Effective magnetic separation of phosphate from natural water by a novel magnetic composite

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ABSTRACT

In this study, we aimed to magnetically separate phosphate from natural water and change its source-to-sink conversion to prevent eutrophication. To this end, a promising material in terms of phosphate removal efficiency and magnetic separability was developed. Nine types of magnetic composite P-removal agents were prepared by changing the types of metal salts (i.e., Zn²⁺, Cu²⁺, Mg²⁺, Al³⁺, Fe³⁺, Zr⁴⁺, Y³⁺, Ce³⁺, and La³⁺), and the optimal agent was determined to be La³⁺/poly(acrylamide-co-acryloyloxyethyl trimethylammonium chloride)/Fe₃O₄ [La³⁺/CPAM/Fe₃O₄] based on phosphate removal efficiency. The optimal synthesis conditions, including reaction time (4 h), reaction temperature (65°C), and the content of metal salts (12.96 mmol), were determined. The synthesized material was characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, and vibrating-sample magnetometry. The results showed that the material featured a core–shell structure and exhibited good magnetic response. The experimental results showed that the removal process was rapid and completed within 20 min. Moreover, the material could greatly reduce P concentration, with phosphate removal efficiency reaching 90.07%. This material could effectively separate phosphate under the action of an external magnetic field and change the source-to-sink conversion of P, thereby preventing the risk of eutrophication.

Keywords: Eutrophication control; Phosphate elimination; Magnetic separation; Source-to-sink conversion; Natural water

1. Introduction

Phosphorus (P) is an essential element of all life forms [1]. Excess P is generally considered to be an important factor for eutrophication in natural water [2]. Eutrophication has been a global environmental problem in natural water, such as in lakes, marshes, and reservoirs [3]. In recent years, great progress has been made in limiting P inputs from the point and non-point contaminant sources [4,5]. External P is released into natural water from sediment, which is deposited at the bottom of the water and serves as a sink of internal P [6]. Therefore, the ability of sediment in natural water to reduce constant P input is limited. Under a variety of complex environmental conditions such as high or low pH environments and redox conditions, P in the sediment will be re-released to the overlying water [7]. Eventually, the sink of internal P becomes the internal source of eutrophication in natural water. The conversion of P in sediment and overlying water occurs annually in natural water. Furthermore, the P concentration in natural water is not reduced mainly because the source-to-sink conversion of P remains unchanged.

Traditional techniques such as sediment dredging, hypolimnetic aeration, and chemical precipitation have been applied to prevent the release of P from sediment in natural water [8,9]. However, sediment dredging is based...
on various preconditioning methods involving an additional expensive infrastructure [10]. The main drawback of hypolimnetic aeration is its high energy cost. Chemical precipitation is another method for reducing the P concentration in natural water, and it has attracted increasing attention because of its high efficiency and stability [11]. However, it requires the consumption of large quantities of chemicals and inevitably produces large quantities of precipitates [12]. The P in these precipitates is re-released into the overlying aqueous phase due to the aging of the chemicals and the complex environmental conditions [13]. To reduce the risk of eutrophication in natural water, effectively preventing the source-to-sink conversion of P in the sediment and the overlying water is critical. Some scholars have controlled the P concentration in overlying water by in-situ capping technology. However, P is not separated from the natural waters and may thus be re-released [14]. Changing the source-to-sink conversion of P in natural water is difficult using traditional methods. Therefore, new methods for effectively separating P from natural water must be explored.

In recent years, magnetic composite materials have been gaining increasing attention due to their unique magnetic properties [15]. Magnetic iron oxide has magnetic properties and low toxicity, and it is easier to separate from natural water than other non-magnetic materials. In some studies [16,17], magnetic composite materials were used to remove dyes, and these materials had high removal efficiencies and recyclability. In addition, some scholars used magnetic composites to remove toxic heavy metals in aqueous solutions [18,19]. There have been a few studies on the separation of P from natural water using magnetic composite materials. Nevertheless, those studies normally used complex methods and expensive materials [20]. Thus, herein, P-removal chemicals were magnetized by hybridization with biocompatible magnetic materials through molecular design, after which they were combined with soluble orthophosphorus to form magnetic P-containing insoluble materials (henceforth referred to as insolubles). Under the action of an external magnetic field, the magnetic P-containing insolubes were attracted to the magnet and could be magnetically separated from natural water. This method is highly efficient and stable because it is based on chemical precipitation. Furthermore, it avoids the large amounts of sludge produced by traditional chemical precipitation methods. Using this method, the source-to-sink conversion of P in natural water can be hindered, and the risk of eutrophication can be avoided.

