of the biochar materials were synthesized using corn stalks as the raw materials, which were collected from farmland in Guiyu Town, Shantou City, China. The corn stalk biomass was washed with deionized water and dried naturally for 2 days before drying at 70°C in an oven for more than 24 h until constant weight. The dried corn stalks were crushed using a ball mill (JX-2G) and passed through a 100-mesh sieve to obtain a constant particle size of 150 µm.

Pristine biochar (PBC) was synthesized by pyrolyzing the corn stalk powder with added KHCO₃ (Yang et al., 2018). Briefly, the corn stalk powder and KHCO₃ were mixed at a mass ratio of 1:1 and pyrolyzed in a tube furnace under N₂ purging (200 mL/min) at 800°C for 3 h, before washing with HCl (0.1 mol/L) to remove the ash. After subsequently washing with deionized water, the PBC product was dried in an oven for further use.

The H₃PO₄-modified PBC (designated as H-PBC) was prepared as described by Jiang et al. (2019). First, 5 g of PBC was mixed with 50 mL of H₃PO₄ solution and soaked for 30 min. The mixture was then transferred to a 100-mL polytetrafluoroethylene lined autoclave and heated at 240°C for 2 h. After cooling to room temperature, the solid product was washed several times with deionized water and then dried overnight in an oven.

The NaOH-modified PBC (designated as O-PBC) was prepared as described by Choudhary et al. (2020). First, 5 g of NaOH was dissolved in 200 mL of deionized water and 5 g of PBC was added. The mixed solution was then stirred for 2 h and dried. The dried O-PBC was calcined at 500°C at a heating rate of 10°C/min for 1 h. Finally, the product was washed with deionized water and dried overnight.

The EDTA-modified PBC (designated as E-PBC) was prepared as described by Li et al. (2019). First, 5 g PBC was mixed with 20 mL of aqueous acetic acid solution and 6.0 g of EDTA was mixed with 100 mL of methanol. The two mixtures were then combined and stirred for 24 h. The solid product was washed with deionized water and dried overnight.

The as-prepared samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and Fourier transform infrared (FT-IR) spectroscopy. The specific surface area (S_{BET}) and pore diameter were calculated based on N₂ adsorption–desorption using the multipoint Brunauer–Emmett–Teller (BET) method. The details of these methods can be found in the Supporting Information.

Pb and Ni adsorption experiments

The heavy metal adsorption experiments were conducted in a home-made reactor. Specific amounts of biochar (5–50 mg) were placed into the reactor containing 20–100 mL Ni(II)/Pb(II) solution (40 mg/L). The pH of the reaction mixture was adjusted to 2.0–9.0 with 0.1 M NaOH/HCl. Subsequently, adsorption was performed by shaking the reactor in a water bath where the temperature was maintained at 288.15–318.15 K. At specific time intervals, samples were removed and centrifuged at 3000 rpm for 10 min. The supernatant obtained was used to determine the Ni(II) and Pb(II) concentrations with a flame atomic absorption spectrometer (SP-3530AA, Shanghai).

The adsorption capacity q_e (mg/g) was calculated for Ni(II) and Pb(II) using Equation (1):

$$q_e = V(C_o - C_e)/m, (1)$$

where C_o and C_e are the heavy metal concentrations (mg/L) at the initial time and adsorption time, respectively, V is the volume (L) of the reaction solution, and m is the dried weight (g) of biochar. All of the adsorption experiments were conducted in triplicate.

Adsorption kinetics and isotherm models

First-order and second-order models were used to study the adsorption kinetics with Equation (2) and Equation (3), respectively:

$$q_t = q_e(1 - e^{-k_1 t}) (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, (3)$$

where q_t (mg/g) is the adsorption capacity at time t (min), q_e (mg/g) is the adsorption capacity at equilibrium, k_1 (min^{-1}) is the first order adsorption rate constant, and k_2 [$\text{g}/(\text{mg} \cdot \text{min})$] is the second order adsorption rate constant.

Langmuir and Freundlich models were used to analyze the adsorption isotherms for Ni(II) and Pb(II) with different initial concentrations (10–100 mg/L). The equations for the Langmuir and Freundlich models are given in Equation (4) and Equation (5):

$$\text{Langmuir: } q_e = \frac{q_m K_L C_e}{1 + K_L C_e} (4)$$

$$\text{Freundlich: } q_e = K_F C_e^{1/n}, (5)$$

where q_e (mg/g) is the adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium concentration, K_L (mg/L) is the Langmuir constant related to the adsorption energy, and K_F and n are the Freundlich constant and nonlinear factor, respectively.

