Pyridinium-functionalized magnetic mesoporous silica nanoparticles as a reusable adsorbent for phosphate removal from aqueous solution

Fang Ma, Hongtao Du, Ronghua Li and Zengqiang Zhang

ABSTRACT

In this work, pyridinium-functionalized silica nanoparticles adsorbent (PC/SiO₂/Fe₃O₄) was synthesized for phosphate removal from aqueous solutions. The removal efficiency of phosphate on the PC/SiO₂/Fe₃O₄ was carried out and investigated under various conditions such as pH, contact temperature and initial concentration. The results showed that the adsorption equilibrium could be reached within 10 min, which fitted a Langmuir isotherm model, with maximum adsorption capacity of 94.16 mg/g, and the kinetic data were fitted well by pseudo-second-order and intra-particle diffusion models. Phosphate loaded on the adsorbents could be easily desorbed with 0.2 mol/L of NaOH, and the adsorbents showed good reusability. The adsorption capacity was still around 50 mg/g after 10 times of reuse. All the results demonstrated that this pyridinium-functionalized mesoporous material could be used for the phosphate removal from aqueous solution and it was easy to collect due to its magnetic properties.

Key words | adsorption, desorption, magnetic separation, phosphate, pyridinium-functionalized adsorbent

INTRODUCTION

Phosphorus is one of the main elements to sustain life in the earth system, and is also an essential element in the metabolic process (Ramasahayam et al. 2012). However, phosphorus containing compounds in water could lead to serious problems such as eutrophication, water degradation and potentially harmful impact on humans or animals (Duranceau et al. 2014). China requires that the maximum level of phosphorus should not exceed 0.5 mg/L, which affects the survival of fish and other aquatic organisms (Chen et al. 2015). Therefore, controlling phosphorus emission is a key factor for preventing eutrophication phenomena in water bodies (Ghaneian et al. 2014; Ge et al. 2015).

To date different technologies have been developed to remove phosphorus from wastewater including chemical precipitation (Zhang et al. 2014), denitrification (Wang et al. 2014), biological removal (Sibag & Kim 2012), and adsorption (Zhong et al. 2014). Among these various methods of wastewater treatment, adsorption is one of the most environmentally friendly, simple and economic methods for phosphorus removal. A variety of adsorbents for phosphorus removal from water such as fly ash (Chen et al. 2007), ion exchange resin (Yoon et al. 2014), silicates (Moharami & Jalali 2013), and bone charcoal (Ghaneian et al. 2014) have been used in water treatment. Many of these adsorbents such as Ti and Al oxides can uptake phosphorus through innersphere complexation (Moharami & Jalali 2014). However, it is difficult to recycle these adsorbents after treatment, especially when the adsorbents are dispersed into water as fine particles. The difficulty in separation substantially limits the practical application of these powered adsorbents.

Recently, magnetic nanoparticles (MNPs) have attracted more attention in water treatment, due to their convenient separation from water with a simple magnetic process and low cost (Tang & Lo 2013). Several studies have reported that heavy metals, phenolic compounds, drugs, and others are adsorbed onto MNPs (Lin et al. 2018). We also notice that exchange quaternary ammonium cations can adsorb anions from water. For example, Qiu et al. (2006) prepared an anion phase with N-methylimidazolium immobilized on silica to separate common inorganic anions. Qiu et al. (2010) reported poly(ionicliquid)-grafted silica hybrid
materials could be exchanged with tetrafluoroborate, hexa-
fluorophosphate, and trifluoromethanesulfonate through a
simple aqueous anion-exchange reaction. Xin et al. (2012)
prepared cetyl pyridine bromide-modified bentonites (CPB-
Bent) to remove benzoic acid from water. Among these
materials, pyridinium modified materials, which have high
adsorption, chemical inertness and low production cost,
have attracted some researchers’ attentions. Therefore, we
designed and synthesized pyridinium modified MNPs, and
they were applied to remove anions from water (Ma et al.
2015). In this study, MNPs modified with pyridinium are
expected to be a promising adsorbent to remove phosphorus
from water, and can be easily separated from water after
treatment. Consecutive cyclic experiments were conducted
to evaluate the reusability of the adsorbent.

MATERIALS AND METHODS

Materials
Ferric chloride hexahydrate (FeCl3·6H2O), tetraethyl ortho-
silicate (TEOS), iron sulfate heptahydrate (FeSO4·7H2O),
ammonia solution (NH3·H2O 25%), KH2PO4 stock solution
(1,000 mg/L), N,N-dimethyl formamide (DMF), and
1,3-dichloropropane (C3H6Cl2) were purchased from New
Sanli Chemical Reagents Company (Xi’an, Shaanxi,
China) in analytical grade and used as received.

