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Effective adsorption of Pb^{2+} on porous carbon derived from functional Octadecahedron ZIF-8

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ABSTRACT:

An adsorbent ZO (oxidized ZIF-8-derived carbon) was prepared on the ZIF-8-derived carbon (ZC) by Hummer's method. The removal rate and adsorption amount of Pb^{2+} was measured on different molar ratio of 2-Hmim to 2, 2 '-bipyridine in ZO, including 1:1 (1:1 ZO) and 1:2 (1:2 ZO). The adsorption experiments show that the best condition to adsorb Pb^{2+} in Pb^{2+} solution for 1:1 ZO is adsorbent dosage of 20 mg, adsorption time of 16 h, initial Pb^{2+}concentration of 15 mg/L, and pH=3; that for 1:2 ZO is adsorbent dosage of 15 mg, adsorption time of 18 h, initial Pb^{2+} concentration of 15 mg/L, and pH=4. The adsorption data fits the quasi-second-order kinetics and the Langmuir adsorption model. The competitive adsorption results show that 1:1 ZO and 1:2 ZO have a superior selectivity for Pb^{2+} competing with Cu^{2+} and Fe^{2+}.This study shows 1:2 ZO is more helpful for the removal of Pb^{2+} than 1:1 ZO.

Keywords: adsorption; derived carbon; octadecahedron; Pb^{2+}; ZIF-8

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1 Introduction

Heavy metals (HMS) are the most common pollutants in sewage [1], including lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), and arsenic (As). They are highly toxic and non-biodegradable, and be harmful to all organisms [2]. So, HMS removal has attracted much attention owing to the high requirement of ecological civilization and health. Pb^{2+} is not only non-degradable, but also the most toxic metal in HMS ions [3]. Even a small amount of Pb^{2+} is toxic to plants and animals [4]. Pb as a raw material is widely used in solar cells, ceramics, coatings, and other industries [5]. However, the emission of Pb^{2+} has led to a serious environmental problem. Thus, effective removal of Pb^{2+} is essential. Common methods to remove Pb^{2+} from sewage include the chemical precipitation method [6], ion exchange method [7], membrane filtration method [8], an adsorption method, and etc. [9, 10].

The adsorption method is widely used in research and industry for the advantages of strong operability, and high efficiency [11]. Common adsorbents for the adsorption of Pb^{2+} are zeolite [12], graphene oxide [13], and biomass [14]. But, they are in high cost for the wide application. Zeolitic Imidazolate Frameworks (ZIFs) as a Nanoporous carbon (Nc) material have a large specific surface area and pore volume. Therefore, they have better applications in the field of adsorption [15].

ZIFs have zeolite or zeolite-like topological structures, with special characteristics, such as strong chemical robustness and good thermal stability [16, 17]. ZIF-8 is a framework formed by zinc ions and imidazole ligands with albite topology and has been widely studied in this type of material [18]. It can be used for gas adsorption/separation, catalysis, etc. [19, 20]. Common ZIF-8 shapes are cube [21], cuboid [22], dodecahedron [23], spherical [24], and leaf-like [25]. After the carbonization of ZIF-8 (zinc-based ZIF) powder in a nitrogen atmosphere, ZIF-8-Derived carbon can be obtained after washing with hydrochloric acid and drying. Related literature reported that the morphology of ZIF-8 before and after carbonization did not be changed [26]. Recently, researchers found that the porous carbon synthesized by the ZIF-8 carbonization method can be used as an efficient adsorbent to remove pollutants [27-29]. However, the Pb^{2+} adsorption by ZIF-8-derived carbons has been rarely investigated.

In this study, ZIF-8-derived carbon was oxidized by Hummer's method used to adsorb Pb^{2+} in aqueous solution. Then, SEM, XRD, FT-IR, Zeta potential and BET five methods were used to characterize the materials. The effects of adsorption time, pH, adsorbent dose, and initial concentration on the removal of Pb^{2+} were studied, and the optimal parameters for material removal of Pb^{2+} were determined. After that, the material was used to adsorb Pb^{2+} solution containing other metal ions to explore the material's selectivity to Pb^{2+}.

2 Materials and methods

2.1 Chemicals and materials

The details of chemical materials used in the research are listed in Table 1. Deionized water (DW) used in all experiments was made in laboratory. All chemical reagents were purchased without further purification.

Table 1 Chemical Sample Table

chemical name	molecular formula	CAS no.	purity (%)	suppliers
sulfuric acid	H_2SO_4	7664-93-9	95.0~98.0	Chongqing Chuan dong Chemical Co., Ltd. (China)
potassium permanganate	$KMnO_4$	7722-64-7		Jintan County Reagent Co., Ltd. (China)
hydrogen peroxide	H_2O_2	7722-84-1	30.0	Chengdu Jinsan Chemical Reagent Co., Ltd. (China)
hydrochloric acid	HCl	7647-01-0	36.0~38.0	Chongqing Chuan dong Chemical Co., Ltd. (China)
sodium hydroxide	NaOH	1310-73-2	96.0	Tianjin Yongda Chemical Reagent Co., Ltd. (China)
absolute ethyl alcohol	CH_3CH_2OH	64-17-5	99.7	Tianjin KGM Chemical Reagent Co., Ltd. (China)
zinc nitrate hexahydrate	$Zn(NO_3)_2.6H_2O$	10196-18-6	99.0	Chengdu Jinsan Chemical Reagent Co., Ltd. (China)
2-methylimidazole	$C_4H_6N_2$ (2-Hmim)	693-98-1	99.0	Tianjin Komiou Chemical Reagent Co., Ltd. (China)
Ammonia solution	$NH_3·H_2O$	1336-21-6	25.0~28.0	Chengdu Jinsan Chemical Reagent Co., Ltd. (China)
2,2'-bipyridine	$C_{10}H_8N_2$	366-18-7	99.0	Aladdin (Shanghai, China)

2.2 Preparation method [30-32]

2.2.1 Synthesis of ZIF-8

1.8 g $Zn(NO_3)_2·6H_2O$ was added to 90 mL CH_3OH, and 0.5 g 2-Hmim was added to 45 mL $NH_3·H_2O$. Then, the zinc ion-containing solution was slowly added to the above solution. Next, the solution was stirred for 5 h at 5°C. Centrifuge at 8000 rpm for 10 min and wash with methanol three times. Drying at 80°C in a vacuum drying oven overnight，ZIF-8 powder was obtained. Finally, the molar ratios of 2-Hmim and 2, 2 '-bipyridine in ZIF-8 include 1:1 (symbol 1:1 ZIF-8) and 1:2 (symbol 1:2 ZIF-8).