In this study, a magnetic composite agent for P-removal was first prepared by aqueous solution polymerization. The optimal synthesis conditions for preparing the magnetic composite agent were determined by an orthogonal design. The best agent was determined. The magnetic composite agent exhibited suitable selective removal of P, and the influences of the pH value, coexisting ions, and initial P concentration, were evaluated. Moreover, the interaction mechanism of the magnetic composite agent and phosphates was investigated by Fourier-transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) analysis was carried out using a D8 ADVANCE with Cu Kα radiation (30 kV, 15 mA). The particle size and saturation magnetization of the agent were characterized by transmission electron microscopy (TEM) and vibrating-sample magnetometry (VSM), respectively.

2. Materials and methods

2.1. Materials

All the chemicals used for the preparation of the magnetic composite P-removal agent were commercially available and were used without further purification. Acrylamide (AM), ammonium persulfate ((NH₄)₂S₂O₈), and zinc sulfate heptahydrate (ZnSO₄·7H₂O) were supplied by Tianjin Damao Reagent Co., Ltd., (Tianjin, China). Ferrous sulfate heptahydrate, sodium bisulfite (NaHSO₃), and gelatin were purchased from Tianjin Bodi Chemical Co., Ltd., (Tianjin, China). Moreover, N,N-dimethylanilnoyl acetyl methyl chloride quaternary (DAC, 80%) was supplied by Wunduxin Chemical Co., Ltd., (Jinan, China). Citric acid, magnesium chloride hexahydrate (MgCl₂·6H₂O), aluminum chloride hexahydrate (AlCl₃·6H₂O), and ferric chloride hexahydrate (FeCl₃·6H₂O) were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Lanthanum chloride heptahydrate (LaCl₃·7H₂O) and cupric chloride (CuCl₂) were purchased from Shanghai Macklin Biochemical Co., Ltd., China. Cerium chloride heptahydrate (CeCl₃·7H₂O), yttrium chloride heptahydrate (YCl₃·7H₂O), and zirconium sulfate tetrahydrate (ZnSO₄·4H₂O) were supplied by Shanghai Aladdin Reagent Co., Ltd., China. Monopotassium phosphate (KH₂PO₄) was obtained from Tianjin Kemioiu Chemical Reagent Co., Ltd., China.

2.2. Synthesis of magnetic composite P-removal agent

Magnette (Fe₃O₄) nanoparticles and poly (AM-co-DAC)–grafted (CPAM) gelatin were successfully prepared in the laboratory [21,22]. The synthesis conditions of the magnetic composite P-removal agent were optimized by orthogonal experiments. Different types of magnetic composite P-removal agents were prepared by changing the types of metal salts (i.e., Zn²⁺, Cu²⁺, Mg²⁺, Al³⁺, Fe³⁺, Zr⁴⁺, Y³⁺, Ce³⁺, and La³⁺) under the best condition, and the best metal ions were determined based on phosphate removal efficiency. The metal ions were supplied by the metal salts, which could combine with phosphate to form P-containing substances. Therefore, the influence of the quantities of metal salts on phosphate removal efficiency was investigated. Moreover, the reaction time and reaction temperature could affect the completion and stability of the agent. Therefore, the agent specimens with various reaction conditions were obtained by altering the reaction time (factor A), reaction temperature (factor B), and amount of metal salt (factor C). It was assumed that no correlation existed between any two factors. An orthogonal matrix L₉ (3⁴) was used, and the levels are presented in Table 1.

