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Fabrication of Fe-coordinated diamino-functionalized SBA-15 with hierarchical porosity for phosphate removal

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Abstract: Hierarchically macroporous–mesoporous SBA-15 phosphate adsorbent was synthesized via a dual-templating approach, followed by diamino-functionalization and Fe(III) impregnation. The resulting Fe(III)-coordinated diamino-functionalized macroporous-mesoporous adsorbent possessed well-defined and interconnecting macroporous and mesoporous networks. Its maximum adsorption was 12.7 mg/g, which was 86.8% greater than that of Fe(III)-coordinated amino-functionalized mesoporous SBA-15. In the kinetic study of macroporous-mesoporous adsorbent, 92.5% of the final adsorption capacity reached in the first 1 min; and the adsorption followed the pseudo-second-order equation well, suggesting the presence of chemisorption. The pH ranging from 3.0 to 6.0 favored the high phosphate adsorption of hierarchically porous adsorbent; however, the coexistence of other anions, especially F\textsuperscript{-}, retarded the adsorption.

Keywords: Porous materials; Phosphate; Adsorption; diamino-functionalization; Fe(III) impregnation
1. Introduction

To date, the increasing discharge of nutrients, especially phosphate, into aquatic environment contributes to eutrophication, leading to a serious world-wide environmental problem – algal bloom. Therefore, there is a need to reduce the phosphate levels in wastewater before its release to the environment. Several methods have been utilized, in which the adsorption-based process is considered as one of the most efficient routes [1].

Ordered mesoporous silicas have attracted considerable attention owing to attractive features, i.e. ultrahigh surface area, a highly ordered and tunable pore structure. However, most of as-prepared ordered mesoporous silicas show a very limited phosphate adsorption. Functionalization of mesoporous silicas and subsequent metal-impregnation can effectively generate specific binding sites for phosphate anions, thus forming phosphate adsorbents with a superior adsorption capacity and a fast adsorption rate [2,3]. For instance, the Fe(III)-coordinated diamino-functionalized SBA-15 exhibited the maximum phosphate capture capacity of 20.7 mg P/g and reached almost 90% of the final adsorption capacity in 10 min [4].

By utilizing such strategy to fabricate phosphate adsorbents, the reduction of mesopore sizes caused by the attachment of functional groups is noticed, which limits the diffusivity through those confined channels [5]. Despite some attempts to tailor SBA-15 which possesses relatively large pores in the class of mesoporous silicas, its long and isolated parallel channels still cause a slow in-pore diffusion and turnover [6]. As compared with single-sized mesoporous materials, the hierarchically macroporous-mesoporous materials have been proven to offer an improved diffusion characteristic and a high specific surface area on the level of fine pore systems [3,7].

The objective of our work is to fabricate and utilize Fe(III)-coordinated diamino-functionalized macroporous-mesoporous SBA-15 for phosphate removal; which, to the best of our knowledge, is reported for the first time. The macropores existing within SBA-15 are
expected to work as the rapid transport conduits for phosphate to the Fe\(^{3+}\)-diamino sites, which in turn reduce the transport obstacles, thus improving adsorption capacity.

2. **Materials and methods**

2.1 Synthesis of Fe(III)-coordinated diamino-functionalized macroporous–mesoporous adsorbents

Macroporous–mesoporous SBA-15 was firstly synthesized via a dual-templating approach by using P123 and monodisperse polystyrene beads (PS) (Fig. S1) as templates [8]. The products were prepared with the mass ratios of P123 : PS : tetraethoxysilane (TEOS) at 1.00 : 0 : 2.15 and 1.00 : 8.60 : 2.15, respectively. By utilizing the post-grafting method, 1.0 g of the afore-prepared silica was added into the mixture consisting of 30.0 mL of toluene and 1.0 mL of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, which was refluxed at 130 °C for 24 h. The resulting diamino-functionalized samples were washed with ethanol and mixed in 0.10 M FeCl\(_3\) solution. Fe(III)-coordinated diamino-functionalized adsorbents were denoted as SBA-NN-Fe-0 and SBA-NN-Fe-8.6, corresponding to their parent SBA-15 silicas which were fabricated with the mass ratios of P123 : PS : TEOS = 1.00 : 0 : 2.15 and 1.00 : 8.60 : 2.15, respectively.

2.2 Characterization and phosphate adsorption

SEM and TEM images were taken by JSM-7401F and JEM2010-HR (JEOL). XRD patterns were recorded on a Bruker D8 Advance diffractometer. FT-IR measurements were performed by using Shimadzu IR Prestige-21 instrument. Nitrogen adsorption-desorption isotherms were measured at 77 K using ASAP 2010 (Micromeritics Inc.). Details of phosphate adsorption analysis were provided in the supporting document.
3. Results and discussion

Fig.1 shows SEM (a) and TEM (b) images of SBA-NN-Fe-0 and SBA-NN-Fe-8.6. SBA-NN-Fe-0 exhibits the typical SBA-15 ropelike shape [9]. The addition of polystyrene beads modifies the SBA-15-like morphology and the SBA-NN-Fe-8.6 shows a more uniform macroporous network. In Fig.1b, SBA-NN-Fe-0 shows a 2D periodically hexagonal mesostructure of SBA-15, which is retained in SBA-NN-Fe-8.6; however, the introduction of macropores breaks up the extended mesoporous channels. In SBA-NN-Fe-8.6, the highly-organized concentric mesoporous channels with high curvature solely locate in the walls of macroporous framework. This is formed after the self-assembly of templated mesoporous channels around polystyrene beads which is promoted by the electrostatic and hydrogen-bonding interactions among beads, P123 and silica precursor [8].

