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Preparation of porous iron hydroxy phosphate by phosphate slag and its application for adsorbing heavy metal Pb^{2+}

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Abstract: Porous iron hydroxy phosphate was prepared by hydrothermal purification, ball milling modification, hydrothermal crystallization and high temperature roasting of phosphating slag, and was used to treat lead-containing wastewater. The adsorbent was characterized by XRD, SEM, FTIR and TG, and the effect of the amount of adsorbent and the pH value of the system on the adsorption performance of PIHP was investigated. The results showed that when the amount of PIHP added was 0.5g, the removal rate of Pb^{2+} could reach 91% after 120min. When the amount of PIHP added was 0.2 g and the pH of the system was 2.15, the removal rate of Pb^{2+} after 120min could reach 95%. This research has opened up a new direction for the resource utilization of phosphating slag.

1. Introduction

With the rapid development of the metal industry, phosphating treatment technology is more and more widely used, but a large amount of by-product phosphating slag is generated in the phosphating process. The phosphating slag contains some heavy metal ions and a large amount of phosphate ions, which easily cause acidification of the soil and eutrophication of water bodies [1]. According to statistics, nearly 900 million tons of phosphating slag is produced every year in China. Most of the phosphating slag treatment methods are piled up or landfilled, which seriously pollutes the water body and also occupies a large amount of land resources [2]. The main component of phosphating slag is $FePO_4$, which also contains some trace metal elements. The extraction of these useful substances from phosphating slag has a very broad application prospect [3, 4].

On the other hand, with the development of industry, heavy metal wastewater has become one of the most serious environmental pollution [5], Pb^{2+} are harmful to the human and cause great damage to the human kidney and immune system [6]. Iron hydroxy phosphate is a derivative of iron phosphate, and significant progress has been made in the study of the removal of heavy metals by the inorganic adsorbent iron hydroxy phosphate in recent years [7,8]. Due to its special crystal chemical characteristics, iron hydroxy phosphate has wide acceptability and adsorption fixation effects on various metal cations, and has good ion exchange and surface adsorption capacity, thus it becomes a new type of environmental mineral material and has a good application prospect in the field of removing heavy metal cations in wastewater and soil pollution [9,10]. In this study, the phosphating slag was used as raw material to synthesize porous iron hydroxy phosphate by precursor thermal



decomposition method [11], and the adsorption performance of heavy metal ions (Pb^{2+}) was studied.

2. Materials and Method

2.1. Materials

Phosphating slag (provided by an automobile parts company in Zhejiang), phosphoric acid (AR, $\geq 85\%$), absolute ethanol (AR, $\geq 99.7\%$), cetyltrimethylammonium bromide (AR, $\geq 99.0\%$), oxalic acid (AR, $\geq 99.5\%$), lead chloride (AR, $\geq 99.5\%$), hydrochloric acid (AR, $\geq 99.5\%$), sodium hydroxide (AR, $\geq 99.5\%$), deionized water from ultrapure water system (UPT-I-60L, Super Pure Technology China)).

2.2. Adsorbent preparation

The catalyst preparation process mainly included three processes which included phosphating slag purification, iron phosphate ball milling, and preparation of porous iron hydroxy phosphate. First, the phosphating slag, deionized water and phosphoric acid were stirred at a mass ratio of 3:3:1 in a beaker for 4 hours, and the heating temperature was 80°C , and then 30 g phosphating slag, 30 g deionized water and 1 g phosphoric acid were hydrothermally purified in a polytetrafluoroethylene reactor at a hydrothermal temperature of 150°C for 4 hours. Then 20 g purified iron phosphate were ball milled with 20 g absolute ethanol and 120 g agate ball for 5 hour. The ball-milled iron phosphate, deionized water, oxalic acid and hexadecyl trimethyl ammonium bromide (CTAB) were hydrothermally reacted at 200°C for 8 hours in a polytetrafluoroethylene reactor at a mass ratio of 5:40:2:2 to prepare iron hydroxy phosphate precursor. The iron hydroxy phosphate precursor was calcined in a nitrogen atmosphere at a calcination temperature of 600°C for 4 hours to form a porous structure.