First, Fe₃O₄ (1.5 g) and the reagents for preparing the poly(AM-co-DAC)-g-gelatin were placed in a three-necked flask and reacted at 80°C for 130 min. The reaction temperature of the system was then changed according to the designed conditions. Next, predetermined amounts of metal salt were added and reacted for a suitable time. The final product was extracted with ethanol and dried at 40°C until the weight was constant.
were conducted by adding certain amounts of competing ions initial pH levels, ranging from 3.0 to 12.0 for the batch dosage of the agent was added to solutions with different removal efficiency of the agent was studied, and a certain phosphate removal experiments, samples were filtered at pH 7.0 ± 0.1 in separate beakers. The molar ratios of phosphate to competitive anions were 1:1, 1:20, and 1:100. The influences of parameters such as the amount of added lanthanum salt. This directly indicated that phosphate removal efficiency had a positive correlation with the quantity of La$^{3+}$ in the La$^{3+}$/CPAM/Fe$_3$O$_4$ for the phosphorus solution treatment. Phosphate removal efficiency was significantly increased by increasing the amount of added lanthanum salt. This directly indicated that phosphate removal efficiency had a positive correlation with the quantity of La$^{3+}$ in the La$^{3+}$/CPAM/Fe$_3$O$_4$. For a given statistical significance level, the standard $F$-value was determined using an $F$-table [24]. If the $F$-variance ratio was higher than the standard $F$-value, the corresponding factors would contribute significantly to the experimental results. As for the inspection level, $a = 0.05$, $F_{(2,2)} = 19$, and $F_{(0.05)} = 59.615$. Thus, $F_{(0.05)} > Fa$. Furthermore, according to the ANOVA results, factor C played the most important role in phosphate removal efficiency, followed by factor B, which had a larger contribution than factor A. This conclusion was consistent with the range analysis. Through the above analysis, the optimal conditions for preparing La$^{3+}$/CPAM/Fe$_3$O$_4$ were determined, and the agent was accordingly re-prepared for subsequent experiments. Thus, the stability and accuracy of the orthogonal experiment were verified. The results showed that the phosphate removal efficiency of La$^{3+}$/CPAM/Fe$_3$O$_4$ prepared under the optimal conditions was 90.07%.

Table 1

<table>
<thead>
<tr>
<th>Factors Levels</th>
<th>Reaction time, (h)</th>
<th>Reaction temperature, (°C)</th>
<th>Amount of metal salt, (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Reaction time</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>(h)</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Reaction temp.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>(°C)</td>
<td>50</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>Amount of</td>
<td>6.48</td>
<td>12.96</td>
<td>19.44</td>
</tr>
<tr>
<td>metal salt</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Optimization strategy of orthogonal experiment

The data from the orthogonal experiments were analyzed to better clarify the relationship between the experimental conditions and results. For example, La$^{3+}$ was used to prepare the magnetic composite P-removal agent (La$^{3+}$/CPAM/Fe$_3$O$_4$) and investigate phosphate removal efficiency under different experimental conditions. Nine selected experiments were used in an L9 (3$^3$) orthogonal table, and the results are shown in Table 2. These experiments were designed to optimize the synthesis conditions of the magnetic composite P-removal agent and increase phosphate removal efficiency.

The maximum and minimum phosphate removal efficiencies of La$^{3+}$/CPAM/Fe$_3$O$_4$ were observed to be 88.86% and 67.19%, respectively. The parameter $K_i$ ($i = 1, 2, 3$) denotes the average value of phosphate removal efficiency in the equal levels of each factor, and $R$ is the interval between the maximum and minimum $K_i$ values. Moreover, the value of $R$ could be used to evaluate the extent to which various factors influenced phosphate removal efficiency. A larger $R$ indicates that the factor had a more significant effect on the phosphate removal efficiency [23]. The $R$ values of factors $A$, $B$, and $C$ were 0.567, 4.294, and 15.471, respectively. Therefore, among these three factors, the amount of metal salt had the greatest impact on phosphate removal efficiency, followed by the reaction temperature, and the reaction time had the weakest impact. The analysis of variance (ANOVA) results are presented in Table 3. In addition, phosphate removal efficiency was investigated by changing the La$^{3+}$ proportion in the La$^{3+}$/CPAM/Fe$_3$O$_4$ for the phosphorus solution treatment. Phosphate removal efficiency was significantly increased by increasing the amount of added lanthanum salt. This directly indicated that phosphate removal efficiency had a positive correlation with the quantity of La$^{3+}$ in the La$^{3+}$/CPAM/Fe$_3$O$_4$. For a given statistical significance level, the standard $F$-value was determined using an $F$-table [24]. If the $F$-variance ratio was higher than the standard $F$-value, the corresponding factors would contribute significantly to the experimental results. As for the inspection level, $a = 0.05$, $F_{(2,2)} = 19$, and $F_{(0.05)} = 59.615$. Thus, $F_{(0.05)} > Fa$. Furthermore, according to the ANOVA results, factor C played the most important role in phosphate removal efficiency, followed by factor B, which had a larger contribution than factor A. This conclusion was consistent with the range analysis.

