Phosphate dsorption from aqueous solution by mesoporous adsorbent Fe-SBA-15

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Abstract. The excessive amount of phosphorus (P) in water could lead to environment pollution such as eutrophication. Thus, an effective and economical way of removing phosphorus must to be developed. In this study, Fe-SBA-15 was synthesized to investigate the adsorption capacity of phosphorus. The structure and morphology of Fe-SBA-15 were tested by scanning electronic microscopy and transmission electron microscope. According to the experiments, the 30%Fe-SBA-15 exhibited the best phosphorus removal efficiency among different percentages of Fe. The influence of time, adsorbent dose, initial phosphorus concentration, pH and comparative ion were tested in this study. The adsorption rate of phosphorus increases with the increase of adsorption dose. The influence of comparative ion followed the order SO4^2-> NO3->Cl-. The optimistic pH for adsorption was 3.2. The adsorption of phosphorus onto Fe-SBA-15 reached equilibrium in about 80 minutes. The results demonstrated that Fe-SBA-15 is a potential candidate for removing phosphorus from contaminated water.

1. Introduction
As an important nutrient, phosphorus (P) can influence the growth of the plant [1]. When there is a high level amount of phosphorus in lakes or rivers, carried by domestic or industrial sewage, it can promote rapid reproduction of algae. The overgrowth of algae caused by phosphorus leads to the eutrophication in waters [2]. Thus, the excessive phosphorus is a key element for environmental pollution. According to an investigation of 25 lakes in China, the total concentration of phosphorus exceeded 0.02 mg/L in 23 lakes and were 0.2-0.97 mg/L in about half of them, which was much higher than the phosphorus concentration of 0.02 mg/L that could result in eutrophication [3]. Another investigation found that the total concentration of phosphorus in the Pearl River was up to 0.126-0.286mg/L, which led to red tides in the Pearl River more than 10 times a year [4]. According to these surveys, the pollution of phosphorus in rivers and lakes in China are getting worse. Hence, an effective removal and capturing method need to be develop.

In the past decades, various physiochemical and biological methods have been developed for phosphorus removal for aqueous systems, including ion exchange method, chemical precipitation, electrolysis, membrane separation, adsorption and biological method, etc. [5-8]. Among these techniques, adsorption has attracted universal attention due to its significant merits. Activated carbon fiber [9], mesoporous materials [10], zeolite [11], metal ion modified carbons [12-13] were tested as adsorbents for practical wastewater treatment. Typically, metal ion modified adsorbents attracted more attention because of the advantages of low cost and environmental friendliness. SBA-15, a kind of mesoporous molecular sieve, possesses large surface area, large aperture and high thermal stability. It can be used...
as adsorbent itself and exhibit excellent ability\textsuperscript{[14]}. Moreover, through modifying by metal ion, the adsorbing ability of this material could be dramatically enhanced\textsuperscript{[15]}.

In this study, Fe-SBA-15 was prepared by using Fe(NO\textsubscript{3})\textsubscript{3} as Fe source and SBA-15 as carrier. Fe adequately modified on the surface of SBA-15. The modification of Fe could exhibit active sites to bind crystal with phosphorus and they hold high removal efficiency for phosphorus. A serious of adsorption experiments were conducted to acquire the adsorbing capacity of Fe-SBA-15. SEM and TEM were used to acquire the characterization and the size of Fe-SBA-15. This study revealed the relationship of adsorbing capacity and modified materials, which provided more technical data for phosphorus removal from waters.

2. Materials and methods

2.1. Materials
Analytical grade reagents KH\textsubscript{2}PO\textsubscript{4}, Fe(NO\textsubscript{3})\textsubscript{3}, NaNO\textsubscript{3}, HCl, NaCl, Na\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4}, NaOH, anhydrous ethanol and ascorbic acid were purchased from Tianjin 4th chemical reagent factory. The stock phosphorus solution with phosphorus concentration of 2000 mg/L was prepared by dissolving KH\textsubscript{2}PO\textsubscript{4} into deionized water.

2.2. Adsorbent synthesis
First, 6.4929 g Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O was dissolved in 100 ml anhydrous ethanol in a 500 ml flask, and 3 g SBA-15 was added in the above solution. Then the flask was put in an ultra-phoncic machine over 30 minutes. After that, the mixture was dried at 30°C in thermostat water bath for 12 hours to remove water. Finally, the dried mixture was transferred in a crucible and was calcinated in a muffle furnace and heated at a rate of 10 K/min to 473 K lasting for 1 hour. Fe-SBA-15 was obtained by cooling the samples to the room temperature.

2.3. Adsorption experiments
Through experiments we investigated the influence of different percentages of Fe, the amount of adsorbent, the initial concentration of phosphorus, pH and competitive ions on absorbing phosphorus.

All the adsorption experiments were prepared in this way: a certain amount of adsorbent was added into the conical flasks containing 50 ml different initial phosphorus concentration. Then the flasks were placed in the shaker equipped with a thermostat at 140 r/min and at 298 K for a certain time. The initial and residual concentrations were determined by ultraviolet spectrophotometer.