2.2.2 Synthesis of ZC

The ZIF-8 powder was calcined at 900°C under N_2 atmosphere for 2 h (temperature rate is 5°C·min^{-1}) to obtain a black solid. 5% HCl was used to remove zinc substances. After washing with a large amount of DW until the solution was neutral, the black solid was dried under vacuum at 80°C overnight. The final ZIF-8 derived carbon was named as ZC. The 1:1 ZIF-8 and 1:2 ZIF-8 after carbonization were abbreviated as 1:1 ZC and 1:2 ZC, respectively.

2.2.3 Synthesis of ZO

First, 5 g ZC was added to 150 mL of mixed acid (135 mL 98% H_2SO_4, 15 mL 85% H_3PO_4). The solution was stirred under an ice bath for 1 h. Then, 30 g $KMNO_4$ was added into the mixture in batches. The solution was stirred for 3 days under a lower stirring speed. Finally, 250 mL of DW and, 10 mL of H_2O_2 were added to the mixed paste. After removing the supernatant, 1 M HCl was added. Until the paste was homogeneous, the diluted mixture was centrifuged at 4000 rpm for 40 min. The paste was reserved after repeated centrifugation three times. Then, it was further washed with DW six times. The final material was obtained in a vacuum drying oven at 60°C overnight, marked as ZO. The 1:1 ZC and 1:2 ZC after oxidation were abbreviated as 1:1 ZO and 1:2 ZO, respectively.

2.3 Adsorption experiment

Adsorbent (1:1 ZO and 1:2 ZO) was added to 20 mL of Pb^{2+} solution. The solution was shaken in a constant temperature oscillator (200 rpm) at room temperature for 12h, and the obtained solution was filtered with a syringe filter, and 5 mL of the supernatant was taken. The concentration of Pb^{2+} after adsorption was measured by atomic absorption spectrometer at a wavelength of 283.3 nm. The adsorption amount of Pb^{2+} adsorbed by 1:1 ZO and 1:2 ZO can be calculated based on the difference between the initial Pb^{2+} concentration and residual concentration. The removal rate of 1:1 ZO and 1:2 ZO adsorption to Pb^{2+} was calculated by the formula [3]:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$Q_t = \frac{(C_0 - C_t)V}{M} \quad (2)$$

Where R is the removal rate of Pb^{2+} (%), C_0 and C_t are the initial and equilibrium concentration of Pb^{2+} (mg/L), Q_t is the adsorption amount when the adsorption reaches equilibrium ($mg \cdot g^{-1}$), V is the volume (L) of the adsorbed solution, M is the mass (mg) of 1:1 ZO and 1:2 ZO used for adsorption.

Each group of the adsorption experiment was measured in parallel 3 times, the average value and standard deviation were calculated, and the error bars were made in the adsorption experiment diagram.

2.4 Adsorption isotherm experiment

In the experiment, 20 mg of 1:1 ZO and 15 mg of 1:2 ZO were added into 20 mL of Pb^{2+} simulated waste liquid with a concentration of 15 mg/L. After stirring at room temperature for 16 h and 18 h, the obtained solution was filtered with a syringe filter. After filtration, 5 mL of the supernatant was taken and its concentration was determined using atomic absorption at a wavelength of 283.3 nm. Two isotherm adsorption models, Langmuir and Freundlich, were used to analyze the adsorption data of 1:1 ZO and 1:2 ZO on Pb^{2+}.

2.5 Characterization

The characterization methods of the materials and the analysis of the characterization data are given in detail in the Supplementary Material.

3 Result and discussion

3.1 Adsorption research

To investigate the effects of the adsorbent dosage on the removal rate and adsorption amount of Pb^{2+}, 5 mg, 10 mg, 15 mg, 20 mg, and 25 mg of 1:1 ZO and 1:2 ZO were added into 20 mL, 15 mg/L Pb^{2+} solution for adsorption observation. The obtained removal rate and adsorption amount are shown in the Fig 1.

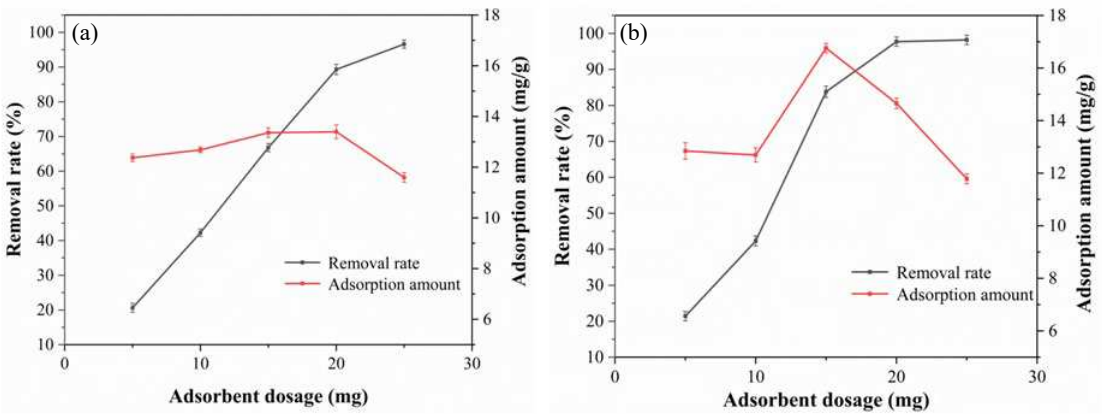

Fig 1 Adsorption dosage (5mg, 10mg, 15mg, 20mg, 25mg) on the adsorption performance of Pb^{2+} (a) 1:1 ZO; (b) 1:2 ZO