Through the above analysis, the optimal conditions for preparing La$^{3+}$/CPAM/Fe$_3$O$_4$ were determined, and the agent was accordingly re-prepared for subsequent experiments. Thus, the stability and accuracy of the orthogonal experiment were verified. The results showed that the phosphate removal efficiency of La$^{3+}$/CPAM/Fe$_3$O$_4$ prepared under the optimal conditions was 90.07%.

\[ R(\%) = \left( \frac{C_f - C_i}{C_i} \right) \times 100 \]
3.2. Determination of metal ions for preparing magnetic composite P-removal agent

Nine kinds of magnetic composite P-removal agents (Mn+/CPAM/Fe3O4) were prepared by changing the metal ions under the optimal synthesis conditions. The best metal ion was determined by comparing the phosphate removal efficiencies of these magnetic composite agents. Fig. 1 shows the phosphate removal efficiency of different types of magnetic composite P-removal agents. The dosages of the different agents were 0.75, 1.75, 2.25, 2.75, and 3.75 g/L. The phosphate removal efficiencies of these agents were compared and the best agent was selected. The results showed that the magnetic composite agents based on Fe3+, Al3+, Mg2+, Cu2+, Zn2+, and Ce3+ had low phosphate removal efficiencies at pH = 7 ± 0.1, which limits the application of these six agents in natural water. However, under the same conditions, lanthanum-, zirconium-, and yttrium-based magnetic composite agents had relatively high phosphate removal efficiencies. Among these agents, La3+/CPAM/Fe3O4 exhibited the highest phosphate removal efficiencies. When the dosage of La3+/CPAM/Fe3O4 was 3.75 g/L, phosphate removal efficiency reached 90.07%.

Phosphate removal efficiency was determined by the stability and magnetic response of the magnetic insolubles formed by the magnetic composite P-removal agent and phosphates. The magnetic response of these agents was affected by the amount of Fe3O4. Different types of magnetic composite agents were prepared with the same amount of Fe3O4 and they had the same magnetic response. Therefore, the stability of the magnetic insolubles was considered to be the main factor in the study of phosphate removal efficiency. The solubilities and bond dissociation energies of the compounds formed by the combination of various metal ions and phosphates can be found in the Rankine chemistry manual. Fig. 1, the solubilities, and the bond dissociation energies of compounds formed indicated that the lower the solubilities of the insoluble were, the higher the phosphate removal efficiencies of these agents were. The ionic radii of rare-earth ions are large, and thus, these ions could combine with more phosphate than the other metal ions, and the phosphate removal efficiency was high [25,26]. The oxygen atoms in the phosphate radicals provided a lone electron pair that formed coordinate bonds with the unoccupied orbitals of the metal ion in the P-removal agent molecule. The stability of the coordination compound was affected by the dissociation energy of the coordination bond. The dissociation energies of the rare-earth ions combined with phosphate were greater than those of the other metal ions combined with phosphate, except for zirconium ions. Therefore, the phosphate removal efficiency of the rare-earth magnetic composite P-removal agents was higher than those of the other P-removal agents. However, the famous lanthanide contraction (that causes a decline in ionic radius from 1.13 Å for La3+ to 1.00 Å for Lu3+) resulted in a subtle change in the properties. Furthermore, due to the lanthanum ions, which were in the 4f subshell, the valence state of lanthanum was stable, and the coordination bonds formed with the ligands were firm [27]. The combination process of the magnetic composite