Adsorbent preparation and characterization
Pyridinium-functionalized magnetic mesoporous silica
(PC/SiO2/Fe3O4) was prepared according to our method
(Ma et al. 2015). Briefly, Fe3O4 nanoparticles were prepared
via a coprecipitation method according to the literature. The
core structured SiO2/Fe3O4 microsphere was synthesized by
a modified Stöber method. Then, PC/SiO2/Fe3O4 was syn-
thesized using 1-(3-chloropropyl) pyridin-1-ium chloride
and SiO2/Fe3O4. Subsequently, the adsorbent was charac-
terized by transmission electron microscopy (TEM) on a
JEOL-2010 microscope (JEOL, Japan), Brunauer-Emmett-
Teller (BET) on a MPMS-XL SQUID magnetometer (Quantum
Design, USA), Fourier transform infrared (FT-IR) spectra
on a BRUKER TENSOR 27 spectrometer (Bruker,
Germany) and X-ray photoelectron spectroscopy (XPS) on
a ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher
Scientific, USA).

Adsorption experiments
The adsorption of phosphorus by PC/SiO2/Fe3O4 was con-
ducted in batch experiments and the effects of adsorbent
dosage, the solution pH, initial phosphate concentration,
temperature, and contact time were investigated. Batch sorp-
tion experiments were performed at 20 °C under neutral pH
conditions in a constant temperature shaker platform at
120 rpm for 2 h. An amount of 20 mg of adsorbent was
added into a capped plastic centrifuge tube containing
20 mL of 100 mg/L phosphate solutions. 0.1 mol/L HCl or
NaOH solutions were used to adjust the pH value. After
the adsorption equilibration, the suspension was separated
by an external magnet. For each flask, 1 mL of the super-
natant was sampled for analysis. The residual total
phosphate concentration in the solutions was measured by
ammonium molybdate spectrophotometry method (Yoon
et al. 2014) at a wavelength of 880 nm using a UV-Vis
NE300 spectrophotometer (Thermo Fisher Scientific,
USA). All the treatments were performed in triplicate.

RESULTS AND DISCUSSION

Adsorbent characterization
The results of adsorbent characterization refer to our
research literature (Ma et al. 2015). The BET surface areas
for SiO2/Fe3O4 and PC/SiO2/Fe3O4 are 52.7 and
51.5 m2/g, pore volumes are 0.052 and 0.046 cm3/g and
pore diameters are 2.6 and 2.2 nm, respectively. Figure 1(a)
represents the TEM microstructure of Fe3O4 (a), (b), and
PC/SiO2/Fe3O4 (c), (d). Figure 1(a) and 1(b) show that
Fe3O4 was dispersed with irregular shape and average
diameter of about 20 nm. Figure 1(c) and 1(d) illustrate
that the dark Fe3O4 nanoparticles were embedded in the
light grey SiO2 with average thickness of about 4 nm. The
result demonstrated that Fe3O4 was coated with SiO2 on
the surface of material successfully, but micrograph could
not confirm that pyridinium was linked to the surface of
SiO2. Therefore, XPS and FT-IR were applied to investigate
the groups and chemical elements on the surface of the
sorbent.

The magnetic hysteresis loops of Fe3O4, SiO2/Fe3O4 and
PC/SiO2/Fe3O4 are shown in Figure 1(b). The saturation
magnetization values were measured to be 85.6, 58.7
and 50.9 emu/g for Fe3O4, SiO2/Fe3O4 and PC/SiO2/
Fe3O4, respectively. The saturation magnetization values
decrease is attributed to the decrease of the magnetite
fraction after silica coating and pyridinium linking (Ren et al. 2013). The adsorbent could be separated from solution with a magnet easily and re-dispersed quickly when the magnet was taken away due to its superparamagnetic property and large saturation magnetization (Zhang et al. 2013).

