

Synthesis of iron phosphate-SAPO-34 composite and its application as effective absorbent for wastewater treatment

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Abstract. High-purity FePO₄ was purified from iron-based phosphating slag as raw material, and FePO₄@SAPO-34 was synthesized by hydrothermal crystallization method under the action of templating agent-diethylamine. The synthesized FePO₄@SAPO-34 samples were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The effects of different crystallization time on the morphology and crystallization of FePO₄@SAPO-34 crystals were investigated. The removal of heavy metal ion wastewater by low-cost FePO₄@SAPO-34 was investigated. The experimental results show that when the reaction time is 180 °C and the reaction time is 72h, the crystallization of FePO₄@SAPO-34 is the best. When the dosage is 0.6g, the removal efficiency of heavy metal ions is the highest.

1 Introduction

Phosphating is a commonly used surface treatment technology. Phosphating slag is a precipitated substance that is produced on the surface of a metal phosphating process. Its main components are metal ions such as phosphate, iron and zinc [1]. In order to effectively control the pollution of phosphating slag, researchers have carried out a lot of research work and made some progress. In this study, the iron phosphate is purified by phosphating slag and has various crystal structures. It is provided with unique catalytic properties, ion exchange properties, etc. Research reports show that iron phosphate is negatively charged (zeta = -30 ~ -40mV) in wastewater, and its electronegative properties produce electrostatic adsorption on positively charged ions [2].

The molecular sieve has a uniform pore structure. According to the molecular size, it can selectively adsorb. Thus, it is mostly used for adsorbents and catalysts [3]. In 1982, SAPO-34 was first synthesized as a SAPOS series molecular sieve by Wilson et al [4]. It has CHA structure and medium strength acid center. SAPO-34 exhibits excellent performance in adsorption and catalysis [5]. Because SAPO-34 has a neutral framework structure, it is difficult to provide the active center required for many reactions [6]. Therefore, it is very important to modify the material. In summary, this study prepared a new catalytic adsorption material of FePO₄@SAPO-34. New materials were applied to remove heavy metal ions from wastewater.

2 Materials and methods

2.1 Materials

Phosphate residue was supplied by an auto components company in Zhejiang, China. Pb(NO₃)₂ (analytical reagent(AR), ≥99.9%), pseudo boehmite (Al₂O₃, ≥67.5%), phosphoric acid (AR, ≥85%) and diethylamine (AR, 99%) were obtained from Sinopharm Chemical Reagent Co. Ltd., of Shanghai, China. Silica solution (SiO₂, ≥30%) was purchased from Qingdao Haiyang Chemical Co.,Ltd[4]. Other chemicals used in the present work were of analytical grade and used without further purification. Deionized water was produced by an ultrapure water system (UPT-I-60L, Super Pure Technology Corporation, China).

2.2 Adsorbent preparation

A certain amount of phosphating slag, water and phosphoric acid were uniformly mixed in an appropriate ratio, and placed in an oven at 80 °C for 4 h, and the sample was suction filtered and dried overnight; after three times of reaction, a phosphating slag was obtained to purify the sample iron phosphate. The experiment used hydrothermal synthesis of FePO₄@SAPO-34. Firstly, the silicon source, the phosphorus source, the aluminum source, the FePO₄ and the appropriate amount of water are uniformly mixed according to a certain ratio, and then

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the templating agent diethylamine is added, and after pretreatment, it is transferred to a polytetrafluoroethylene reactor, and heated to 180 °C, and is self-generated[5]. Crystallize under pressure for different times, after suction filtration, washing and drying. Then, it was baked in a muffle furnace at 550 °C for 6 h to obtain a modified new material.

2.3 Heavy metal ion removal experiment

The experiment of removal of heavy metal ions in simulated wastewater was carried out with a material dosage of 0.6 g, lead-containing (Pb(NO₃)₂) wastewater concentration of 100 mg/L. Adesignated intervals, samples of the solution were collected and immediately filter to monitor the adsorption efficiency by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ICAP 6000, Thermo Corporation, USA). All adsorption experiments were stirred at 350 r/min. After adsorption experiment, the FePO₄@SAPO-34 adsorbent was collected with strong acid and then reused.