2.4. Analytical method
The Fe-SBA-15 sample was characterized by SEM (Hitachi S-3400N II) and TEM (JEOL JEM-200CCX) for investigating the modified surface. After the adsorption experiments, all the solution was measured at 700 nm by an ultraviolet spectrophotometer. The removal rate $R$ (%) of phosphorus and equilibrium adsorption capacity $Q_e$ (mg/g) were calculated as follow:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where, $C_0$ (mg/L) is the initial phosphorus concentration, $C_e$ (mg/L) is the phosphorus concentration at equilibrium, $V$ (L) is the volume of the solution, $m$ (g) is the adsorbent mass.

3 Results and discussion

3.1 Material Characterization
The TEM and SEM images of 30%Fe-SBA-15 were shown in Figures 1 and 2 respectively. In Figure 1, the particles with holes are SBA-15 and some flaky crystals were adhered to the surface of SBA-15. It presented that the length of the crystals was about 6 μm. Fe has been loaded onto the surface of mesoporous molecular sieve SBA-15 successfully and the loaded particles were between 50 nm to 200 nm. In figure 2(a), it could be seen that there were plenty of particles distributed on the surface of the material irregularly. Each irregular particle was about 300 nm long which might be the main reason for the excellent adsorption capacity with 30%Fe-SBA-15. In figure 2(b), the short rod-like particles with narrow particle size were mushy and the morphologies are uniform. Those images showed that the load of Fe did not change the porous structure of the raw material.

Figure 1. The TEM of 30%Fe-SBA-15.  
Figure 2. The SEM of 30%Fe-SBA-15.

3.2 Effect of iron loading on material properties
Five kinds of Fe-SBA-15 were prepared with Fe percentage of 5%, 10%, 15%, 20% and 30%. In this experiment the initial concentration of phosphorus was 10 mg/L and the adsorbent dose was 0.025 g/L. Different percentages of Fe showed different adsorption capacities for phosphorus. The result was shown in Figure 3.

Figure 3. Effect of Fe percentage on material properties. (Adsorbent dose 0.025 g/L, initial phosphorus concentration 10 mg/L at 298 K)

The result indicated that the removal efficiency increased with increasing percentage of Fe in material. The maximum adsorption efficiency was nearly 45%, which was obtained at the Fe percentage of 30%. Thus, the 30%Fe-SBA-15 was chosen for further adsorption experiments.

3.3 Performance experiment
3.3.1 Adsorption kinetics. To investigate the influence of time on adsorption, kinetics experiment was carried out at room temperature. The result was shown in Figure 4. From Figure 4, it could be seen...
that phosphorus was initially adsorbed on 30%Fe-SBA-15 at a faster rate in the first 50 min, then the adsorption rate began to slow down and adsorption of phosphorus on 30%Fe-SBA-15 reached the equilibrium within 80 min. The rapid adsorption showed that the material has an excellent adsorption capacity for phosphorus. The saturated adsorption efficiency of the hybrid adsorbent was 42%.

In addition, the adsorption kinetics models pseudo-first-order and pseudo-second-order were used to describe the adsorption property of phosphorus on 30%Fe-SBA-15. The kinetics models are listed as follows:

the pseudo-first-order model:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

(3)

the pseudo-second-order model:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

(4)

where, \( q_e \) (mg/g) and \( q_t \) (mg/g) present the adsorption capacities in equilibrium and time \( t \) (min) respectively, and \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (mg/min) are the adsorption kinetics parameters and the values calculated in the experiment were shown in Table 1. From the table, it could be concluded that the adsorption of phosphorus onto 30%Fe-SBA-15 were well described by the pseudo-second-order model as compared to the pseudo-first-order model.

Table 1. Kinetics parameters for phosphorus adsorption onto 30%Fe-SBA-15 at 298K.

|               | the pseudo-first-order model | the pseudo-second-order model |
|---------------|-----------------------------|------------------------------|
| \( q_e \) (mg/g) | \( k_1 \) (min\(^{-1}\))  | \( R^2 \) | \( q_e \) (mg/g) | \( k_2 \) (mg/min)  | \( R^2 \) |
| 40.51         | 0.6651                      | 0.9552                       | 41.65         | 0.0295                      | 0.9850             |

3.3.2 Effect of adsorbent dosage. The influence of adsorbent dosage on adsorption was investigated. The initial phosphorus concentration was 10 mg/L. The dosage of SBA-15 and 30%Fe-SBA-15 were ranged from 0 to 0.08 g. The experiment result was shown in Figure 5. It could be seen that as the dosage of 30%Fe-SBA-15 increased, the removal efficiency increased rapidly. The maximum removal efficiency was up to 100% at the 0.08 g. However, when the amount of SBA-15 further increased, the removal efficiency kept at a lower rate which indicated the SBA-15 could not adsorb more phosphorus from solution, which indicated that the load of Fe obviously improved the adsorption performance of SBA-15.