Recyclability analysis

Five consecutive adsorption–desorption experiments were conducted in order to explore the reusability of the as-prepared modified biochar samples. First, 0.2 g of biochar was placed into a reactor containing 200 mL of $\text{Ni}(\text{NO}_3)_2/\text{Pb}(\text{NO}_3)_2$ (40 mg/L) solution. The suspension was stirred for 9 h to reach adsorption equilibrium. The used adsorbent was then collected by filtration, washed with ultrapure water, and re-used in the next run for Ni(II) and Pb(II) desorption.

Results and discussion

Characteristics of adsorbents

The morphologies of the as-prepared samples were studied based on SEM images. Figure S1(A) shows that the PBC had a hierarchical porous structure similar to that of carbon foam. Large amounts of chelating agents were attached to the surface of E-PBC, which resulted in significant aggregation (Fig. S1(B)). Rectangular crystals spread all over the surface of PBC in O-PBC (Fig. S1(C)). The hierarchical porous structure of PBC was retained in H-PBC and projections were observed on its surface (Fig. S1(D)). The existence of porous structure marched well with the result of BET analysis.

Figure 1(A) shows the N_2 adsorption–desorption isotherms determined for the as-prepared samples. The adsorption–desorption curves for PBC and H-PBC were type IV adsorption/desorption isotherms with H4 type hysteresis loops, and they suggested the existence of a mesoporous structure according to a previous study (Yang et al., 2018). By contrast, the curves for E-PBC and O-PBC were type I

adsorption/desorption isotherms due to their microporous filling. As shown in Fig. 1(B), most of the pores in PBC and H-PBC were mesopores. The BET surface areas determined for PBC, H-PBC, O-PBC, and E-PBC were 360.41, 344.17, 3.66, and 1.64 m²/g, respectively (Table 1). Compared with PBC, the surface area was clearly much lower for E-PBC, possibly because the micropores were covered by EDTA. The surface area of O-PBC was also significantly reduced. Interestingly, H-PBC maintained a high surface area in a similar manner to PBC, thereby indicating that modification with H₃PO₄ retained the porous structure of the raw material, as well as maintaining the high surface area of the biochar through the formation of mesopores.

The XRD patterns obtained for the PBC samples are illustrated in Fig. 1(C). For PBC, the characteristic peaks at 29.81°, 32.72°, and 41.12° corresponded to the (112), (103), and (220) planes, respectively (Yang et al., 2018). For O-PBC, a weak peak around 48° was related to (100) diffraction and another weak peak at around 43° was related to (101) diffraction by the activated biochar (Liu et al., 2017). For E-PBC and H-PBC, the peak observed at 23° corresponded to the (002) planes of the graphite lattice (Xu et al., 2014).

FTIR analysis was conducted to identify the functional groups on the surfaces of the prepared PBC samples and the results are shown in Fig. 1(D). For PBC, the adsorption peak around 3430 cm⁻¹ could be attributed to the stretching of -NH groups in acidic and aliphatic compounds. The peak at 1049 cm⁻¹ was due to the stretching vibration of C-O (Yang et al., 2018). For O-PBC, the signals detected at 3430 cm⁻¹ and 1442 cm⁻¹ corresponded to the stretching vibrations of -OH and chromene, thereby, suggesting that O-PBC was successfully synthesized. For H-PBC, the peaks at 1223 cm⁻¹, 1185 cm⁻¹, and 500 cm⁻¹ could be assigned to the stretching vibrations of C-O-C, P-O-C (Chu et al., 2018), and C-P bonds (Yang et al., 2011), respectively. In addition, the bands at 1610 cm⁻¹ and 833 cm⁻¹ could be assigned to the stretching vibrations of aromatic C=C and =C-H, respectively (Jiang et al., 2019), thereby indicating the high aromaticity of H-PBC. For E-PBC, the absorption peaks near 2925 cm⁻¹, 1627 cm⁻¹, and 1390 cm⁻¹ could be attributed to the asymmetric stretching of -CH₂- (Xu et al., 2015), C=O (Lv et al., 2018), and -NH₂, thereby indicating that EDTA was successfully grafted onto PBC.