2.4 Characterization methods

The morphology of the samples was characterized by scanning electron microscopy (SEM) (S-4800, Hitachi Corporation, Japan) with the accelerating voltage at 10 kV and current at 10 mA. X-ray diffraction (XRD) (D8-Advance, Bruker Corporation, Germany) measurements were undertaken to record the phase composition and crystalline structure of the powder samples, operating at 40 kV and 40 mA with a monochromatized Cu K α radiation ($\lambda = 0.15418$ nm) source. The chemical bonds on the surface of the samples were examined by Fourier transform infrared spectroscopy (FTIR) (Vertex70, Bruker Corporation, Germany). KBr was chosen as a diluent. The surface area was measured based on the Brunauer Emmett Teller (BET) (ASAP-2020M, Micromeritics Corporation, USA) model over a relative pressure range of 0.05–1.

3 Results and discussion

3.1 XRD characterization

Figure 1 is an XRD pattern of a sample synthesized at different crystallization times. Crystallization plays a role in transforming metastable materials into stable crystals. So crystallization time is one of the most important factors that affect the synthesis of zeolite. Fig1. shows five peaks at 9.48°, 16.2°, 20.7°, 25° and 31°, corresponding to (101), (211), (104), (401) of SAPO-34

(JCPDS), respectively [6-7]. With the extension of time, the peak intensity gradually increased. When t=72 h, the peak intensity was the strongest, but when the time was extended to 84 h, the peak intensity weakened and the impurity peak began to appear. The crystallinity of SAPO-34 was set to 100%. The relative crystallinity of FePO₄@SAPO-34 is calculated as follows [7-8]:

$$X_i(\%) = X_s \frac{\sum I_i}{\sum I_s} \quad (1)$$

Where, X_i is relative crystallinity of the sample; X_s is equivalent to 100%; $\sum I_i$ is the sum of the five characteristic peak intensities of the sample; $\sum I_s$ is the sum of the five characteristic peak intensities of the standard sample.

From Fig. 3, the relative crystallinity of FePO₄@SAPO-34 increased from 40% to 98%, indicating that the crystallinity of the sample increased with the crystallization time. But when the time is too long, it could lead to the formation of other crystals. Too short or too long crystallization time was not conducive to the synthesis of FePO₄@SAPO-34. The crystallization time was the most favourable for the synthesized FePO₄@SAPO-34 at 72 h.

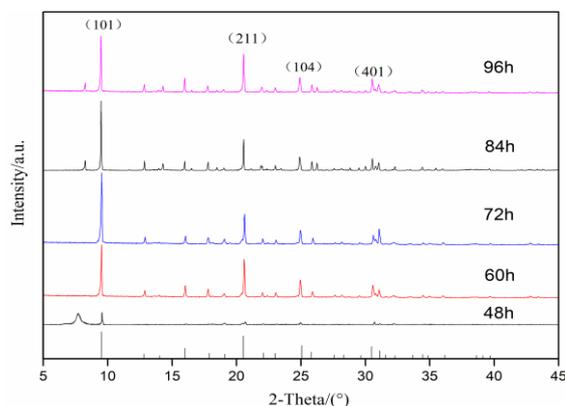


Figure 1. –X-ray diffraction (XRD) patterns of FePO₄@SAPO-34 at different crystallization times