As shown in Fig 1, with the increase of adsorbent dosage (5mg~25mg), the removal rate of Pb^{2+} increases from 20.62% to 96.62% by 1:1 ZO and from 21.41% to 98.21% by 1:2 ZO. The Pb^{2+} adsorption amount of 1:2 ZO first increases from 12.8 mg/g to 16.76 mg/g, and then decreases to 11.79mg/g, while that of 1:1 ZO firstly increases from 12.37 mg/g to 13.36 mg/g and then decreases to 11.59 mg/g. Thus, 1:1 ZO and 1:2 ZO have the same trend in the removal rate and adsorption amount. Reaching the maximum adsorption amount, the dosage of 1:2 ZO (15 mg) is less than that of 1:1 ZO (20 mg). Under this condition, the removal rate of Pb^{2+} by both materials can reach more than 90%.

When the dosage is less than a certain value (15 mg of 1:2 ZO and 20 mg of 1:1 ZO), the active sites on the adsorbent are insufficient, the adsorption not reach a saturated state, and the removal rate is low. On the contrary, the adsorption is saturated and the adsorption amount decreases.

To research the effects of the initial concentration in Pb^{2+} solution on the removal rate and adsorption amount, Fig 2 shows 1:1 ZO and 1:2 ZO adsorption following the concentrations of Pb^{2+} solution. The volume of the Pb^{2+} solution is 20 mL and the

concentrations include 5 mg/L, 10 mg/L, 15 mg/L, 25 mg/L, and 35 mg/L. 20 mg of 1:1 ZO and 15 mg of 1:2 ZO were used as the adsorbent in the experiment.

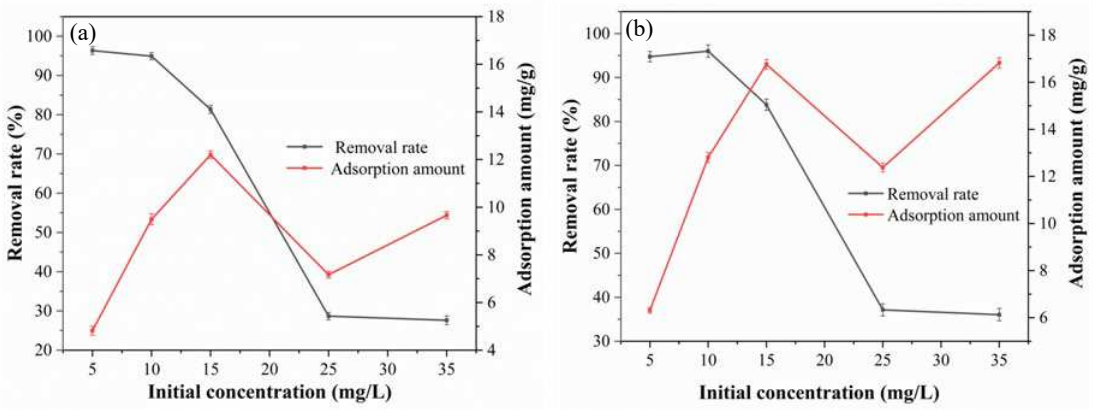

Fig 2 Effect of different initial concentrations (5 mg/L,10 mg/L,15 mg/L,25 mg/L,35 mg/L) on the adsorption performance of Pb^{2+} (a)1:1 ZO; (b) 1:2 ZO

As shown in Fig 2, with the increase of the initial concentration of Pb^{2+} (5mg/L~25mg/L), the adsorption amount of Pb^{2+} by 1:1 ZO (Fig 2(a)) first increases from 4.81mg/g to 12.01mg/g. Then, it decreases to 7.17mg/g, and finally increases to 9.67mg/g. The removal rate continues to decrease (96.35%~27.62%). For comparison, the adsorption amount of Pb^{2+} by 1:2 ZO (Fig 2(b)) first increases from 6.32 mg/g to 12.81 mg/g. Then, it decreases to 12.38 mg/g, and finally increases to 16.82 mg/g. The removal rate continues to decrease by 58.71%. Thus, the optimum initial concentration of Pb^{2+} to obtain the maximum adsorption amount and the peak removal rate removal rate is 15mg/L for 1:1 ZO and 1:2 ZO. Significantly, the adsorption amount and removal rate of 1:2 ZO are higher than those of 1:1 ZO at the same initial Pb^{2+} concentration. So, 1:2 ZO has a better removal effect of Pb^{2+}.

For the same adsorbent, when the concentration of Pb^{2+} in the solution is less than 15 mg/L, it is easy to chelate with Pb^{2+} or produce electrostatic adsorption due to enough carboxyl groups. However, if the concentration of Pb^{2+} is greater than 15 mg/L, the

carboxyl groups available for adsorption are insufficient, and sufficient active sites could not be provided for the adsorption of Pb^{2+}, so the removal rate decreases.

To research the effects of the pH in Pb^{2+} solution on the removal rate and adsorption amount, 20 mg 1:1 ZO and 15 mg 1:2 ZO were added into 20 mL of simulated waste liquid with a Pb^{2+} concentration of 15 mg/L. 1 M NaOH and 1 M HCl were used to adjust the pH value containing 2, 3, 4, 5, 6, 7, and 8. The experiments are shown in the Fig 3.