These results indicate that the E-PBC, O-PBC, and H-PBC were successfully synthesized according to previous studies.

Ni(II)/Pb(II) adsorption efficiency

Effect of adsorbent dosage

Figure 2(A) shows the efficiency of Ni(II) and Pb(II) adsorption using different adsorbents. In general, the Ni(II) removal efficiency improved significantly as the amount of adsorbent increased. When the adsorbent dosage was 50 mg, the Ni(II) removal efficiencies using PBC, H-PBC, E-PBC, and O-PBC were 11.2%, 43.1%, 22.6%, and 39.8%, respectively. The efficiency of Ni(II) removal by H-PBC was significantly higher than that by PBC, possibly due to the presence of more binding sites on the surface of H-PBC (Munagapati et al., 2010). Similarly, the concentration of the adsorbent greatly affected the adsorption of Pb(II). The Pb(II) removal efficiency increased rapidly as the adsorbent dosage increased. At a dosage of 20 mg, the Pb(II) removal efficiencies with H-PBC, E-PBC, and O-PBC were 70.0%, 37.5%, and 63.3%, respectively, which were far higher than that with PBC (10.8%). Therefore, the modifications of PBC greatly enhanced the efficiency of heavy metal removal.

Effect of pH

In general, the adsorption process associated with surface functional groups is influenced by the pH of

the solution (Wang et al., 2018). In the present study, the effect of the pH on the uptake of heavy metals was investigated in the pH range from 2 to 9. As shown in Fig. 2(B), the Ni(II) removal efficiency improved dramatically as the pH increased from 2 to 9. This change might have occurred because the functional groups on the surfaces of the adsorbents were negatively charged due to deprotonation as the pH increased, and thus, they combined with Ni(II) via electrostatic attraction, so the removal efficiency increased (Li et al., 2019). When the pH increased to 9, the Ni(II) removal efficiencies with H-PBC, O-PBC, E-PBC, and PBC were 12.8%, 11.8%, 7.6%, and 4.3%, respectively. Moreover, the effect of the pH on Pb(II) was similar to that on Ni(II), where the adsorption capacity improved as the pH increased (Fig. 2(B)). When the pH increased to 9, the Pb(II) adsorption efficiencies with H-PBC, O-PBC, E-PBC, and PBC were 42.5%, 41.4%, 25.7%, and 12.1%, respectively.

Thermodynamic analysis

Temperature is an important parameter in the adsorption process. The effects of temperature on the adsorption of Ni(II) and Pb(II) are shown in Fig. 2(C). The heavy metal removal efficiencies gradually improved as the temperature increased. Moreover, H-PBC had the highest capacity for adsorbing Ni(II) and Pb(II). When the temperature reached 55°C, the Ni(II) and Pb(II) removal efficiencies with H-PBC were 11.3% and 40.4%, respectively. The thermodynamic behavior was investigated further using Equations (6)–(8) (Kumar et al., 2010):

$$\Delta G^0 = -RT \ln K_C \quad (6)$$

$$K_C = \frac{C_{Ae}}{C_e} \quad (7)$$

$$\ln K_C = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (8)$$

where ΔG^0 is the Gibbs free energy (kJ/mol), ΔS^0 is the entropy change (J/mol·K), ΔH^0 is the enthalpy change (kJ/mol), R is the general gas constant (J/mol·K), T is the solution temperature (K), C_e is the concentration of the compound at equilibrium (mg/L), and C_{Ae} is the amount adsorbed after reaching equilibrium at a specific temperature (mg/g).

The values of ΔH^0 and ΔS^0 were calculated from the plot of $\ln K_C$ versus $1/T$ (Fig. S2). The thermodynamic parameters are presented in Table S1 and Table S2. The negative values of ΔG^0 for the adsorption of Ni(II) and Pb(II) indicated the spontaneous nature of the adsorption process. The adsorption of heavy metals was more efficient at high temperatures because ΔG^0 decreased as the temperature increased. ΔH^0 was positive in the cases of Ni(II) and Pb(II) adsorption, thereby indicating the endothermic nature of their adsorption. The positive values of ΔS^0 reflected increased randomness on the adsorbents/solution surface and the affinity of Ni(II) and Pb(II) for the adsorbents (Yang and Jiang, 2014).