Fig.2 shows XRD patterns (a), FT-IR spectra (b), N$_2$ adsorption–desorption isotherms (c) and BJH pore size distribution plots (d) of SBA-NN-Fe-0 and SBA-NN-Fe-8.6. In Fig.2a, three SBA-15 characteristic diffraction peaks (100), (110) and (200) are distinguishable, suggesting a well-ordered hexagonal arrangement of mesoporous silica framework [9]. However, a decrease in the intensities of peaks was observed for the sample SBA-NN-Fe-8.6 synthesized with the addition of PS. This may be caused by the introduction of macropores which breaks up the long-range order of mesoporous channels [10]. In Fig.2b, the peaks at 1081, 803, and 466 cm$^{-1}$, which are attributed to the vibrations of condensed silica network, and the peak at 961 cm$^{-1}$, which is ascribed to the Si-OH groups, are observed for both of SBA-NN-Fe-0 and SBA-NN-Fe-8.6 samples [11]. In particular, in the FTIR spectra of SBA-NN-Fe-0 and SBA-NN-Fe-8.6, the band appearing at 1408 cm$^{-1}$ corresponds to the NH$_2$ vibration [11], thus confirming the successful functionalization of mesoporous and macroporous-mesoporous silicas via the post-grafting method. Both of the N$_2$ adsorption–desorption isotherms (Fig.2c) exhibit a type IV model with a H1 hysteresis loop, suggesting the samples with uniform and even mesopores [12].
However, the loop size of isotherm decreases with increasing macropore character, which is attributed to the limited gas diffusion caused by the disruption of extended mesopore networks [8]. The pore diameters of SBA-NN-Fe-8.6 (Fig.2d) are slightly smaller than that of SBA-NN-Fe-0, which may be caused by the high curvature of mesoporous channels, as shown in Fig.1b. The specific surface areas for SBA-NN-Fe-0 and SBA-NN-Fe-8.6 are 247.40 m²/g and 233.68 m²/g, respectively.

In Table 1, both of Langmuir and Freundlich equations can satisfactorily describe the experimental data (R² > 0.93). In particular, q₀ of SBA-NN-Fe-8.6, 12.7 mg P/g, is significantly greater than that of SBA-NN-Fe-0, proving the presence of macropores can promote the diffusion of phosphate into the active sites and in turn improve the adsorption efficiency. Fig.3 further examines the adsorption behaviors of SBA-NN-Fe-8.6. The fitted pseudo-second-order kinetic model with a high correlation coefficient (Fig.3a) reveals that the adsorption is chemisorption. 92.5% of the adsorption capacity reaches in the first 1 min (Fig.3b). In Fig.3c, the highest adsorption of SBA-NN-Fe-8.6 is about 9.0 mg P/g in the pH from 3.0 to 6.0, indicating the Fe³⁺– diamino complex provides a great affinity to the main species of phosphate H₂PO₄⁻ [13]. The adsorption capacity dramatically decreases at pH ≥ 7.0; which is ascribed to the competitive adsorption between OH⁻ and the predominant species of phosphate HPO₄²⁻, as well as the precipitation of Fe³⁺ out of Fe³⁺– diamino complex [4]. The presence of open and interconnected macroporous-mesoporous framework in SBA-NN-Fe-8.6 may promote the diffusion of relatively smaller ions. Therefore, in comparison to HCO₃⁻, its phosphate adsorption capacity seems much easier to be affected by the existence of F⁻, Cl⁻ or NO₃⁻ (Fig.3d).

4. Conclusion

Fe-coordinated diamino-functionalized SBA-15 with hierarchical porosity was synthesized and used to remove phosphate for the first time. SBA-NN-Fe-8.6 possessed a
uniform macroporous network with highly-organized concentric mesopores, which contributed to the high phosphate adsorption capacity and rate. Therefore, our study offers a simple and scalable approach to fabricate adsorbents with improved phosphate adsorption performance by tailoring their porous structure.

Acknowledgements

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References and Notes


Figure captions:

Fig.1. (a) SEM and (b) TEM images of SBA-NN-Fe-0 and SBA-NN-Fe-8.6.

Fig.2. (a) XRD patterns, (b) FT-IR spectra, (c) N\textsubscript{2} adsorption-desorption isotherms and (d) BJH pore size distributions of SBA-NN-Fe-0 and SBA-NN-Fe-8.6.

Fig.3. (a) Pseudo-second-order plot for the phosphate adsorption; (b) effect of contact time, (c) pH, and (d) co-existing anions on the phosphate adsorption capacity of SBA-NN-Fe-8.6.
Tables

Table 1. Langmuir and Freundlich isotherm parameters in the phosphate adsorption of SBA-NN-Fe-0 and SBA-NN-Fe-8.6. (Dosage: 0.1 g/100 mL; pH=5.0; reaction time: 2h)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_0 (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td>SBA-NN-Fe-0</td>
<td>6.8</td>
<td>0.755</td>
</tr>
<tr>
<td>SBA-NN-Fe-8.6</td>
<td>12.7</td>
<td>0.405</td>
</tr>
</tbody>
</table>

**Highlights**

► Fe-coordinated functionalized macro-mesoporous SBA-15 was used to remove phosphate. ► The P adsorption of SBA-NN-Fe-8.6 was 86.8% higher than the mesoporous SBA-NN-Fe-0. ► 92.5% of the adsorption capacity of SBA-NN-Fe-8.6 reached within the first 1 min. ► High phosphate adsorption of SBA-NN-Fe-8.6 was recorded from pH 3.0 to 6.0. ► The coexistence of anions retarded the phosphate adsorption of SBA-NN-Fe-8.6.