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Application of magnetic nano-particles for phosphorus removal/recovery in aqueous solution

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ABSTRACT

To remove or recover phosphorus (P) efficiently from various aqueous solutions is important as P is an essential nutrient and a key element to cause eutrophication. This study examines the feasibility of P removal/recovery using Fe_3O_4 nano-particles, generated from ferrite process. A rapid increased of P adsorption (0.17 to 2.38 mg/g) was detected when the solution pH decreased from 11.09 to 2.77. A maxima adsorption capacity was estimated to be 3.65 mg/g P at 318 K and pH 2.77, much higher than other iron-based adsorbents. Additionally, P adsorption increases with the increase of ionic strength from 0.001 to 1.0 N, indicating that the inner-sphere mechanism was importantly involved in the P adsorption. This P adsorption is spontaneous and endothermic, supported by the negative changed standard free energy with temperatures ($\Delta G^o = -4.33, -4.56, -4.80, -5.02$ kJ/mol at 288, 298, 308, and 318 K, respectively) and the positive ΔH^o values (0.28 kJ/mol). The positive ΔS^o (2.79 J/mol K) further indicates that the randomness increased at solid-solution interface during P adsorption. These results reveal potential applications of Fe_3O_4 nano-particles for P removal/recovery in wastewaters or freshwaters.

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1. Introduction

Phosphate is an essential nutrient for the growth of photosynthetic cyanobacteria and algae [1]. Excess of phosphorus (P) in aquatic systems may cause serious eutrophication, overgrowth of algae or aquatic plants to cause dissolved oxygen depletion [2,3]. On the other hand, P is a limiting element for organisms growth in ecosystems [2,4,5] in the form of phosphate, plays an important role in RNA/DNA or cellular metabolism [6]. Nevertheless, most P sources (rock-phosphate) are not renewable resources in nature and could be consumed because of the increasing demands by different agricultural or industrial usages [7,8].

It is evident that various P sources enter water bodies (rivers or lakes) from household, agricultural, or industrial wastes [1,9–12]. In wastewater, P is in the forms of phosphate ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}), organic phosphate and polyphosphate [4]. The dissolved phosphate is easily absorbed by algae while the polyphosphates and organic phosphate could be hydrolyzed into the phosphate forms [13,14]. Therefore, to remove/recover P from wastewaters not only can prevent the loss of this scarce resource but also to protect natural waters from pollution.

Typical technologies, such as adsorption, precipitation, and activated-sludge process, are employed for removing high concentration (hundred to thousand mg/L) of phosphate in wastewaters. However, in the case of low concentration (several mg/L) phosphates, precipitation or activated-sludge method is not much effective [1]. In addition, the developed adsorbents have been investigated widely due to their high efficiency and low cost even if the chemical precipitation is suitable for the higher concentrations in industrial wastewaters [2,3,5].

Magnetic nano-particles (Fe_3O_4), synthesized from ferrite process, have a cubic close-packed arrangement of the oxygen ions with Fe^{2+} and Fe^{3+} at two different crystallographic sites. It should be noticed that ferrite process is used to treat heavy metals bearing wastewater [15–19]. The product generated from ferrite process could be described by the following equation [16,20]:

$$3Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow Fe_3O_4 + 3H_2O \tag{1}$$

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Our precious study reported that Fe_3O_4 has the potential to remove toxic elements such as arsenic from water [21]. With the advantage of its magnetism, the synthesized Fe_3O_4 could be recovered by an external magnetic field. Compared to the conventional separation method such as filtration or centrifugal technique, magnetic separation could be regarded as a more rapid and effective technology. However, it is still rare to find the investigation of removal/recovery of P by using Fe_3O_4.

This work aims to understand the P adsorption behaviors using the magnetic nano-particles synthesized from ferrite process. The adsorbent properties and the adsorption mechanisms were evaluated in detail. In addition, issues related to P adsorption kinetics and thermodynamics were also investigated. The information obtained shows great potential for designing a new and effective adsorbent for removing/recovering P using the magnetic nano-particles.

2. Materials and methods

2.1. Preparation of the magnetic nano-particles

The magnetic nano-particles were produced following the same procedures as our previous study [21]. Briefly, 27.8 g reagent grade $FeSO_4 \cdot 7H_2O$ was dissolved into 1000 mL water and the solution pH was subsequently adjusted to 8.0 by adding 0.1 N NaOH or 0.1 N HNO_3. Under continuous air purging (flow rate = 3 L/min), this process was proceeded at 353 K for 60 min while the solution pH was maintained constant at 8.0. The corresponding reaction is described as Eq. (1).