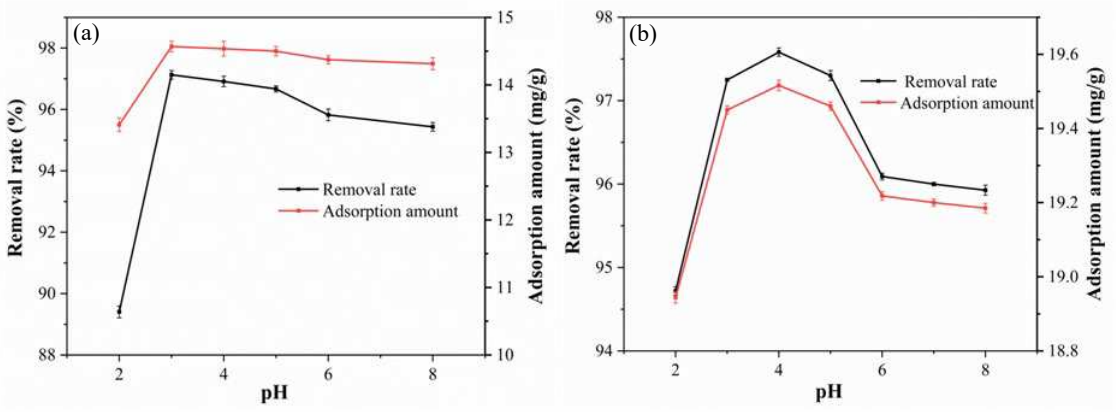

Fig 3 Effect of materials on the adsorption performance of Pb^{2+} at different pH values (2, 3, 4, 5, 6, 7, 8,) (a) 1:1 ZO; (b) 1:2 ZO

The pH value affects the interaction between adsorbates and adsorbents by changing the charge distributing on the surface of the adsorbates and adsorbents [33]. When the pH ＜ 5, lead mainly exists in Pb^{2+} and $Pb(OH)^{+}$, and when 5＜pH＜ 10, lead mainly exists in the form of $Pb(OH)_2$, $Pb(OH)_4^{2-}$ and $Pb(OH)_3^{-}$.

As shown from Fig 3, the adsorption amount and removal rate of 1:1 ZO and 1:2 ZO for Pb^{2+} are first increased and then decreased with the increase of pH. The Pb^{2+} adsorption amount (14.57 mg/g) and the Pb^{2+} removal rate (97.13%) of 1:1 ZO reach the peak at pH=3, shown in Fig 3(a). Because pH_{PZC} of 1:1 ZO is 2.38 (shown in Fig S6), when pH ＜ 2.38, 1:1 ZO is positively charged, there are Pb^{2+} and $Pb(OH)^{+}$ exist, and there is electrostatic repulsion between them. When 2.38 ＜ pH ＜5, the negative

charge of 1:1 ZO is enhanced, and Pb^{2+} has a positive charge and attracts each other.

As shown from Fig 3(b), both the Pb^{2+} adsorption amount (19.52 mg/g) and the Pb^{2+} removal rate (97.58%) of 1:2 ZO reach the peak at pH=4. Since pH_{PZC} of 1:2 ZO is 3.78 (shown in Fig S6), When pH ＜ 3.78, the 1:2 ZO is positively charged. At this time, lead mainly exists in Pb^{2+} and $Pb(OH)^{+}$, while the Pb^{2+} and $Pb(OH)^{+}$ are mutually repellent to the 1:2 ZO. When 3.78 ＜ pH＜4, 1:2 ZO is negatively charged, it electrostatically attracts with Pb^{2+} and $Pb(OH)^{+}$. When 5＜pH, 1:2 ZO is negatively charged. The adsorption amount and the removal rate significantly decrease due to that lead mainly exists in the form of $Pb(OH)_2$ and $Pb(OH)_4^{2-}$, and mutual repulsion occurs between them.

To investigate the effects of the adsorption time on the Pb^{2+} removal rate and the Pb^{2+} adsorption amount, 20 mg 1:1 ZO and 15 mg 1:2 ZO were added into 20 mL of simulated waste liquid with a Pb^{2+} concentration of 15 mg/L, and the solutions were shaken at room temperature (200 rpm) in a constant temperature oscillator for 1h, 2h, 3h, 4h, 5h, 6h, 8h, 10h, 12h, 16h, 18h, 24h, 32h, and 36h. The experiment results are shown in Fig 4.

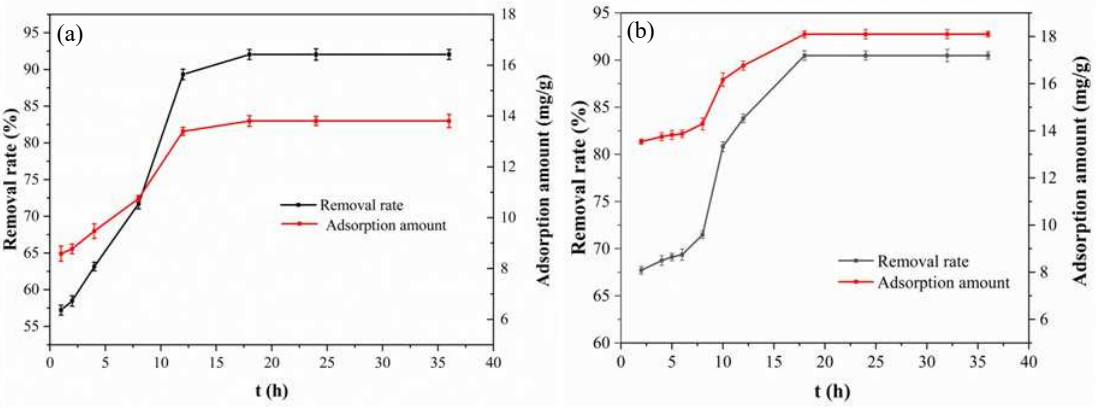

Fig 4 Effects of materials on the adsorption performance of Pb^{2+} at different time (1h, 2h, 3h, 4h, 5h, 6h, 8h, 10h, 12h, 16h, 18h, 24h, 32h, 36h) (a) 1:1 ZO; (b) 1:2 ZO

As shown from Fig 4, the Pb^{2+} removal rate of 1:1 ZO and 1:2 ZO gradually increase

when increasing the adsorption time. The adsorption time of 1:1 ZO and 1:2 ZO to reach the saturation (13.81 mg/g for 1:1 ZO and 18.09 mg/g for 1:2 ZO) of Pb^{2+} adsorption is 16 h and 18 h, respectively. Significantly, at the same adsorption time, the adsorption amount of 1:2 ZO is much higher than that of 1:1 ZO, that is, the adsorption effect of 1:2 ZO is better.