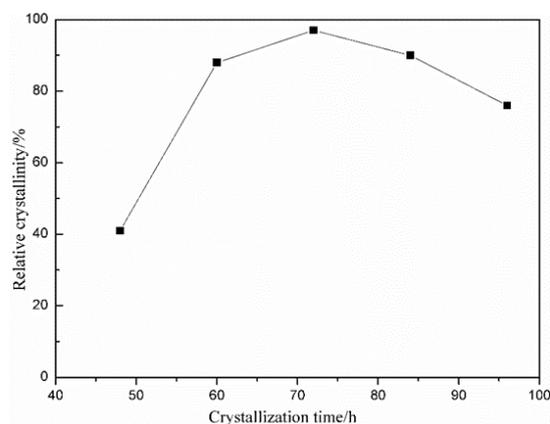


Figure 2.Crystallinity of FePO₄@SAPO-34 at different crystallization times

3.2 SEM characterization

The scanning electron microscopy (SEM) images showed, as the time increased from 48 h to 72 h, the shape of the material became more and more complete. At 180 °C, t=72 h, FePO₄@SAPO-34 had a typical cubic small square structure of chabazite-based molecular sieves, indicating that the crystal growth was perfect [9-10]. When the time was gradually increased to 84-96 h, the morphology of FePO₄@SAPO-34 particles was destroyed, and some amorphous substances appeared in the synthesized product.

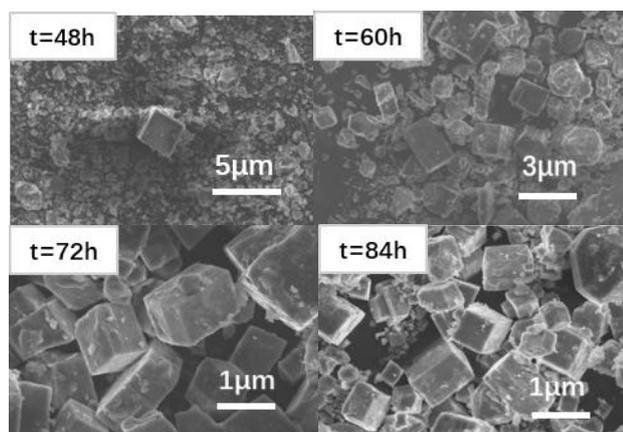


Figure 3. Scanning electron microscopy (SEM) images of FePO₄@SAPO-34 at different crystallization times

3.3 FT-IR and BET characterization

FT-IR analysis was further carried out to verify FePO₄@SAPO-34 in the reaction process. FT-IR spectrum was sensitive to the skeletal structure of the molecular sieve, and could better detect the molecular sieve crystallite structure. SAPO-34 has a periodic arrangement of PO²⁺, AlO₄ and SiO₄ tetrahedral framework structures. As shown in Fig 4, the spectrum of FePO₄@SAPO-34 was basically consistent with the spectrum of SAPO-34. Peak at 2320 cm⁻¹ could be ascribed to the bending vibration of CO₂, while those at 730cm⁻¹, 640cm⁻¹, 575cm⁻¹ and 530cm⁻¹ could be assigned to the stretching vibration of OPO (O-Al-O), the double six-membered ring vibration peak and PO₄. It may be due to moisture in the air during the test. When FePO₄ was doped, since the electron energy of iron was smaller than the electron energy of silicon, the bonding strength of the sample was enhanced, and the corresponding frequency was increased[11-13].

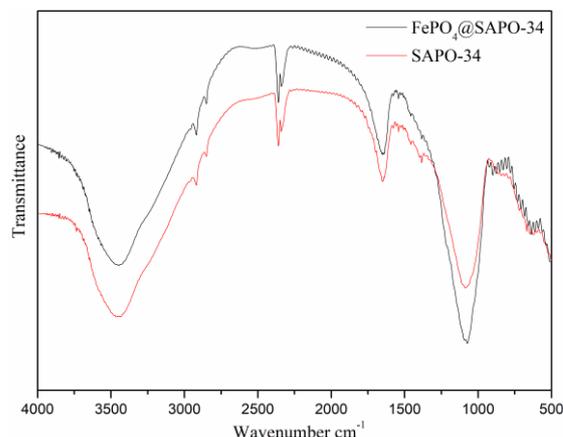


Figure 4. FT-IR image of FePO₄@SAPO-34 and SAPO-34 samples

From Table 1, the specific surface of SAPO-34 was 391.2 m².g⁻¹, and the specific surface of FePO₄@SAPO-34 was 362.8 m².g⁻¹. It had little difference and large specific surface area.