Table 2
Results of orthogonal experiment

<table>
<thead>
<tr>
<th>Experimental number</th>
<th>A (h)</th>
<th>B (°C)</th>
<th>C (mmol)</th>
<th>Phosphate removal efficiency (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>67.19</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>88.86</td>
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<td>3</td>
<td>79.35</td>
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<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>84.45</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>81.43</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>70.19</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>78.47</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>72.70</td>
</tr>
<tr>
<td>9</td>
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<td>83.20</td>
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<td>k1</td>
<td>78.467</td>
<td>76.703</td>
<td>70.027</td>
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<td>k2</td>
<td>78.690</td>
<td>80.997</td>
<td>85.503</td>
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<td>k3</td>
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</tr>
<tr>
<td>r</td>
<td>0.567</td>
<td>4.294</td>
<td>15.476</td>
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</tr>
</tbody>
</table>

Best level

Amount of metal salt > reaction temperature > reaction time

Table 3
Analysis of variance (ANOVA) of phosphate removal efficiency

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.486</td>
<td>2</td>
<td>0.079</td>
<td>0.926</td>
</tr>
<tr>
<td>B</td>
<td>30.875</td>
<td>2</td>
<td>5.013</td>
<td>0.166</td>
</tr>
<tr>
<td>C</td>
<td>367.171</td>
<td>2</td>
<td>59.615</td>
<td>0.016</td>
</tr>
<tr>
<td>Error</td>
<td>6.16</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SS: sum of squared deviations; df: degrees of freedom; F: F ratio; P: probability value test.
P-removal agent with phosphate to form insolubles could be affected by the coexisting ions in natural water. However, due to their special electronic structures, the rare-earth magnetic composite P-removal agents had strong affinities and selectivities for phosphate [28]. Hence, the phosphate removal efficiency of La$^{3+}$/CPAM/Fe$_3$O$_4$ was higher than those of the other eight agents. Thus, La$^{3+}$/CPAM/Fe$_3$O$_4$ was selected as the best agent to remove phosphate in natural water.

3.3. Characterization of materials

3.3.1. Characterization by transmission electron spectroscopy

To determine the morphology and average size of the as-synthesized La$^{3+}$/CPAM/Fe$_3$O$_4$, the material was analyzed using TEM (Fig. 2). As shown in Fig. 2, the La$^{3+}$/CPAM/Fe$_3$O$_4$ nanoparticles were nearly spherical, with their diameters ranging from about 15 to 40 nm. During the preparation of La$^{3+}$/CPAM/Fe$_3$O$_4$, the Fe$_3$O$_4$ nanoparticles were entrapped by the macromolecular compounds, forming a core–shell-like structure. A large number of nanoparticles attracted each other and converged, due to their high surface energy and the mutual magnetic interaction of Fe$_3$O$_4$ [29].

3.3.2. Characterization by XPS

To further investigate the chemical compositions and states of La$^{3+}$/CPAM/Fe$_3$O$_4$ before and after it bonded with phosphate, XPS surface characterizations of the La$^{3+}$/CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ + P were performed. Fig. 3 shows the XPS spectra of La$^{3+}$/CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ + P. The pristine La$^{3+}$/CPAM/Fe$_3$O$_4$ consisted mainly of carbon, nitrogen, chlorine, lanthanum, and iron (Fig. 3a). As shown in Fig. 3b, additional photoelectron lines at a binding energy (BE) of about 132.9 eV, which were attributed to the P 2p species, appeared after phosphate removal. This phenomenon demonstrated that phosphate was successfully loaded onto the La$^{3+}$/CPAM/Fe$_3$O$_4$ [30]. The distinctly contrasting XPS spectra of the La 3d before and after phosphate removal are illustrated in Fig. 3c.