At the beginning of adsorption, there are a large number of active sites on the surface of the adsorbent. So, 1:1 ZO and 1:2 ZO can well combine with Pb^{2+}, resulting in the high removal rate. With the decrease of active sites, the adsorption rate gradually slows down, and the adsorption reaches saturation after a certain time.

3.2 Adsorption kinetics

The pseudo-first-order kinetic model (3) and the pseudo-second-order kinetic model (4) were used to calculate the adsorption rate. The equations are as follow s:

$$log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \qquad (4)$$

Where q_e and q_t (mg/g) are the equilibrium adsorption amount and adsorption amount at time t, respectively, K_1 (min^{-1}) and K_2 (min^{-1}) are the pseudo-first-order kinetic constant and the pseudo-second-order kinetic constant, respectively.

The fitting curves and the related parameters are shown in Fig 5 and Table 2. It can be clearly seen from Table 2 that the fitting effect of the quasi-second-order kinetic has the fitting coefficient of 0.99998, which is significantly higher than that of the quasi-first-order kinetic. Moreover, the maximum adsorption amount calculated by the quasi-second-order kinetics equation is closer to the experimental value. Thus, it is indicated that the pseudo-second-order kinetics can better describe the adsorption kinetics of 1:1 ZO and 1:2 ZO for Pb^{2+}, so the adsorption process is mainly a chemisorption adsorption process.

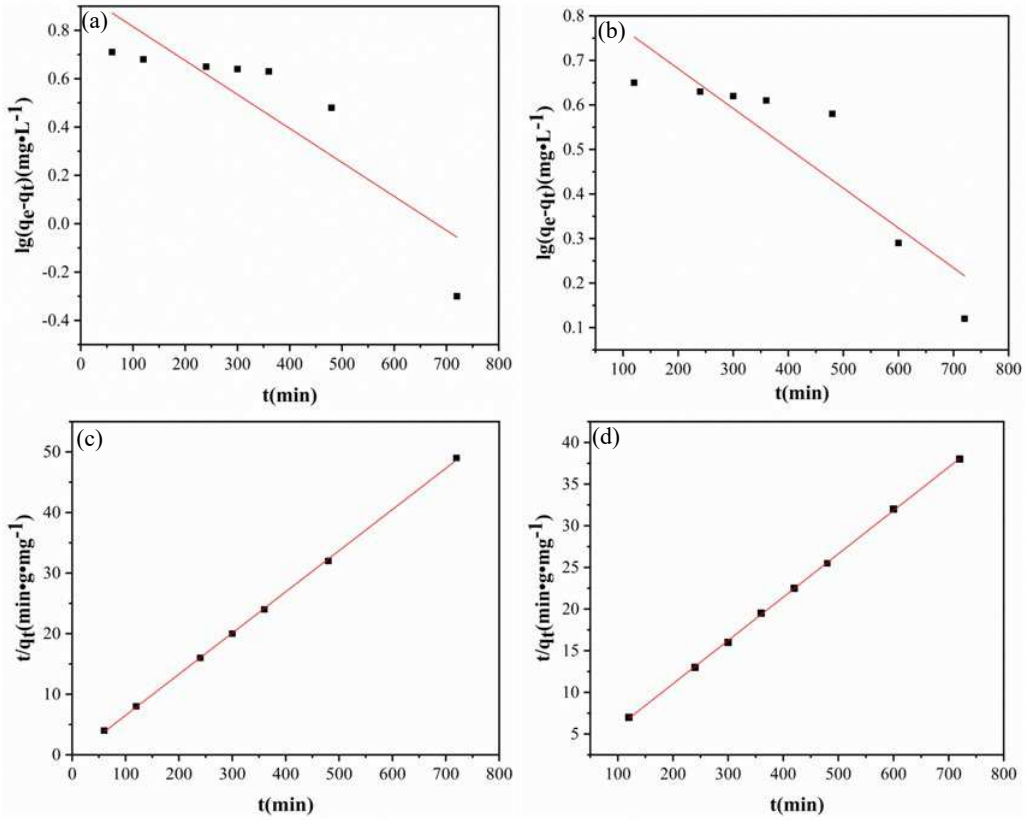

Fig 5 Quasi-first-order kinetics (a) 1:1 ZO, (b) 1:2 ZO and quasi-second-order kinetics (c) 1:1 ZO, (d) 1:2 ZO

Table 2 Kinetic parameters of 1:1 ZO and 1:2 ZO adsorption of Pb^{2+}

material	Initial concentration C_0 (mg/L)	Saturation adsorption amount q_e (mg/g)	quasi-first-order kinetic			quasi-second-order kinetic		
			K_1 (min^{-1})	$Q_{e,cal}$ (mg/g)	R^2	K_2 (min^{-1})	$Q_{e,cal}$ (mg/g)	R^2
1:1 ZO	15	13.80650	0.00357	10.0970	0.75779	0.07243	13.80640	0.99998
1:2 ZO	15	18.09590	0.00207	7.47460	0.81858	0.05526	18.09620	0.99998

3.3 Adsorption isotherm

The adsorption isotherm is employed to evaluate the adsorption characteristics of an absorbent. In this work, the Langmuir adsorption isotherm (5) and the Freundlich adsorption isotherm (6) were used to understand the Pb^{2+} adsorption behavior of 1:1 ZO and 1:2 ZO. The equations of the Langmuir model and the Freundlich model are as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

Where q_e (mg/g) is the equilibrium adsorption amount of 1:1 ZO and 1:2 ZO; C_e (mg/L) is the concentration of the Pb^{2+} when the adsorption is in equilibrium; q_m (mg/g) is the maximum adsorption amount of 1:1 ZO and 1:2 ZO; K_L is the Langmuir constant; K_f and n are the Freundlich constant, which is related to the adsorption strength of the adsorbent; C_0 is the initial concentration of the Pb^{2+} (mg/L).