Table 1. BET of FePO₄@SAPO-34 and SAPO-34

| Sampal | FePO ₄ @SAPO-34 | SAPO-34 |
|---|----------------------------|---------|
| BET surface area/(m ² .g ⁻¹) | 362.8 | 391.2 |

3.4 Adsorption of pb²⁺ experiments

The removal effect of Pb²⁺ by SAPO-34 and FePO₄@SAPO-34 materials has been shown in Fig.5. It can be seen that SAPO-34 has better absorbing capacity than FePO₄@SAPO-34 in the first 45min, which was ascribed to the large specific surface area for pure SAPO-34 with a uniform pore structure[13-15]. However, the removal efficiency of two materials has been changed. The removal efficiency of FePO₄@SAPO-34 exceeded to that of SAPO-34 due to the electrostatic effect of FePO₄ in aqueous solution, further attracting cations which has been reported in other papers. Thus, the FePO₄@SAPO-34 showed excellent adsorption performance in pollution removal.

On this basis, this experiment studied the effect of FePO₄@SAPO-34 dosage on Pb²⁺ adsorption. As shown in Figure 6, as the amount of material increases, it can be seen that, the amount of Pb²⁺ adsorption increases. The increase was larger and then tended to be flat. The adsorption efficiency is calculated as follows:

$$\eta = \frac{C_0 - C_i}{C_0} \times 100\% \quad (2)$$

Where, C₀ is original concentration; C_i is concentration during dynamic adsorption equilibrium. η is adsorption efficiency. When the addition amount was 0.2 g, the adsorption rate was only 67.3%. When the amount added was increased to

0.6 g, the removal rate of Pb^{2+} was 89%. When the amount added was 1 g, the adsorption rate was 92%. As the number of exchanged active particles increases, the amount of adsorption of metal ions becomes large[14-16]. Therefore, the amount of adsorbent has a great influence on the adsorption effect.

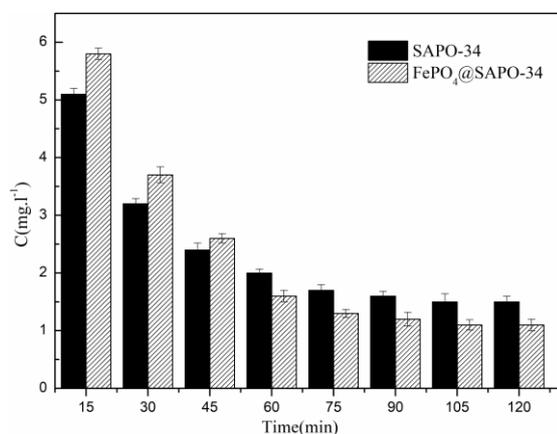


Figure 5. Pb^{2+} removal effect image of $FePO_4@SAPO-34$

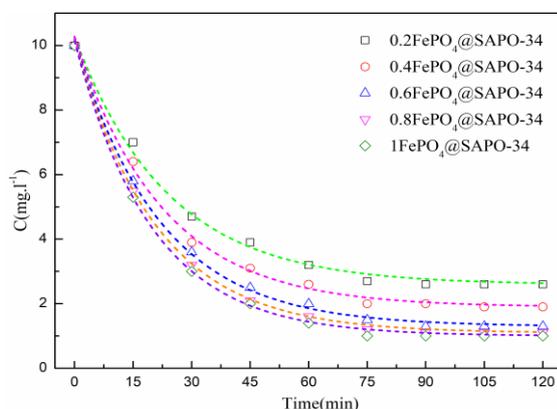


Figure 6. Adsorption effect diagram for different adsorbent dosages

Conclusions

In this study, an effective phosphate residue recovery method was proposed and be used to fabricate a $FePO_4@SAPO-34$ adsorbent. Experiments were conducted to investigate the effect of different crystallization times on the crystal form of the adsorbent. The results showed that the synthesized sample crystal form was more complete at 72 h. Experiments have found that new materials can effectively remove heavy metal ions from wastewater. Compared with SAPO-34, the new synthetic material passes through the electro-negative properties of $FePO_4$, so it electrostatically adsorbs positively charged ions. And $FePO_4$ provides a metal active center for SAPO-34. The synergy between SAPO-34 and $FePO_4@SAPO-34$ improves the adsorption performance of new materials.

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