2.3. Heavy metal ion removal experiment

The lead-containing wastewater was simulated with 100 mg/L PbCl_2 solution, different masses of PIHP were added to 200 mL lead-containing wastewater, and the pH value of the system was adjusted by HCl and NaOH. 10 mL solution was filtered through a needle and the residual Pb^{2+} concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (ICAP 6000, Thermo, USA), then the lead ion removal rate of the lead-containing wastewater and the amount of adsorption of the adsorbent were calculated. All adsorption experiments were stirred at 350 r/min. The calculation formula of the lead ion removal efficiency η and the adsorption amount q of the adsorbent are as follows:

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

$$q = \frac{V(C_0 - C_t)}{m} \quad (2)$$

η is the removal efficiency of lead ions and q is the adsorption amount. C_0 is the initial concentration of lead ions in the solution and C_t is the concentration of lead ions in the solution at a certain moment, and V is the volume of the solution.

2.4. Characterization method

The phase composition and crystal structure of the powder sample were measured by X-ray diffraction (XRD) (D8-Advance, Bruker Corporation, Germany), and operation was carried out at 40 kV and 40 mA with aminobrominated Cu K α radiation ($\lambda = 0.15418 \text{ nm}$) source. The composition of the sample was analyzed by a synchronous thermogravimetric analyzer (TG) (STA 449C, NETZSCH instrument Corporation, Germany) under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The surface morphology of the sample was analyzed by a scanning electron microscope (SEM) (S-4800, Hitachi Corporation, Japan) with an acceleration voltage of 10 kV and a current of 10 mA. The functional groups and the chemical bonds in the samples were analyzed by fourier transform infrared spectroscopy (FTIR) (Vertex 70, Bruker, Germany), and the KBr was chosen as a medium.

3. Results and discussion

3.1. XRD characterization

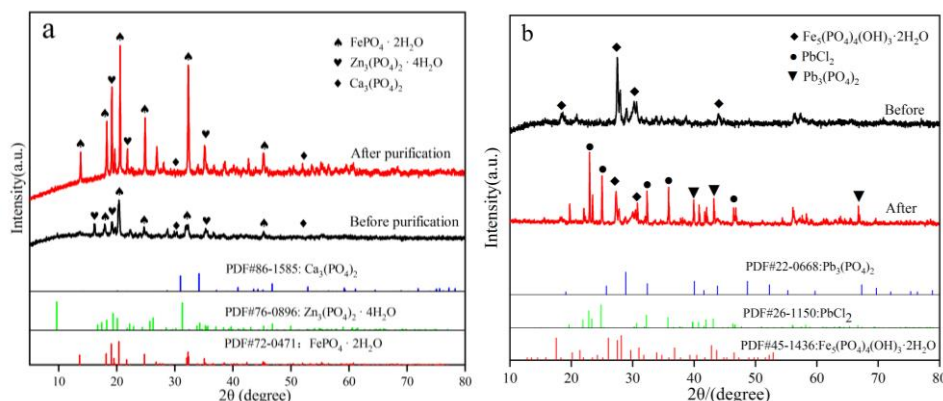


Figure 1. (a) the xrd diagram before and after phosphating slag purification and (b) the xrd diagram before and after PIHP adsorption of Pb^{2+}

The results of XRD analysis before and after purification of phosphating slag were shown in Fig a, the diffraction peaks of the three crystals which appeared in the phosphating slag before purification were matched with the PDF#72-0471, PDF#76-0896 and PDF#86-1585 standard cards respectively, indicating that the phosphating slag contained $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$. The XRD diffraction peak became sharper after the phosphating slag was hydrothermally purified, indicating that the content and crystallinity of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ was greatly improved after hydrothermal purification. As shown in Figure b, the main component of PIHP was iron hydroxy phosphate which was matched with the standard card of PDF#45-1436 before the adsorption of Pb^{2+} . PbCl_2 and $\text{Pb}_3(\text{PO}_4)_2$ appeared after the adsorption of Pb^{2+} which matched with the standard cards of PDF#26-1150 and PDF#22-0668. It was indicated that the absorption of PbCl_2 by PIHP had two effects of adsorption and ion exchange.

