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Removal of phosphate from aqueous solution by activated siderite ore: Preparation, performance and mechanism

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ABSTRACT

Activated siderite ore (ASO) was prepared by annealing siderite ore at different temperatures for different durations. The performance of ASO on the removal of phosphate from aqueous solution and the effects of particle size, contact time, pH, initial phosphate concentration, temperature, and coexisting anions on phosphate removal were investigated. X-ray diffractometer, thermogravimetric analyzer (TGA), transmission electron microscopy (TEM), surface area analyzer, Fourier transformed infrared spectra and other techniques were utilized to characterize ASO before and after adsorption. The results showed that a large amount of CO₂ was released meanwhile the siderite began to transform to hematite when the annealing temperature increased to 450 °C. The specific surface area of annealed product increased from 4.17 m²/g to 57.5 m²/g as the temperature came to 470 °C. Phosphate can be removed efficiently by ASO in a relatively wide pH range between 3.0 and 11.0. The effects of coexisting anions were not significant within the experimental concentration ranges except HCO₃⁻. The adsorption process of phosphate on ASO fitted pseudo-second order kinetics model. ASO showed a high-efficient adsorption capacity of 9.24 mg/g estimated from Langmuir isotherm at 30 °C. Results of TEM and FTIR analysis suggested that under the condition of pH = 6.5 and phosphate concentration (100 mg/L), two different monoprotonated phosphate complexes exist at ASO, with one surface complex coordinated in a monodentate binuclear (bridging) fashion, and the other as a monodentate mononuclear complex. A small amount of co-precipitation is most likely to be another mechanism for the removal of phosphate. These fundamental data indicate that siderite is a promising precursor for preparing porous material at least for adsorption of phosphate.

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1. Introduction

Along with the development of the economy, environmental pollution has become a global issue. Among all the pollution problems, eutrophication has been considered as one of the most serious environmental problems. From the previous research, eutrophication could result from the excess of nitrogen, phosphorus, and other nutrients in the water [1,2]. In recent years, the efficiency of various types of wastewater and sewage treatment has been improved significantly, and the urban sewage has achieved the emission standard (for example, 0.5 mg/L in China) after secondary treatment. However, due to the constraints of underdeveloped economic conditions and limited technical methods, the phosphorus concentration of effluent is still higher than II criterion (for example, 0.025 mg/L in China) of environmental quality for surface water. Moreover, secondary treatment for the effluent cannot work solely to curb eutrophication effectively. Therefore, regarding the

treatment of phosphorous-containing wastewater, low concentration, namely deep treatment, has overtaken high concentration [3–5]. Up to now, biological methods and physicochemical methods are widely regarded as the most effective methods for the removal of phosphate. Furthermore, the physicochemical methods mainly include chemical precipitation and adsorption method. It should be noted that in both methods the removal of phosphorus via biological method is not stable enough, because the process of removal is complex, and the results can be influenced by various factors, such as pH, temperature, and so on [6–13]. Chemical precipitation method requires a lot of flocculants, which will produce a lot of chemical sludge. In addition, this method costs more, meanwhile, it is likely to cause secondary pollution [14–18]. Consequently, adsorption method has become one of the most effective methods to remove phosphate from aqueous solution due to its low cost, relatively easy operation, and no secondary pollution [19–25].

Adsorption method is characterized by the use of certain porous or adsorbents of a large area on the surface of which phosphorus can be attached through ion exchange or surface precipitation [20–23]. The porosity and surface activity of natural sorbents can be modified so that the efficiency of the phosphorous removal

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could be improved. With the development of mineralogy, natural minerals have become a major resource of adsorbents due to their low cost, easy operation, and no secondary pollution [26–30].

As a traditional iron mineral resource, siderite (FeCO_3) was used for smelting iron and steel. As reported, siderite is rich in China with reserves up to 2 billion ton. However, only 10% of the total siderite reserves were used up to now [31]. Recently, Guo et al. [32–34] and Jönsson and Sherman [35] investigated how to use siderite to remove arsenic from groundwater, but the removal of other contaminants has not been reported yet. It can be observed that the oxidation rate of natural siderite in water is so slow that the product of hydroxides of iron is insufficient to adsorb pollutants [36]. On the other hand, siderite has a high thermal chemical activity. Therefore, siderite ore was activated by heat treatment to improve its surface activity for the adsorption of phosphate.

In this study, siderite ore was activated for batch experiments by heat treatment. The main objectives are to (1) characterize the activated siderite ore (ASO); (2) evaluate effects of particle size, contact time, pH, initial phosphate concentration, temperature, and coexisting anions on phosphate adsorption; and (3) investigate adsorption mechanism by means of microscopic technologies.

2. Materials and methods

2.1. Materials preparation

Siderite ore used in our experiments was obtained from Tongling city, Anhui province, China. The siderite ore was crushed and ground into the desired particle size (less than 0.098 mm) as samples for the annealing experiment. The samples were annealed at different temperatures (300 °C, 350 °C, 400 °C, 450 °C, 470 °C, 500 °C, 550 °C, 600 °C and 700 °C) for different times (1 min, 10 min, 20 min, 30 min and 60 min).