3.3.3. Characterization by FT-IR spectrum analysis

The functional groups of the Fe$_3$O$_4$/CPAM, La$^{3+}$/CPAM/Fe$_3$O$_4$, and La$^{3+}$/CPAM/Fe$_3$O$_4$ + P, determined by FT-IR characterization, are compared in Fig. 4. For the La$^{3+}$/CPAM/Fe$_3$O$_4$ spectra, a large peak of the primary amine –NH$_2$ (m) was observed at 3,360 cm$^{-1}$, and two sharp peaks were observed for primary amide (s) and –COO$^-$ at 1,662 and 1,419 cm$^{-1}$, respectively. The stretching vibration peak of N$^+$-linked –CH$_2$–N–(CH$_3$)$_3$ was observed at 1,454 cm$^{-1}$. The results indicated that dimethyl groups were present in the hybrid polymers. A small peak of C–C was observed at 1,168 cm$^{-1}$, and a broad and low peak was found for Fe–O at 590 cm$^{-1}$ [32]. This proved that Fe$_3$O$_4$ was present in the La$^{3+}$/CPAM/Fe$_3$O$_4$. Moreover, the La$^{3+}$/CPAM/Fe$_3$O$_4$ spectrum featured a lower peak intensity of the primary amine than the CPAM/Fe$_3$O$_4$ spectrum, and the range was also smaller. This was mainly due to the metal ions compounded on the La$^{3+}$/CPAM/Fe$_3$O$_4$, which hindered the absorption of infrared light. Meanwhile, a blue shift occurred at the peaks of the carboxylate group on the La$^{3+}$/CPAM/Fe$_3$O$_4$ from 1,643 and 1,392 cm$^{-1}$ to 1,662 and 1,419 cm$^{-1}$, respectively, which was mainly caused by La$^{3+}$ taking part in the reaction. Moreover, a new intense peak appeared at 1,056 cm$^{-1}$. This was attributed to the antisymmetric stretching vibrations of the P–O bonds.
After the La$^{3+}$/CPAM/Fe$_3$O$_4$ combined with phosphate, a new peak of the O–P–O bending modes formed at 540 cm$^{-1}$, which was attributed to the presence of phosphate [34].

3.3.4. Characterization by vibrating-sample magnetometry spectrum analysis

Fig. 5a shows the magnetic response of the La$^{3+}$/CPAM/Fe$_3$O$_4$. Under the action of the carboxylic groups, the La$^{3+}$/CPAM/Fe$_3$O$_4$ solution was homogeneously dispersed and attracted by an external magnet. The phenomenon indicated that the La$^{3+}$/CPAM/Fe$_3$O$_4$ exhibited a good dispersity and magnetic response.

The magnetic properties of the La$^{3+}$/CPAM/Fe$_3$O$_4$ were studied in an external magnetic field from −10 to 10 kOe. The hysteresis loops of the CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ are shown in Fig. 5b. The results indicated that both samples exhibited superparamagnetism. The saturation magnetization values of CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ were 1.77 and 1.66 emu/g, respectively. Increasing the La$^{3+}$ content resulted in a smaller saturation magnetization value, which was because the non-magnetic matter attenuated the magnetization of the Fe$_3$O$_4$. Moreover, CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ exhibited superparamagnetism, mainly because of the presence of nanoscale magnetite particles in the core [35]. This superparamagnetic La$^{3+}$/CPAM/Fe$_3$O$_4$ with high magnetic properties could be used to achieve rapid solid–liquid separation in natural water. Fig. 5c shows the magnetic response of the final product. The La$^{3+}$/CPAM/Fe$_3$O$_4$ combined with phosphate to form magnetic
insolubles and could be attracted to a magnet placed at the side of the beaker. This phenomenon shows that solid–liquid separation could be effectively realized under the action of a magnetic field, and the P contents were removed. This advantage further promotes the practical application of La$^{3+}$/CPAM/Fe$_3$O$_4$ in natural water.

### 3.3.5. Characterization by XRD patterns

The wide-angle XRD profiles of the Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ are shown in Fig. 6. The crystal structure of Fe$_3$O$_4$ was determined based on its diffraction peaks, in which the strong peaks appeared at 20 values of 30.1°, 35.4°, 43.1°, 57.1°, and 62.4° (JCPDS card 99-0073) [36]. After being coated with the polymer, the La$^{3+}$/CPAM/Fe$_3$O$_4$ particles exhibited an almost identical diffraction pattern to that of Fe$_3$O$_4$, indicating the formation of an amorphous polymer layer. This indicated that the polymer and lanthanum(III) on the surface of Fe$_3$O$_4$ could be regarded as an amorphous phase without a crystal structure. In addition, the presence of the maghemite magnetic phase in the iron oxides with the polymer could not be excluded, because the reaction experiment was conducted in an open system. In fact, the color of the resulting magnetic composite P-removal agent could be an indication of the coexistence of magnetic maghemite. The Fe$_3$O$_4$ was black, whereas the magnetic composite P-removal agent was maroon. This result agrees with previous literature [4,37].