3.2. SEM characterization

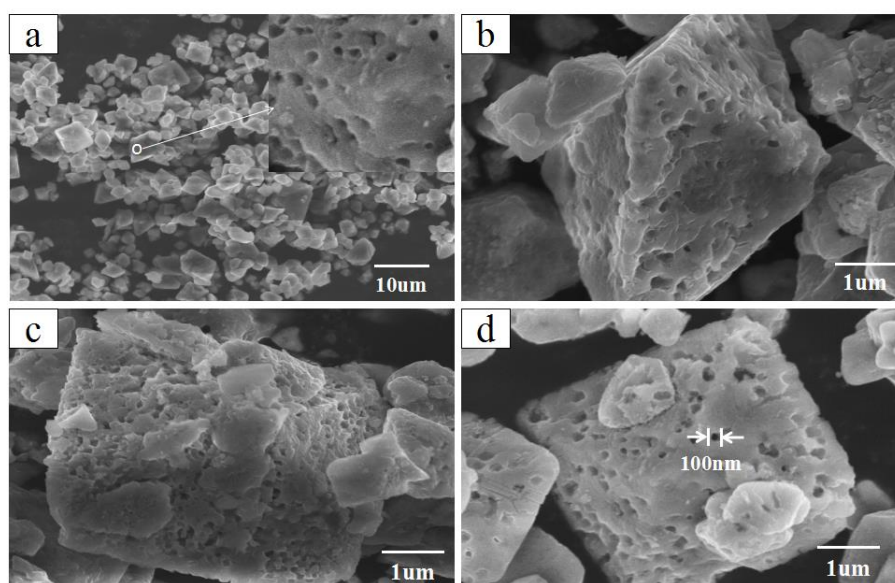


Figure 2. SEM image of porous iron hydroxy phosphate

Figure 2 was the SEM image of porous iron hydroxy phosphate. The iron hydroxy phosphate had a regular octahedral structure, but the surface structure changed to form a porous structure after high-temperature calcination, this was mainly because some iron ions and oxalates form iron oxalate complexes during the preparation of iron hydroxy phosphate, and the iron oxalate decomposed and released CO and CO₂ during the high temperature roasting process, and formed a porous structure on the surface of iron hydroxy phosphate [12], the pore size was about 100 nm.

3.3. FTIR and TG characterization

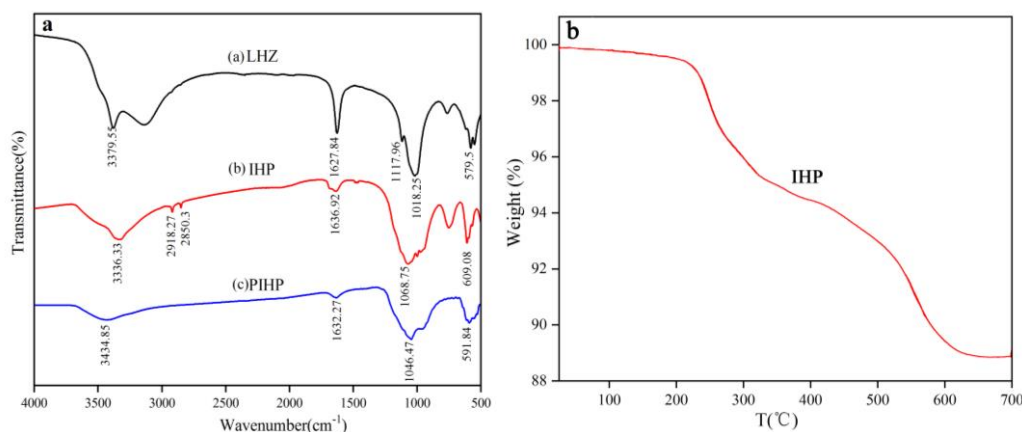


Figure 3. (a) the infrared image of phosphating slag, iron hydroxy phosphate, porous iron hydroxy phosphate and (b) the thermogravigram of iron hydroxy phosphate