Fig 6 shows the Langmuir adsorption isotherm equation and the Freundlich adsorption isotherm equation. As shown from Table 3, Langmuir's fitting coefficients (1:1 ZO R^2=0.95058 1:2 ZO R^2=0.97488) are better than Freundlich's (1:1 ZO R^2=0.91288 1:2 ZO R^2=0.82627). Thus Langmuir is more suitable to describe the adsorption of 1:1 ZO and 1:2 ZO for Pb^{2+}, indicating that the adsorption of 1:1 ZO and 1:2 ZO for Pb^{2+} belongs to monolayer adsorption.

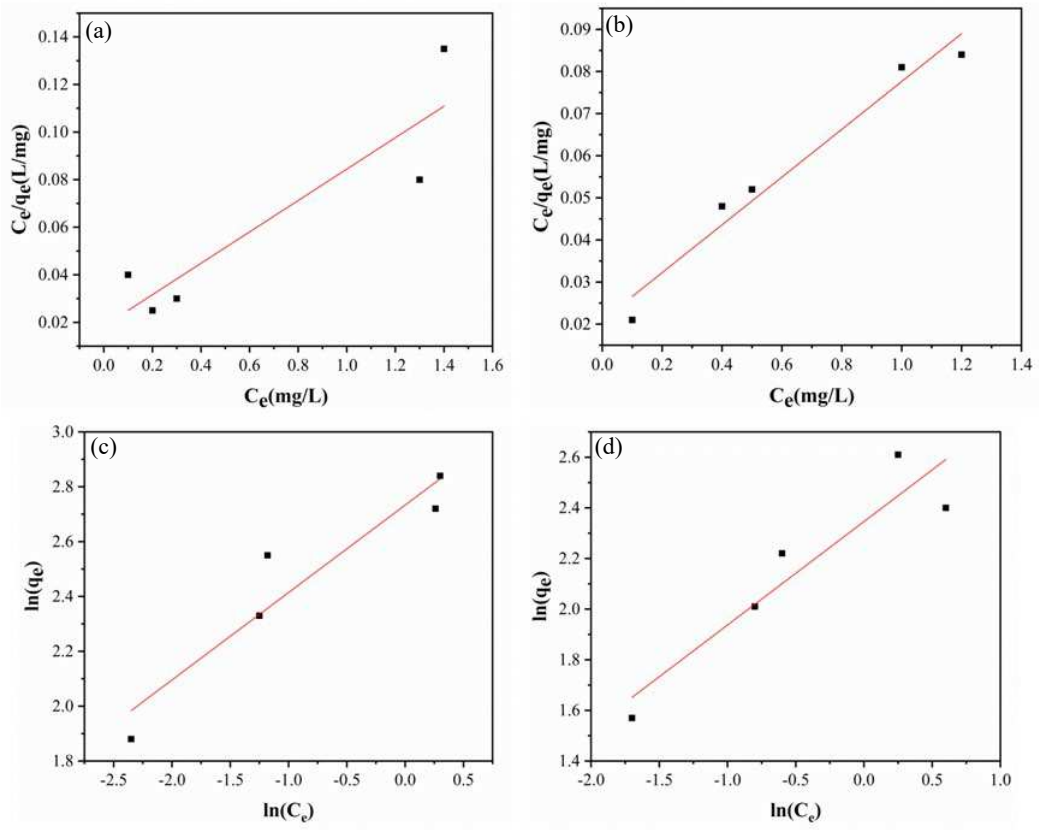

Fig 6 Langmuir adsorption isotherm equation (a) 1:1 ZO, (b) 1:2 ZO and Freundlich adsorption isotherm equation (c) 1:1 ZO, (d)1:2 ZO

Table 3 Adsorption isotherm parameters of 1:1 ZO and 1:2 ZO adsorption for Pb^{2+}

material	temperature	Langmuir adsorption isothermal equation			Freundlich adsorption isothermal equation		
	(K)	q_m (mg/g)	K_L (L/m)	R^2	1/n	K_F (L/mg)	R^2
1:1 ZO	298	15.22	2.5575	0.95058	0.5650	2.5346	0.91288
1:2 ZO	298	17.80	2.0271	0.97488	1.3480	0.9792	0.82627

Adsorption thermodynamics can be used to calculate the driving force of the

adsorption process. The enthalpy change (ΔH^0) and the entropy change (ΔS^0) can be obtained by multiplying the slope to the intercept of the lnK versus 1/T fitted curve (Equations 7 and 9) with the gas molar constant R. The value of ΔG^0 can be calculated from ΔH^0 and ΔS^0 at a temperature (Equation 8). The specific equations involved in the fitting curve are as follows:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

$$K_d = \frac{q_e}{C_e} \quad (9)$$

Where K_d is the adsorption equilibrium constant (L/kg); R is the gas molar constant (8.314 J/mol•K); T is the absolute temperature (K); ΔS^0 (kJ/mol), ΔH^0 (kJ/mol) and ΔG^0 (kJ/mol) are entropy change, enthalpy change and Gibbs free energy, respectively.