### 3.4. Effect of pH on P-removal

The effect of the initial pH on the phosphate removal by La$^{3+}$/CPAM/Fe$_3$O$_4$ was further investigated, and the results are illustrated in Fig. 7. When the pH was <4.0, phosphate removal efficiency was low. When the initial pH was 4–12, phosphate removal efficiency gradually increased to 100%. This phenomenon has also been observed during phosphate removal by other La-based P-removal agents [38]. The variation of the phosphate species in the aqueous solution could influence the phosphate removal efficiency of La$^{3+}$/CPAM/Fe$_3$O$_4$. Based on the phosphate species distribution vs. the pH, some of the H$_3$PO$_4$ was present in the aqueous solution at pH = 3. However, the H$_3$PO$_4$ state could not be effectively loaded onto the La$^{3+}$/CPAM/Fe$_3$O$_4$. As the pH increased from 3 to 7, the H$_3$PO$_4$ was gradually converted into monovalent H$_2$PO$_4^-$ species, and the H$_2$PO$_4^-$ could rapidly combine with La$^{3+}$/CPAM/Fe$_3$O$_4$. The combination could form P-containing magnetic insolubles, which improved the phosphate removal efficiency [30]. As the pH was increased to 11, the quantity of HPO$_4^{2-}$ species decreased and the quantity of HPO$_4^{2-}$ species increased. The corresponding ligand binding between HPO$_4^{2-}$ and La$^{3+}$/CPAM/Fe$_3$O$_4$ was strengthened, and an intra-spherical phosphate complex was formed [28]. When the pH was increased to 12, the phosphate removal efficiency of La$^{3+}$/CPAM/Fe$_3$O$_4$ decreased. This result was attributed to the increased content of OH$^-$ groups competing with HPO$_4^{2-}$ to bind with the active sites of La$^{3+}$/CPAM/Fe$_3$O$_4$, thereby weakening the coordination between HPO$_4^{2-}$ and La$^{3+}$/CPAM/Fe$_3$O$_4$. 

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Fig. 5. (a) Magnetic separation of La$^{3+}$/CPAM/Fe$_3$O$_4$ under external magnetic field, (b) magnetic hysteresis loops of CPAM/Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$, and (c) magnetic separation of La$^{3+}$/CPAM/Fe$_3$O$_4$ under an external magnetic field.

Fig. 6. XRD patterns of Fe$_3$O$_4$ and La$^{3+}$/CPAM/Fe$_3$O$_4$. 

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3.5. Effects of coexisting ions

Potentially competing anions such as Cl\(^-\), HCO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), and NO\(_3\)\(^-\) are present in natural water, and these anions could interfere with the phosphate removal efficiency of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\). Therefore, to evaluate the selectivity of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) for phosphate, the influences of various anions on phosphate removal efficiency were studied, and the results are presented in Fig. 8. As the molar ratios of phosphate to Cl\(^-\), SO\(_4\)\(^{2-}\), and NO\(_3\)\(^-\) increased to 1:100, the phosphate removal efficiency of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) slightly decreased. This was because the three anions competed with the phosphate ions for the active sites of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\), thereby reducing phosphate removal efficiency [39]. In addition, the increase in the HCO\(_3\)\(^-\) concentration had a positive effect on the phosphate removal efficiency of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\). This may have been because a high NaHCO\(_3\) concentration caused an increase in the electric potential at the interface, which promoted the combination of the negatively charged phosphate anions with La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) and was thus favorable for the magnetic separation. Moreover, sodium bicarbonate is the salt of a strong alkali weak acid, and its solution is alkaline [33,38]. Thus, the pH of the reaction system increased with the increase in the sodium bicarbonate concentration, which may have affected the existence state of phosphate and ultimately the phosphate removal efficiency of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\). Therefore, the strong selectivity of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) to phosphate in natural water was conducive to the magnetic separation of phosphate, which further supports the application potential of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) in natural water.