Adsorption kinetics

Pseudo-first order and pseudo-second order models were employed to describe the kinetic adsorption processes. As shown in Fig. 3(A) and Fig. 3(B), the pseudo-first order model did not obtain a good linear relationship, but the experimental data were in agreement with the pseudo-second order model. For Ni(II), the correlation coefficients (R^2 values) obtained for the pseudo-first order models for PBC, H-PBC, E-PBC, and O-PBC were 0.967, 0.960, 0.871, and 0.812 (Table 2), respectively, which were lower than those for the pseudo-second order models (0.994, 0.995, 0.993, and 0.983). The experimental results obtained for Pb(II) were consistent with those for Ni(II). For Pb(II), the correlation coefficients (R^2 values)

obtained for the pseudo-first order models for PBC, H-PBC, E-PBC, and O-PBC were 0.883, 0.822, 0.880, and 0.867 (Table 3), respectively, which were lower than those for the pseudo-second order models (0.989, 0.987, 0.993, and 0.993). Furthermore, the values calculated for q_{e2} were consistent with the experimental $q_{e,exp}$ values for the pseudo-second order models based on Ni(II) and Pb(II). The pseudo-second order kinetic constants (k^2 values) were small for Ni(II) and Pb(II), thereby indicating that the adsorption rate decreased as the contact time increased and it was proportional to the amount of adsorption sites (Li et al., 2019). These results suggest that the adsorption process was controlled by chemical adsorption instead of physical adsorption.

Adsorption isotherms

The Langmuir and Freundlich models were used to simulate the adsorption equilibria for heavy metals by the adsorbents. The fitted models and experimental data are shown in Fig. 4, and the calculated parameters are presented in Tables 4–5. As shown in Table 4 and Table 5, the Langmuir model obtained a high coefficient of determination ($R^2 \geq 0.99$) and it was more suitable than the Freundlich model, where it suggested the homogeneous adsorption of Ni(II) and Pb(II). The maximum monolayer adsorption capacities for H-PBC were determined as 64.94 mg/g for Ni(II) and 243.90 mg/g for Pb(II). According to the Freundlich isotherm, the value of $1/n < 1$ indicated the favorable adsorption of heavy metals. Moreover, the dimensionless separation factor R_L was employed to check the favorability of the adsorption process. Based on $R_L = 1/(1 + K_L C_0)$ (Al-Othman et al., 2012), the Ni(II) and Pb(II) adsorption processes were thermodynamically favorable because the values of R_L ranged from 0 to 1.

The Ni(II) and Pb(II) adsorption capacities of various adsorbents are compared in Table S3 and Table S4. The adsorption capacity of H-PBC was similar to or superior to those of previously reported adsorbents. The greater capacity of H-PBC for adsorbing heavy metals may be explained by the following reasons. First, characterization of H-PBC showed that it had a larger S_{BET} value and higher aromaticity than the other adsorbents. Second, the abundance of oxygen-containing functional groups was conducive to ion exchange between H-PBC with Ni(II) and Pb(II). Jiang et al. (2019) synthesized H_3PO_4 -HC via a hydrothermal carbonization process and found that the oxygen-containing functional groups on H_3PO_4 -HC, such as C=O groups, played the main role in Pb(II) adsorption. Finally, the adsorption process was affected by the phosphonic and pyrophosphate groups on H-PBC. In a previous study, Chen et al. (2020) prepared H_3PO_4 -modified biochar (BCP) via an *in situ* pyrolysis method and found that the C-P bonds on BCP could remove Cr(VI). In summary, the results showed that H-PBC was more effective than the other adsorbents.

Regeneration study

Figure 5 shows the recyclability of the adsorbents. Five cycles of adsorption were conducted. The adsorption efficiency generally remained unchanged in the first three cycles. Furthermore, after three cycles of adsorption and desorption, H-PBC maintained a high capacity for adsorbing Ni(II) and Pb(II), with 32.32 mg/g and 137.35 mg/g, respectively, thereby indicating that the H-PBC composite material is a stable adsorbent for use in heavy metal removal. The adsorption efficiency decreased in the fourth and fifth cycles, probably due to the use of ultrapure water as the desorption agent since it is inefficient compared with traditional desorption agents such as NaOH.