Annealing method: Firstly, a plain ceramic tile as a tray was placed in a muffle furnace followed by opening the muffle furnace after it reached the required temperature; Then, the samples (10 g) mentioned in the last paragraph were sprinkled on the panel quickly and evenly, then the plain ceramic tiles were placed in the muffle furnace rapidly and the temperature was kept at the required time; Finally, the ceramic plate was taken out by tongs, cooled to room temperature in air and then preserved samples in a drier.

2.2. Materials characterization

X-ray diffractometer (D/max-RB) was utilized to analyze the phase composition of each sample. The tube voltage was 40 kV and the current, 40 mA. The XRD diffraction patterns were taken in the range of $2\theta = 3^\circ\text{--}70^\circ$ at a scan speed of 2 min^{-1} . Phase identification was carried out by comparison with those included in the Inorganic Crystal Structure Database (ICSD).

A surface area and pore size analyzer (NOVA 3000e) was used for the measurement of specific surface area, pore volume, and average pore size. All samples were degassed over 24 h at 110 °C before analysis. S_{BET} (the specific surface area) of the sample was calculated by using the multiple point Brunauer–Emmett–Teller (BET) method, and V_{pore} (the total pore volume) was evaluated by the nitrogen uptake at a relative pressure of *ca.* 0.99.

Thermal analyzer (EXSTAR S II TG/DTA 7300) measurement was performed in air atmospheres under a stable gas flow at 100 mL/min with a heating rate of 10 °C/min from 30 °C to 900 °C.

Field emission transmission electron microscope (JEOL-2100F) was used to observe and analyze the morphology of all samples. Each sample was mixed with alcohol and deposited on a Cu grid. Images of the microstructure were acquired using an analytical electron microscope.

Fourier transformed infrared spectra (VERTEX-70) was used to analyze the species of the surface complexes on the ASO before and after adsorption. The KBr/sample discs were prepared by mixing 1.0 wt% of finely ground samples in KBr. The measurement resolution was set at 4/cm and the spectra were collected in the range of 400–4000/cm.

2.3. Phosphate removal

All reagents used were of analytical grade. Phosphate-enriched sewage was prepared by addition of 0.4394 g KH_2PO_4 to 0.8 L deionized water. Then, 0.1 mol/L NaOH was used to regulate the pH up to a neutral condition; then, some deionized water was added up to 1 L. Finally, the desired phosphate concentration (100 mg P/L) was achieved with a pH of 6.8. All of the adsorption experiments were carried out by a batch method at ambient temperature (23 ± 2 °C). Phosphate concentration in the solutions was measured by the molybdenum blue method with a spectrophotometer at 700 nm (UV-2550, Shimadzu, Japan).

Batch experiments were carried out at a fixed dose of 2 g/L, with 0.1 g adsorbent in 50 mL solution in 150 mL conical flask. These bottles were placed in a shaking water bath with a temperature controller, at a shaking rate of 160 r/min. After the reaction, the phosphate concentrations in the supernatant solution obtained by centrifugation were measured by the ammonium molybdate spectrophotometric method.

Adsorption kinetics studies were conducted with contact time from 10 min to 24 h. Batch experiments were carried out with an initial phosphate concentration of 5 mg/L at 20 °C. Effect of particle size was studied using phosphate solutions containing 0.05–0.1, 0.1–0.4, 0.4–0.85, 0.85–3.35 mm of ASO, respectively. Effect of solution pH on phosphate adsorption was investigated with initial pH between 3.0 and 11.0, which were adjusted by using 0.1 mol/L HCl and 0.1 mol/L NaOH. In addition, the effect of co-existing anions (including Cl^- , HCO_3^- , NO_3^- , NO_2^- and SO_4^{2-}) was investigated. Adsorption isotherm studies were performed by varying initial phosphate concentrations (5, 10, 20, 50, 100 mg/L) at different temperatures (*i.e.*, 10, 15, 20, and 30 °C). It is remarkable that all batch experiments were conducted in duplicate and reported as a mean value.

3. Results and discussion

3.1. Characterization of adsorbent

The mineralogical component analysis was carried out with XRF and chemical phase analysis at the early stage, the results indicated that the pristine siderite ore sample is composed of 66.3 wt% siderite, 22.4 wt% clay minerals and quartz, and 11.3 wt% goethite [36]. Siderite has a hardness of 3.75–4.25, as measured on the Mohs scale, and a specific gravity of 3.9.

3.1.1. XRD analysis

The XRD patterns of siderite ore and its annealed products under different temperatures (400 °C, 450 °C, 470 °C, 500 °C, 550 °C, 600 °C and 700 °C) for 10 min (the data of other annealed time are not listed here) are shown in Fig. 1. These peaks are observed in the XRD pattern of siderite ore and identified as siderite when compared with the standard pattern (ICDD (29-0696)). The reflection intensities of siderite decreased with increasing temperature, indicating that the increased temperature favored the decomposition of siderite. The characteristic reflections of siderite disappeared as the temperature reaching 500 °C and the peaks were replaced by several new reflections. The new reflections with low intensity appear after heating at 450 °C and can be identified as hematite after compared with the standard pattern (ICDD

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