According to the thermodynamic analysis in the temperature range (298 K, 308 K, 318 K), the adsorption amount data at each concentration can be calculated, and a scatter plot of lnK vs. 1/T is fitted shown in Fig 7. From the slope and the intercept of the fitted curve to the gas mole constant, the value of ΔH^0 and ΔS^0 can be obtained, as shown in Table 4. It can be seen from Fig 7 that as the temperature of the system increases, the adsorption amount of Pb^{2+} by 1:1 ZO and 1:2 ZO both decrease, and the $\triangle H^0$ is a negative value in Table 4, indicating that the adsorption of Pb^{2+} by 1:1 ZO and 1:2 ZO is an exothermic process. In addition, $\triangle G^0$ is a negative value, indicating that the adsorption process of Pb^{2+} by 1:1 ZO and 1:2 ZO is spontaneous. A negative value of ΔS^0 indicates that the disorder of the solid-liquid interface is reduced during the adsorption process.

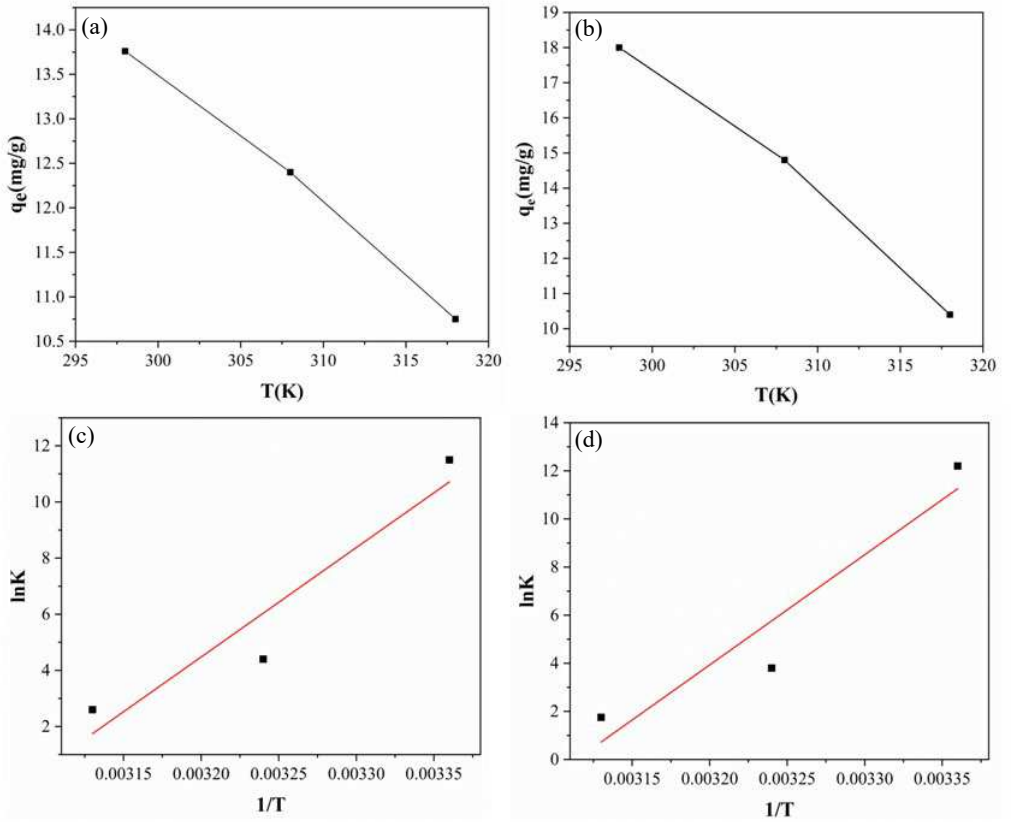

Fig 7 Adsorption amount of ZO for lead ions at different temperatures (a) 1:1 ZO, (b) 1:2 ZO and the fitting curve (c) 1:1 ZO, (d) 1:2 ZO

Table 4 Thermodynamic parameters of adsorption of Pb^{2+} by 1:1 ZO and 1:2 ZO

Material	T (K)	$\triangle G^0$ (kJ/mol)	$\triangle H^0$ (kJ/mol)	$\triangle S^0$ (kJ/mol)
1:1 ZO	298	-6.1741	-15.1439	-0.0301
	308	-5.8731		
	318	-0.5721		
1:2 ZO	298	-6.26578	-11.7311	-0.01834
	308	-6.0824		
	318	-5.8990		

3.4 Competitive Adsorption

In the experiment, Cu^{2+} and Fe^{2+} were selected as heavy metal ions to compete with Pb^{2+} during adsorption. The adsorption results of 1:1 ZO, 1:2 ZO for Pb^{2+} in different mixtures are shown in Fig 8. When Cu^{2+} and Fe^{2+} exist simultaneously, the removal rates of Pb^{2+} by 1:1 ZO and 1:2 ZO both reach more than 98%. It shows that the existence of Cu^{2+} and Fe^{2+} has little effect on the adsorption of Pb^{2+} by 1:1 ZO and 1:2 ZO. The results show that 1:1 ZO and 1:2 ZO have a superior selectivity for Pb^{2+}.

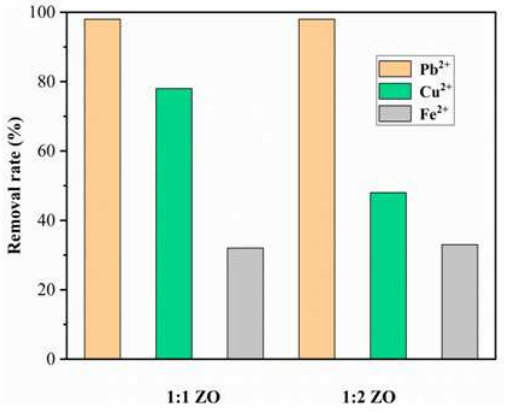

Fig 8 Competitive adsorption of 1:1 ZO and 1:2 ZO for heavy metal ions (Pb^{2+}, Cu^{2+} and Fe^{2+})