Conclusions

In this study, three methods for modifying biochar to improve the adsorption of Ni(II) and Pb(II) were

systematically compared. H-PBC, E-PBC, and O-PBC were prepared, characterized, and applied for Ni(II) and Pb(II) adsorption. The results obtained in adsorption experiments showed that the efficiencies of Ni(II) and Pb(II) removal were higher with H-PBC, E-PBC, and O-PBC than PBC. In addition, a high adsorbent content, high pH, and high temperature were favorable for the adsorption of Ni(II) and Pb(II). The adsorption kinetics and the adsorption isotherms fitted a pseudo-second order model and the Langmuir adsorption model, respectively. Due to the large specific surface area, abundant oxygen-containing functional groups, and abundant phosphorus-containing functional groups of H-PBC, its adsorption capacity was greater than those of the other adsorbents. The results obtained in this study demonstrate that the modification of porous biochar can yield highly efficient materials for the removal of heavy metals.

Funding

This project was supported by the Key-Area Research and Development Program of Guangdong Province (2019B110207002), Science and Technology Planning Project of Guangdong Province (200106105876892, 190807115560881, and 190325224778589), National Natural Science Foundation of China (NSFC-41907299), Research Project of Chemistry and Chemical Engineering Guangdong Laboratory (2032008), Science and Technology Program of Guangzhou (202002030177), and Guangdong Basic and Applied Basic Research Foundation for Distinguished Young Scholars (2021B1515020063).

Declarations

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent for Publish

Not applicable.

Author Contributions

Y.Y. and W.J.W. designed the experiments. C.C.L. and J.X.L. conducted most of the experiments and analyzed the data. C.C.L. and J.X.L. drafted the manuscript. H.J.C., W.J.W., and Y.Y. revised the manuscript.

Availability of data and materials

The data and materials used and analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare no competing interests.

Supplementary Information

The supplementary information and data associated with this article are shown in Tables S1–S4 and Fig. S1–S2.

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Figures

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Fig. 1 (A) Brunauer – Emmett – Teller spectra, (B) pore size distributions, (C) X-ray diffraction patterns, and (D) Fourier transform infrared spectra obtained for PBC, E-PBC, O-PBC, and H-PBC

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Fig. 2 (A) Effect of adsorbent dosage on Ni^{2+} and Pb^{2+} removal efficiency. Experimental conditions: $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; $\text{pH} = 5.0$; temperature = 298.15 K ; adsorption time = 9 h . (B) Effect of pH on Ni^{2+} and Pb^{2+} removal efficiency. Experimental conditions: adsorbent dosage = 10 mg ; $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; temperature = 298.15 K . (C) Effect of temperature on Ni^{2+} and Pb^{2+} removal. Experimental conditions: adsorbent dosage = 10 mg ; $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; $\text{pH} = 5.0$; adsorption time = 9 h .

Fig. 3 Adsorption kinetic equations fitted for (A) Ni^{2+} and (B) Pb^{2+} with PBC, H-PBC, E-PBC, and O-PBC. Experimental conditions: adsorbent dosage = 10 mg; $[\text{Ni}^{2+}]$ and $[\text{Pb}^{2+}] = 40 \text{ mg/L}$; pH = 5.0; temperature = 298.15 K.

Fig. 4 Sorption isotherms for (A) Ni^{2+} and (B) Pb^{2+} with PBC, H-PBC, E-PBC, and O-PBC. Experimental conditions: adsorbent dosage = 10 mg; pH = 5.0; temperature = 298.15 K; adsorption time = 9 h.

443 **Fig. 5** Recyclable analysis for the adsorption of (A) Ni^{2+} and (B) Pb^{2+} by PBC, H-PBC, E-PBC, and O-
444 PBC. Experimental conditions: adsorbent dosage = 200 mg; $[\text{Ni}^{2+}]$ and $[\text{Pb}^{2+}]$ = 40 mg/L; adsorption time
445 = 9 h.
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Tables

Table 1 Main textural properties for PBC, H-PBC, O-PBC, and E-PBC

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
PBC	360.41	0.213	25.8
H-PBC	344.17	0.234	26.9
O-PBC	3.66	0.002	91.5
E-PBC	1.64	0.005	122.7

Table 2 Kinetic parameters for pseudo-first order and pseudo-second order models of Ni(II) adsorption by PBC, H-PBC, E-PBC, and O-PBC