Figure a was the infrared spectrum analysis diagram of iron phosphate, iron hydroxy phosphate and porous iron hydroxy phosphate. As shown in (a), the iron phosphate had vibration peaks at 33789.55, 1627.84, 1117.66, 1018.25, 579.5 cm⁻¹. 3375.55 and 1627.84 cm⁻¹ were corresponded to the stretching vibration and bending vibration of O-H in crystallization water, and 1117.96 and 579.5 cm⁻¹ were correspond to the anti-expansion vibration and asymmetric bending vibration of P-O bond, and 1018.25 cm⁻¹ were corresponded to the stretching vibration of Fe-O-P. As shown in (b), the iron hydroxy phosphate had vibrational peaks at 3336, 2918, 2850, 1636, 1068, 751, and 609 cm⁻¹, 3336 and 1636 cm⁻¹ were corresponded to the stretching vibration and bending vibration of O-H in the crystallization water, 2918 and 2850 cm⁻¹ were corresponded to the stretching vibration of -CH₃ and -CH₂, and 1068 cm⁻¹ and 609 cm⁻¹ were corresponded to the anti-expansion vibration and asymmetric bending vibration of P-O bond. The analysis results showed that iron hydroxy phosphate contained crystal water, hydrocarbon compound on the surface was presumed to be CTAB remaining on the surface in the process of preparing iron hydroxy phosphate. As shown in (c), the porous iron hydroxy phosphate showed weak vibration peaks at 3134 and 1632 cm⁻¹, which were corresponded to the stretching vibration and bending vibration of O-H in crystal water, and the 1046 and 591 cm⁻¹ were corresponded to the anti-expansion vibration and asymmetric bending vibration of the P-O bond. The result showed that the porous iron hydroxy phosphate contained a small amount of crystal water, and its main component was iron hydroxy phosphate.

Fig b was the TG analysis diagram of adsorbent PIHP precursor, the mass was reduced by 5.4% between 250°C and 400°C, in which the crystallization water was lost, and the mass was reduced by 5.8% between 400°C and 620°C, in which the iron oxalate decomposed to form Fe₂O₃, CO and CO₂.

3.4. Pb²⁺ adsorption experiment

3.4.1. Effect of adsorbent dose on adsorption effect

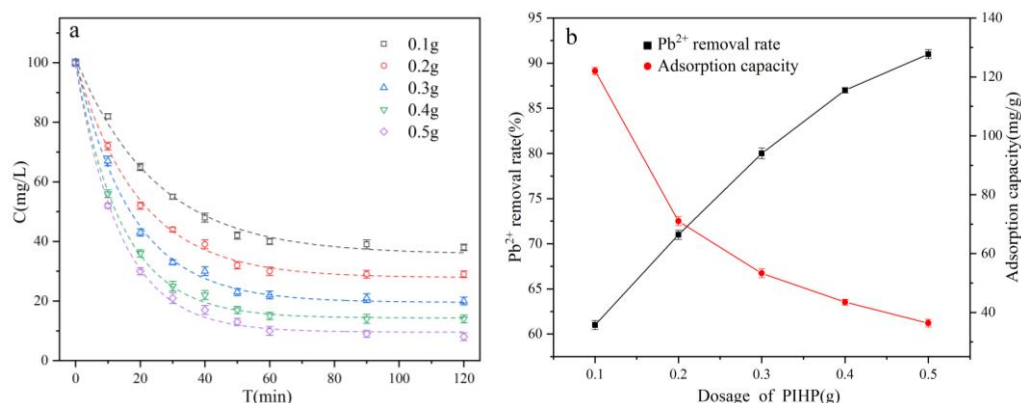


Figure 4. Effect of the amount of adsorbent added on the removal rate of Pb^{2+} and the amount of adsorbent adsorbed

The concentration of Pb^{2+} gradually decreased with the increase of adsorption time and reached the adsorption equilibrium at 60 min. The removal rate of Pb^{2+} after 120 min was 61% when the amount of PIHP added was 0.1 g, the removal rate of Pb^{2+} increased to 91% when the amount of PIHP added increased to 0.5 g. The removal rate of Pb^{2+} in the solution increased with the increase of PIHP addition, but the unit adsorption amount of the adsorbent decreased, which may be due to the increase of the active sites of adsorption as the adsorbent increased, the excess active sites could not exert its adsorption effect when the amount of the adsorbent was too much, resulting in a decrease in the unit adsorption capacity of the adsorbent [13].