4 Conclusion

In this work, 1:1 ZO and 1:2 ZO were prepared and used to adsorb Pb^{2+}. The best conditions for 1:1 ZO to adsorb Pb^{2+} are m (adsorption dosage) = 20 mg, t (adsorption time) =16 h, C_0 (initial concentration) = 15 mg/L, and pH=3. The best conditions for 1:2 ZO to adsorb Pb^{2+} are m=15 mg, t= 18 h, C_0= 15 mg/L, and pH= 4. It shows that 1:2 ZO is more helpful for the removal of Pb^{2+} than 1:1 ZO. The adsorption mechanism of 1:1 ZO and 1:2 ZO on Pb^{2+} has been discussed. The Pb^{2+} adsorption process of ZO accords with the quasi-second-order kinetics (R^2=0.99998), indicating that chemical adsorption plays a leading role. The fitted isotherm adsorption curve is more consistent with the Langmuir adsorption model (1:1 ZO: R^2=0.95058; 1:2 ZO: R^2=0.97488). The maximum adsorption amount of Pb^{2+} is 15.52 mg/g by 1:1 ZO, and 18.09 mg/g by 1:2 ZO.

Thermodynamic analysis shows that the Pb^{2+} adsorption process is spontaneous. Competitive adsorption experiments show that the removal rate of Pb^{2+} by 1:1 ZO and 1:2 ZO is more than 98% in the presence of other heavy metal ions, which indicates that the investigated materials have a high selectivity for Pb^{2+}.

Supplementary Material

Supplementary Material for this article can be found under DOI:

Acknowledgment

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Declaration of competing interest

The authors report no conflict of interests.

Symbols used

D_a	[nm]	average pore size
$\triangle G^0$	[KJ/mol]	Gibbs free energy change
$\triangle H^0$	[KJ/mol]	enthalpy change
K_1, K_2	[-]	kinetic coefficient
K_L, K_F,n	[-]	equilibrium constant
Q_t	$mg \cdot g^{-1}$	adsorption amount
R	[-]	removal rate
R^2	[-]	fitting coefficient
R_c	[-]	removal rate after cycle
S_{BET}	$[m^2/g]$	specific surface area
$\triangle S^0$	[KJ/mol]	entropy change
V_a	$[cm^3/g]$	pore volume

C_0	[mg/L]	initial concentration
C_t	[mg/L]	equilibrium concentration
V	[L]	volume
M	[mg]	mass
q_e	[mg/g]	equilibrium adsorption amount
q_m	[mg/g]	maximum adsorption amount
K_d	[L/kg]	adsorption equilibrium constant

Abbreviations

BET	Brunauer-Emmett-Teller
FT-IR	Fourier transform infrared Spectrometer
HMS	heavy metals
Nc	nanoporous carbon
SEM	scanning electron microscopy
XRD	X-ray diffraction
ZC	ZIF-8 after carbonization
ZO	ZC after oxidation
ZIFs	Zeolite imidazole-based frameworks
DW	distilled water

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Table and Figure captions

Table 1 Chemical Sample Table

Table 2 Kinetic parameters of 1:1 ZO and 1:2 ZO adsorption of Pb^{2+}

Table 3 Adsorption isotherm parameters of 1:1 ZO and 1:2 ZO adsorption for Pb^{2+}

Table 4 Thermodynamic parameters of adsorption of Pb^{2+} by 1:1 ZO and 1:2 ZO

Fig 1 Adsorption dosage (5mg, 10mg, 15mg, 20mg, 25mg) on the adsorption performance of Pb^{2+} (A) 1:1 ZO；(B) 1:2 ZO

Fig 2 Effect of different initial concentrations (5 mg/L,10 mg/L,15 mg/L,25 mg/L,35 mg/L) on the adsorption performance of Pb^{2+} (A)1:1 ZO；(B) 1:2 ZO

Fig 3 Effect of materials on the adsorption performance of Pb^{2+} at different pH values (2, 3, 4, 5, 6, 7, 8,) (A) 1:1 ZO; (B) 1:2 ZO

Fig 4 Effects of materials on the adsorption performance of Pb^{2+} at different time (1h, 2h, 3h, 4h, 5h, 6h, 8h, 10h, 12h, 16h, 18h, 24h, 32h, 36h) (A) 1:1 ZO; (B) 1:2 ZO

Fig 5 Quasi-first-order kinetics (A) 1:1 ZO; (B) 1:2 ZO and quasi-second-order kinetics (C) 1:1 ZO; (D) 1:2 ZO

Fig 6 Langmuir adsorption isotherm equation (A) 1:1 ZO; (B) 1:2 ZO and Freundlich adsorption isotherm equation (C) 1:1 ZO; (D)1:2 ZO

Fig 7 Adsorption amount of ZO for lead ions at different temperatures A (1:1 ZO);B (1:2 ZO) and the fitting curve C (1:1 ZO) D (1:2 ZO)

Fig 8 Competitive adsorption of 1:1 ZO and 1:2 ZO for heavy metal ions (Pb^{2+}, Cu^{2+} and Fe^{2+})

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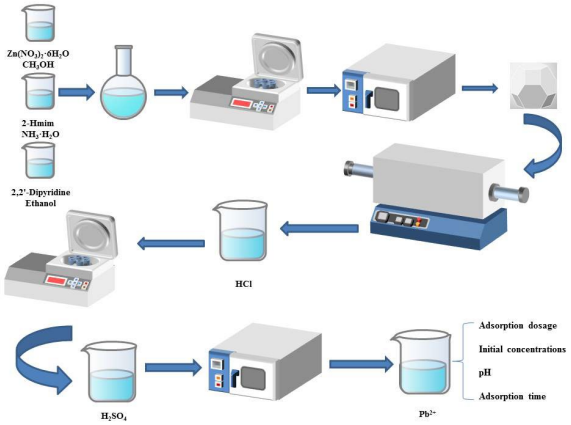

Title:

Effective adsorption of Pb^{2+} on porous carbon derived from functional Octadecahedron ZIF-8

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