Samples	Q _{e,exp} (mg/g)	Pseudo first-order			Pseudo second-order		
		q _{e1} (mg/g)	K ₁ (h ⁻¹)	R ²	q _{e2} (mg/g)	K ₂ (mg.(gh) ⁻¹)	R ²
PBC	8.39	7.95	2.91	0.967	8.40	0.57	0.994
H-PBC	33.52	31.79	4.54	0.960	33.44	0.24	0.995
E-PBC	16.75	15.80	4.95	0.871	16.56	0.54	0.993
O-PBC	30.21	29.08	6.36	0.812	30.21	0.42	0.983

Table 3 Kinetic parameters for pseudo-first order and pseudo-second order models of Pb(II) adsorption by PBC, H-PBC, E-PBC, and O-PBC

Samples	Q _{e,exp} (mg/g)	Pseudo first-order			Pseudo second-order		
		q _{e1} (mg/g)	K ₁ (h ⁻¹)	R ²	q _{e2} (mg/g)	K ₂ (mg.(gh) ⁻¹)	R ²
PBC	22.21	21.13	3.85	0.883	22.22	0.293	0.989
H-PBC	138.57	132.14	5.57	0.822	138.89	0.077	0.987
E-PBC	71.86	68.62	4.53	0.880	71.94	0.113	0.993
O-PBC	130.47	125.05	5.03	0.867	137.58	0.072	0.993

Table 4 Parameters fitted to Langmuir and Freundlich models of Ni(II) adsorption by PBC, H-PBC, E-PBC, and O-PBC

	Langmuir			Freundlich		
	q _m (mg/g)	K _L (L.mg ⁻¹)	R ²	K _F	1/n	R ²
PBC	19.80	0.017	0.998	0.704	0.633	0.875
H-PBC	64.94	0.0295	0.996	4.225	0.548	0.885
E-PBC	47.17	0.0158	0.998	1.323	0.669	0.995
O-PBC	60.24	0.0262	0.999	3.493	0.563	0.978

Table 5 Parameters fitted to Langmuir and Freundlich models of Pb(II) adsorption by PBC, H-PBC, E-PBC, and O-PBC

	Langmuir			Freundlich		
	q _m (mg/g)	K _L (L.mg ⁻¹)	R ²	K _F	1/n	R ²
PBC	38.31	0.037	0.999	3.368	0.491	0.981
H-PBC	243.90	0.0514	0.999	23.58	0.500	0.875
E-PBC	156.25	0.031	0.968	9.34	0.579	0.975
O-PBC	192.31	0.0935	0.997	31.907	0.403	0.939

Figures

Figure 1

(A) Brunauer-Emmett-Teller spectra, (B) pore size distributions, (C) X-ray diffraction patterns, and (D) Fourier transform infrared spectra obtained for PBC, E-PBC, O-PBC, and H-PBC

Figure 2

(A) Effect of adsorbent dosage on Ni^{2+} and Pb^{2+} removal efficiency. Experimental conditions: $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; $\text{pH} = 5.0$; temperature = 298.15 K ; adsorption time = 9 h . (B) Effect of pH on Ni^{2+} and Pb^{2+} removal efficiency. Experimental conditions: adsorbent dosage = 10 mg ; $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; temperature = 298.15 K . (C) Effect of temperature on Ni^{2+} and Pb^{2+} removal. Experimental conditions: adsorbent dosage = 10 mg ; $[\text{Ni}(\text{II})]$ and $[\text{Pb}(\text{II})] = 40 \text{ mg/L}$; $\text{pH} = 5.0$; adsorption time = 9 h .

Figure 3

Adsorption kinetic equations fitted for (A) Ni^{2+} and (B) Pb^{2+} with PBC, H-PBC, E-PBC, and O-PBC. Experimental conditions: adsorbent dosage = 10 mg; $[\text{Ni}^{2+}]$ and $[\text{Pb}^{2+}] = 40 \text{ mg/L}$; pH = 5.0; temperature = 298.15 K.

Figure 4

Sorption isotherms for (A) Ni^{2+} and (B) Pb^{2+} with PBC, H-PBC, E-PBC, and O-PBC. Experimental conditions: adsorbent dosage = 10 mg; pH = 5.0; temperature = 298.15 K; adsorption time = 9 h.

Figure 5

Recyclable analysis for the adsorption of (A) Ni^{2+} and (B) Pb^{2+} by PBC, H-PBC, E-PBC, and O-PBC. Experimental conditions: adsorbent dosage = 200 mg; $[\text{Ni}^{2+}]$ and $[\text{Pb}^{2+}]$ = 40 mg/L; adsorption time = 9 h.

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