3.4.2. Effect of PH on adsorption effect

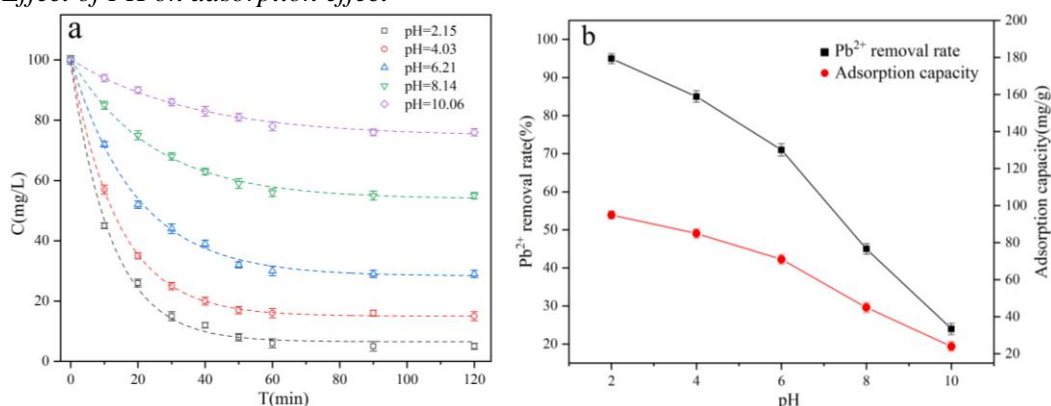


Figure 5. Effect of pH of the system on Pb^{2+} removal rate and adsorbent adsorption capacity

0.2 g PIHP was added to 200 mL of $PbCl_2$ solution and the pH value of the solution was changed by adding HCl or NaOH to study the effect of pH value on the adsorption of Pb^{2+} . As shown in Figure a, the effect of pH on the adsorption of Pb^{2+} was very obvious, and the adsorption amount increased with the decreased of pH value. The decrease of Pb^{2+} concentration in the system was mainly due to the three main functions of dissolution-precipitation, ion exchange and surface physical adsorption [14]. The adsorption of Pb^{2+} by PIHP depended on the concentration of phosphate dissolved, the phosphate dissolved by PIHP gradually decreased with the increased of pH, the ability to remove Pb^{2+} by dissolution-precipitation was weakened and some hydroxides also appeared, which changed the adsorption mechanism and inhibited the adsorption of Pb^{2+} by PIHP [15].

4. Conclusion

This study used industrial solid waste phosphating slag as raw material to prepare porous iron hydroxy phosphate for treating lead-containing wastewater, the porous iron hydroxy phosphate was prepared

by hydrothermal purification, ball milling modification, hydrothermal crystallization and calcination treatment, the particle size was about 3 μm and the pore size was about 100 nm. The adsorption results showed that the removal rate of Pb^{2+} increased gradually with the increased of PIHP, but the unit adsorption amount of PIHP decreased, the removal rate of Pb^{2+} could reach 91% when the addition amount of PIHP was 0.5 g. The adsorption capacity of PIHP for pb^{2+} increased with the decreased of pH value of the solution, the removal rate of pb^{2+} after 120 min could reach 95% when the amount of PIHP added was 0.2 g and the pH value of the system was 2.15. The results showed that the heavy metal ion adsorbent which prepared by the solid waste phosphating slag exhibited excellent performance in the treatment of Pb^{2+} -containing wastewater, and achieved the purpose of waste treatment.

Acknowledgements

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