Table S1 displays the physical/chemical properties of the adsorbent. Briefly, the XRD pattern indicates the main diffraction peaks of the adsorbent are at d-spacing of 2.966, 2.530, 2.422, 2.098, 1.713, 1.615, 1.483, and 1.280 Å, matched well with the Fe_3O_4 crystals (JCPDS file number 03-065-3107). No other crystalline phases were detected in the XRD pattern. The primary particle size and the point of zero charge (PZC) of the synthesized adsorbent were found to be around 30–90 nm, and 7.1, respectively. Furthermore, the magnetic nano-particles not only show their high BET surface area (40.3 m^2/g), also have high saturation magnetization, 82.5 emu/g.

In addition, the synthesized particles can be collected using a magnetic separation method by taking advantage of its inherited magnetism. The ferrite product was then washed with Milli-*Q* water for several times until the solution pH reached 7. The solids were dried at 323 K for 24 h in an oven and then stored for further tests.

2.2. Batch adsorption experiments

The batch experiments were carried out in order to evaluate the adsorption processes and the equilibrium states of P mobilization. The P solution was prepared by dilution of the stock standard solution (1000 mg/L). All batch adsorption experiments were performed according to the following procedures: 10 mL P solution and a fixed amount of magnetic nano-particles were poured into a 15 mL centrifuge tube. The centrifuge tubes were then put on a shaft of a rotary shaker after the caps were tightened.

2.2.1. Effect of pH and ionic strength

To evaluate the influence of the solution pH and the ionic strength on the P adsorption, various experiments were performed by adding 0.05 g of the adsorbent into a 15 mL centrifuge tube, containing 10 mL 20 mg/L P solution at 298 ± 1 K. The pH of the solutions was adjusted using 0.1 N HNO_3 or NaOH solution to the designated values (2.77 ± 0.01, 3.92 ± 0.01, 4.91 ± 0.01, 6.58 ± 0.01, 8.32 ± 0.01, and 11.09 ± 0.01) and the ionic strength of the solutions was designed at 0.001, 0.01, 0.05, 0.1, 0.5, and 1.0 N by adding 1.0 N NaCl solution.

2.2.2. Adsorption equilibrium and kinetics

All equilibrium adsorption experiments were individually conducted by shaking 0.05 g of the magnetic nano-particles with 20 mg/L P solution using a thermostated shaker at a speed of 30 rpm for 2 h. Adsorption kinetics for P were measured by taking 20 mg/L P solution with 0.05 g of the magnetic nano-particles and shaking the mixture at pH 2.77 (temperature was controlled at 288 ± 1 to 318 ± 1 K). The P uptake rate of q_t (mg/g) was determined by the following equation:

$$q_t = \frac{(C_o - C_t) \times V}{m} \tag{2}$$

where C_o and C_t are the metal concentration in liquid phase at the initial and at time t (mg/L), respectively; m is the adsorbent amount (g); V is the volume used in the adsorption process (L).

The solid and liquid phases were magnetically separated using a 4000 Gauss magnet. The P concentrations in the filtrate were determined by ICP-OES (iCAP 6500, Germany). The amount of P adsorbed on the synthesized nano-particles was determined using the differences between the initial and the equilibrium concentrations in solutions. Prior to analysis, the supernatant was acidified with concentrated HNO_3 and stored in acid-washed bottles. Finally, the exhausted adsorbents were taken out for further desorption investigation.

2.3. Desorption experiments

The regeneration of adsorbents is an important aspect in any adsorption research. Thus, the adsorption–desorption processes were repeated three times for evaluating the reusability of the synthesized nano-particles. Desorption experiments were carried out using NH_4OH and NaOH solutions of 0.001, 0.01, 0.02, 0.05, and 0.1 N. 0.05 g nano-particles adsorbed P were put together with 10 mL NH_4OH or NaOH solution and then shaken for 30 min at room temperature. The adsorption performance in each cycle was measured and the desorption efficiency was calculated by the following equation:

$$\text{desorption efficiency} = \frac{C \times V}{X} \times 100\% \tag{3}$$

where C (mg/L) is the concentration of P in the desorption solution, V (L) is the volume of the desorption solution, and X (g) is the amount of P adsorbed.

3. Results and discussion

3.1. Effect of pH and ionic strength

It is well known that pH and ionic strength act as an important factor during adsorption process [22]. The amount of P adsorbed onto magnetic nano-particles at various pH values is illustrated in Fig. 1. A fast decreased P adsorption capacity, from 2.38 to 0.17 mg/g, was found when the solution pH increased from 2.77 to 11.09 at 298 K. This phenomenon is consistent with the results reported in Lin et al. [9] and Sarkar et al. [23]. On the other hand, the speciation in solution and the surface charge of the synthesized nano-particles play important roles in the P adsorption. It should be noted that the dissociation constants pKa_1, pKa_2, and pKa_3 of H_3PO_4 is 2.15, 7.20 and 12.33, respectively [24]. At higher pH values, there is always competition between hydroxylic ions (OH^-) and phosphate anions ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) for the adsorption

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