![Figure 5. Effect of adsorbent dosage. (Initial phosphorus concentration 10 mg/L at 298 K)](image.png)

![Figure 6. Effect of initial concentration of phosphorus. (Adsorbent dose 0.05 g/L at 298 K)](image.png)
3.3.3 Effect of initial phosphate concentration. The influence of initial concentration of phosphorus on adsorbing capacity was shown in Figure 6. The adsorbent dosage was 0.05 g/L. As depicted in Figure 6, the adsorbing capacity increased rapidly as the initial phosphorus concentration increased from 10 to 80 mg/L, the saturated adsorption capacity of 30%Fe-SBA-15 was 26 mg/g, which was obtained at the initial phosphorus concentration of 80 mg/L. When the phosphorus concentration increased to 100 mg/L, the adsorbed amount of phosphorus on 30%Fe-SBA-15 did not improve furthermore, which showed the adsorption saturation of phosphorus.

3.3.4 Effect of solution pH. The influence of solution pH on adsorption was examined and the result was presented in Figure 7. The initial phosphorus concentration was 10 mg/L and the adsorbent dosage was 0.05 g/L. The uptake capacity of phosphorus increased as the solution pH in equilibrium increased from 1.4 to 3.2, and the optimum solution pH was about 3.2 with the removal efficiency of phosphorus up to 77.3%. When the pH increased beyond 3.2, the uptake capacity decreased rapidly. According to the experimental data, the pH-dependent trend might be relevant with the ion exchange between phosphorus and 30%Fe-SBA-15. As pH increased, the OH⁻ in the solution probably competed with the phosphorus on the surface of 30%Fe-SBA-15 for adsorption sites.

3.3.5 Effect of competitive ions. Taking the fact that a relatively high level of competing ions in waste water into account, Cl⁻, SO₄²⁻ and NO₃⁻ were added in the system to investigate the selective adsorption of phosphorus into 30%Fe-SBA-15. Figure 8 indicated the increasing concentration of competing ions inevitable resulted in the decreasing of phosphorus removal efficiency. Compared with Cl⁻ and NO₃⁻, SO₄²⁻ had a relative lower competitive effect. 30%Fe-SBA-15 displayed higher selective preference over SO₄²⁻ than the other ions. However, as the concentration of competing ions increased to 500 mg/L, 30%Fe-SBA-15 did not show an excellent selectivity. The lower adsorption selectivity of the anions further confirmed the contention that there was a competition as discussed in 3.3.4 and the ion selectivity should be improved in further works.

4. Conclusions
In this work, the 30%Fe-SBA-15 was prepared and its excellent adsorption performance towards phosphorus was reported. The morphology of 30%Fe-SBA-15 was investigated by SEM and TEM which indicated Fe has been loaded on SBA-15 successfully. The rapid adsorption of the material reached equilibriums within 80 min. Various solution pH were investigated and the maximal points of removal efficiency was 77.3% at equilibrium pH 3.2. Additionally, for high phosphorus concentration, 30%Fe-SBA-15 exhibited an excellent adsorption capacity. The promising results in adsorption experiments indicated that the 30%Fe-SBA-15 had a great application potential in phosphorus removal from waters.
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References
[1] Cordell D, Drangert J and White S 2009 *J. Global Environ. Change* 19 292-305
[2] Cooper J, Lombardi R, Boardman D and Carliell-Marquet C 2011 *J. Resour. Conserv. Recycl.* 57 78-86
[3] Zhang G, Xue J, Ni Z W and Li J C 2018 *J. soil. sediment.* 18 887-96
[4] Jiang S, Lu H L, Liu J C, Lin Y S, Dai M Y and Yan C L 2018 Influence of seasonal variation and anthropogenic activity on P cycling and retention in mangrove sediments: A case study in China. *Preprint* gr-qc
[5] Barbosa S G, Peixoto L, Meulman B, Alves M M and Pereira M A 2016 *J. Chem. Eng. J.* 298 146-53
[6] Carvalho W S, Martins D F, Gomes F R, Leite I R and Gustavo da Silva 2011 *J. Biomass Bioenergy* 35 3913-9
[7] Koilraj P and Sasaki K 2017 *J. Chem. Eng. J.* 317 1059-68
[8] Nancharaiah Y V, Venkata Mohan S and Lens P N 2016 *J. Bioresour. Technol.* 215 173-85
[9] Liu J Y, Qi Z, Chen J H, Zhang L and Chang N 2013 *J. Chem. Eng. J.* 215-216 859-67
[10] Liu H L, Sun X F, Yin C Q and Hu C 2008 *J. J. Hazard. Mate.* 151 616-22
[11] Zhang Y, Kou X and Lu H 2014 *J. Desalin. Water. Treat* 52 4298-304
[12] Cui X, Dai X, Li T and Yang X 2016 *J. Bioresour. Technol.* 218 1123-32
[13] Ren Z, Shao L and Zhang G 2012 *J. Water Air Soil Pollut.* 223 4221-31
[14] Boukoussa B, Hakiki A, Moulai S, Chikh K and Kherroub, D E 2018 *J. Mater. Sci.* 53 7372-86
[15] Fristak V, Pipiska M, Duriska L and Soja, G 2017 *J. Environ. Sci. Pollut. Res.* 24 463-75