The spectra FT-IR are shown in Figure 1(c). The typical adsorption peak for Fe$_3$O$_4$ at 585 cm$^{-1}$ was due to the Fe–O stretching vibration peak (Idris 2015). A broad strong band at 1,090 cm$^{-1}$ contributes to the Si–O–Si stretching vibration peak, while bands at 800 cm$^{-1}$ and 465 cm$^{-1}$ due to the Si–O bending and stretching mode were obvious (Idris 2015), which confirmed the successful coating of silica layers on Fe$_3$O$_4$. The broad adsorption peak at around 3,425 cm$^{-1}$ resulted from O–H stretching vibration, and 1,633 cm$^{-1}$ and 958 cm$^{-1}$ were characteristic bending bands of O–H. Adsorption peaks around 1,644 cm$^{-1}$, 1,571 cm$^{-1}$ belonged to C= N and C–N bonds respectively, and 1,329 cm$^{-1}$ was attributed to the –CH$_2$ bending of the connecting nitrogen ion (Ren et al. 2013), demonstrating pyridinium was successfully grafted to the surface of SiO$_2$/Fe$_3$O$_4$ particles.

The wide-scan XPS spectra for PC/SiO$_2$/Fe$_3$O$_4$ are shown in Figure 1(d). The elements of Si2s (154.8 eV), Si2p (103.5 eV), C1s (285.9 eV), Cl2p (196.9 eV), N1s (400.8 eV), and O1s (532.7 eV) were detected on the surface of PC/SiO$_2$/Fe$_3$O$_4$ (Konno & Yamamoto 1987; Hernández-Morales et al. 2012). The results agreed with the TEM micrograph of the sorbent. The results indicated that PC/SiO$_2$/Fe$_3$O$_4$ was prepared successfully.
Determination of adsorption parameters

The effect of pH range of 2–10 at 20 °C on phosphate removal is shown in Figure 2(a). The results indicated that the solution pH was a significant parameter controlling the process of adsorption. It can be observed that the adsorption of phosphate increased rapidly within the pH range from 2.0 to 4.0, and maintained a high adsorption at pH in the range of 4.0 to 8.0. However, the adsorption decreased obviously at pH above 8.0. The reason for this phenomenon may be that the main form of phosphorus is H₃PO₄ as the solution pH value was lower than 3.0, which is difficult to adsorb by the adsorbent. The existing forms of phosphorus are H₂PO₄⁻ and HPO₄²⁻ within the pH range from 3.0 to 8.0, which are easily absorbed through ion exchange by the adsorbent. Contrarily, more OH⁻ exists in the solution and competes with HPO₄²⁻ and PO₄³⁻ at higher pH (above pH 8.0).

Figure 2(b) expresses the effect of temperature in the range of 20–40 °C for the adsorption of phosphate on the PC/SiO₂/Fe₃O₄ under neutral pH for 60 min. The equilibrium sorption capacity slightly decreased with the solution temperature increased from 20 to 40 °C, indicating that adsorption process had an exothermic nature (Keränen et al. 2015).

The effect of adsorbent dosage in the range of 10–60 mg on the adsorption of phosphate was carried out at 20 °C under neutral pH for 60 min, as shown in Figure 2(c). The equilibrium adsorption capacity gradually decreased, with the increment of adsorbent dosage. While the removal rate was rising suggesting that phosphate adsorption onto adsorbent depended on availability of positively charged adsorption sites. This is consistent with the expectation that higher adsorbent dosages will result in lower adsorption efficiencies per gram, as the adsorbed phosphate is distributed among more available binding sites. Hence, the optimal adsorbent dosage for the investigation of maximum adsorption capacity is very important. According to the experimental results, the adsorption isotherm experiments were performed with 20 mg of phosphate.

![Figure 2](https://iwaponline.com/wst/article-pdf/74/5/1127/459669/wst074051127.pdf)
Adsorption isotherms

Solutions of different initial concentrations 100, 150, 200, 250, 300, 350, 400, 500, 600 mg/L KH2PO4 were used to evaluate the effect of concentration on the phosphate removal with 20 mg of adsorbent in 20 mL of solution and shaken in a thermostat at 120 rpm for 60 min under 20 °C. Figure 3 shows the adsorption isotherm of phosphate by PC/SiO2/Fe3O4. The data were fitted by Langmuir isotherm and Freundlich isotherm, the results are shown in Table 1. From Figure 3 and Table 1, it is evident that the maximum adsorption capacity of PC/SiO2/Fe3O4 was 94.16 mg/g, and the Langmuir isotherm model showed more significant correlation ($R^2 = 0.999$) than the Freundlich isotherm model ($R^2 = 0.912$). Therefore, the adsorption process could be described as a monolayer adsorption due to the homogenous and negligible interaction between adsorbed molecules (Ge et al. 2015).

Adsorption kinetics

To illustrate the adsorption kinetics and the rate determining step of phosphate by PC/SiO2/Fe3O4, the pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model were employed (El-Khaiary 2007). The description of the pseudo-first-order equation is following:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where $k_1$ (min$^{-1}$) is the rate constant of sorption equilibrium in the first order reaction, $q_e$ (mg/g) is the amount of phosphate at the equilibrium state, $q_t$ (mg/g) is the amount of phosphate on the surface of the sorbent at any time.

The description of the pseudo-second-order equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $k_2$ (g/(mg min)) is the rate constant of sorption equilibrium in the second order reaction.

The intra-particle equation is as follows:

$$q_t = k_p t^{0.5}$$

where $k_p$ (g/(mg min$^{0.5}$)) is the intra-particle rate constant.

To distinguish which of the three models was more appropriate, a comparison between adsorption capacity calculated ($q_{e, \text{cal}}$) and experimental adsorption capacity from the kinetic adsorption test was carried out. From Table 2, although high correlation coefficients ($R^2$) were obtained, the correlation coefficients ($R^2$) of pseudo-second-order (Figure 4(c)) were higher than those of pseudo-first-order (Figure 4(b)). The equilibrium adsorption capacity calculated ($q_{e, \text{cal}}$) by the pseudo-second-order equation is closer to the experimental ones from the pseudo-first-order model, which proved that the phosphate adsorption on adsorbents is probably controlled by chemisorptions (Moattari et al. 2015).

Due to the mesoporous structure of adsorbent, diffusion was also tested. Figure 4(d) shows the intra-particle diffusion plot of phosphate on PC/SiO2/Fe3O4. As could be seen, the adsorption process appeared as three linear portions which were not linear during the whole time. The diffusion rate

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Parameters for Langmuir and Freundlich equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>$Q_{\text{max}}$ (mg/g)</td>
</tr>
<tr>
<td>PC/SiO2/Fe3O4</td>
<td>94.16</td>
</tr>
</tbody>
</table>

$q_{\text{max}}$: maximum adsorption capacity; $b$: energy of adsorption; $K$: proportionality constant; $n$: dimensionless exponent; $R^2$: correlation coefficient.
Constants in every step follow the order of $k_{p,1} > k_{p,2} > k_{p,3}$, which are described in Table 2. It can be demonstrated that the first portion with high slope showed the instant diffusion stage, in which large numbers of phosphate were adsorbed rapidly by adsorbent. After almost every active bonding site was filled, the phosphate entered into the pores of the adsorbent, then the phosphate was absorbed by the interior surface of pores, which appeared in the second stage. In the third stage, the intra-particle diffusion rate constants were almost zero, demonstrating equilibrium was reached finally. The regression did not pass through the origin, indicating that the intra-particle diffusion was not the only rate controlling step and that some other kinetic processes were also involved.

Results of phosphate adsorption onto different materials from other researchers are shown in Table 3. It can be seen that the maximum adsorption capacity of PC/SiO$_2$/Fe$_3$O$_4$ for phosphate is matched and even higher than that of...
other adsorbents, which maybe contribute to more pyridinium cations coated on the surface per unit mass MNP. Moreover, due to the absorbing process being mainly controlled by an ion exchange process (Ma et al. 2015), the rate of adsorption is relatively fast. In addition, the adsorbent with magnetic properties could be separated easily from solution with a magnet. So, this material has advantages of high adsorption capacity, rapid adsorption, and easy separation in removing phosphate in aqueous solution.

**Desorption and reusability**

To achieve the reusability of adsorbent, the phosphate loaded on the adsorbents should be desorbed carefully without damaging the structure of the adsorbents. Different consumption of NaOH (0.2 mol/L) was applied to desorb phosphate (KH₂PO₄ 64.1 mg/g) after the adsorbent (20 mg) was separated from solution with a magnet and the supernatant was decanted. The results (Figure 5(a)) showed that over 90% of adsorbed phosphate could be desorbed with NaOH (12 mL), therefore, we chose 12 mL NaOH (0.2 mol/L) for desorption in the next experiments.

Phosphate adsorbed on the adsorbents was desorbed with desorption solution, and the adsorbents were collected and rinsed with deionized water thoroughly for reuse. The reusability of PC/SiO₂/Fe₃O₄ is shown in Figure 5(b). The adsorption capacity was 64.1 mg/g in the first use of adsorbents, and it decreased to around 54.8 and 50.9 mg/g in the second and third use. The decrease of the adsorption capacity in the first two reuses might result from some of

<table>
<thead>
<tr>
<th>Adsorbent name</th>
<th>qₘ (mg/g)</th>
<th>Equilibrium time (min)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/SiO₂/Fe₃O₄</td>
<td>94.2</td>
<td>10</td>
<td>This work</td>
</tr>
<tr>
<td>Iron/reduced iron oxide nanoparticles</td>
<td>43.7</td>
<td></td>
<td>Ramasahayam et al. (2012)</td>
</tr>
<tr>
<td>Bone charcoal (BC)</td>
<td>30.2</td>
<td>120</td>
<td>Ghaneian et al. (2014)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>28.3</td>
<td>180</td>
<td>Moharami &amp; Jalali (2014)</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>24.4</td>
<td>180</td>
<td>Moharami &amp; Jalali (2014)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.5</td>
<td>180</td>
<td>Moharami &amp; Jalali (2014)</td>
</tr>
<tr>
<td>Wheat straw anion exchanger (WS–AE)</td>
<td>45.7</td>
<td>150</td>
<td>Xu et al. (2010)</td>
</tr>
<tr>
<td>Nano-bimetal ferrites</td>
<td>41.4</td>
<td>120</td>
<td>Tu &amp; You (2014)</td>
</tr>
<tr>
<td>Fe₃O₄@Zn–Al–LDH</td>
<td>36.9</td>
<td>60</td>
<td>Yan et al. (2015)</td>
</tr>
<tr>
<td>Fe₃O₄@Mg–Al–LDH</td>
<td>31.7</td>
<td>40</td>
<td>Yan et al. (2015)</td>
</tr>
<tr>
<td>Fe₃O₄@mZrO₂</td>
<td>119.8</td>
<td>200</td>
<td>Sarkar et al. (2010)</td>
</tr>
<tr>
<td>Magnetic iron oxide nanoparticles</td>
<td>83.2</td>
<td>&gt;100</td>
<td>Yoon et al. (2014)</td>
</tr>
<tr>
<td>Fly ashes</td>
<td>130.4</td>
<td>&gt;100</td>
<td>Chen et al. (2007)</td>
</tr>
</tbody>
</table>

qₘ: maximum adsorption capacity.

Figure 5 | (a) Desorption of phosphate with NaOH and (b) reusability of the PC/SiO₂/Fe₃O₄ for phosphorus adsorption.
the phosphate entering into the pores of the adsorbent, which was not an irreversible adsorption. With the reduction of this kind of irreversible adsorption process, the adsorption capacity remained stable in the following reuse. The adsorption capacity was still around 50 mg/g after 10 times of recycle, indicating excellent reusability of the adsorbents.

CONCLUSION

In this study, a magnetic adsorbent PC/SiO2/Fe3O4 was successfully synthesized. Containing a magnetic core, PC/SiO2/Fe3O4 could be conveniently separated from water in short time by using a simple magnetic process. The PC/SiO2/Fe3O4 exhibited excellent capacity for phosphate removal within the pH range from 3.0 to 8.0, and its maximum adsorption calculated by Langmuir model was 94.16 mg/g. The phosphate adsorption reached the equilibrium state within 10 min, and the kinetic data were well fitted by pseudo-second-order model, and intra-particle pore diffusion process which confirmed the phosphate adsorption was limited by the chemisorption of phosphate on the porous structure of adsorbent. The PC/SiO2/Fe3O4 with sorbed phosphate can be effectively regenerated in NaOH solution, and the regenerated PC/SiO2/Fe3O4 can be used at least 10 times in the sorption–desorption cycles without any significant loss of the adsorption capacities. Therefore, we consider that PC/SiO2/Fe3O4 adsorbent can be reused as a promising, effective and magnetic separation adsorbent for phosphorus removal from aqueous solution.

ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China under Grant No. 41101288; and Northwest A&F University PhD Degree Scholar Research Projects under Grant No. 2013BSJJ120.

REFERENCES

Idris, S. A. M. 2015 Adsorption, kinetic and thermodynamic studies for manganese extraction from aqueous medium using mesoporous silica. J. Colloid Interface Sci. 440, 84–90.
Sarkar, A., Biswas, S. K. & Pramanik, P. 2010 Design of a new nanostructure comprising mesoporous ZrO2 shell and magnetite core (Fe3O4@mZrO2) and study of its phosphate ion separation efficiency. J. Mater. Chem. 20, 4417–4424.

First received 29 November 2015; accepted in revised form 27 April 2016. Available online 20 June 2016