3.6. Influence of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) dosage

To investigate the influence of the La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) dosage on phosphate removal efficiency, a test was conducted with an La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) dosage of 0.25–4.75 g/L, initial phosphate concentration of 50 mg/L, initial pH of 7, and contact time of 30 min (Fig. 9). By increasing the La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) dosage, the removal efficiency of phosphate increased. This was due to an increase in the number of lanthanum ions that could react with the phosphate. As shown in Fig. 9, with an increase in the dosage from 0.25 to 3.75 g/L, phosphate removal efficiency increased from 36.5% to 90.07%. As the dosage of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) increased from 3.75 to 4.75 g/L, the removal efficiency of phosphate was not altered. This was mainly attributed to the precipitation reaction between La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) and the phosphate reaching saturation. Since the dosage of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) in the aqueous solution was constant, not all the lanthanum ion reacted with the phosphate. Furthermore, as the La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) dosage was increased, the removal efficiency of phosphate was reduced. When the dosage of La\(^3+\)/CPAM/Fe\(_3\)O\(_4\) was in excess, the residual pH of solution changed, and the amount of phosphate decreased [40].
3.7. Effect of reaction time and phosphate concentration

The effects of the reaction time and initial phosphate concentration on the phosphate removal efficiency of La\(^{3+}/\)CPAM/Fe\(_3O_4\) were investigated, and the results are presented in Fig. 10. The tests were performed with a reaction time in the range of 5–40 min, an initial phosphate concentration of 10–60 mg/L, an La\(^{3+}/\)CPAM/Fe\(_3O_4\) dose of 3.75 g/L, and an initial pH of 7. Based on the results, the trends of phosphate removal efficiency were similar for all initial phosphate concentrations. By increasing the reaction time, the removal efficiency of the phosphate was performed quickly. However, after 20 min, phosphate removal efficiency was almost constant and did not change significantly. The initially high removal efficiency was attributed to the phosphate in the solution having sufficient time to react with La\(^{3+}/\)CPAM/Fe\(_3O_4\). By increasing the reaction time, the precipitation reaction between the La\(^{3+}/\)CPAM/Fe\(_3O_4\) and phosphate reached saturation. The optimal reaction time for the removal of phosphate was determined to be 20 min. Fig. 10 shows that the phosphate removal efficiency of La\(^{3+}/\)CPAM/Fe\(_3O_4\) was gradually decreased by increasing the initial phosphate concentration. Due to the chemical relationship between the phosphate and P-removal agent, an increase in the phosphate concentration would cause the chemical reaction to reach saturation. After reaching saturation, excess phosphate could not be combined with the La\(^{3+}/\)CPAM/Fe\(_3O_4\). This result agrees with previous literature [40].

4. Conclusion

In this study, a magnetic composite P-removal agent was synthesized by aqueous solution polymerization, and magnetic separation of the phosphate from the aqueous solution was achieved. The optimal magnetic composite P-removal agent was prepared with a reaction time of 4 h, a reaction temperature of 65°C, and a metal salt content of 12.96 mmol. Nine types of agents were prepared by changing the types of metal salts (i.e., Zn\(^{2+}\), Cu\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\), Zr\(^{4+}\), Y\(^{3+}\), Ce\(^{4+}\), and La\(^{3+}\)), and the optimal agent was determined to be La\(^{3+}/\)CPAM/Fe\(_3O_4\) based on phosphate removal efficiency. The FT-IR and XPS analysis results showed that La\(^{3+}/\)CPAM/Fe\(_3O_4\) featured a combination of La–O and Fe–O, indicating that it was successfully prepared. The TEM analysis results showed that the optimal product had a core–shell structure. In addition, the VSM results demonstrated that La\(^{3+}/\)CPAM/Fe\(_3O_4\) exhibited a better magnetic response compared to other agents, and it could be separated from natural water under the action of an external magnetic field. Moreover, it could greatly reduce the P concentration, with phosphate removal efficiency reaching 90.07%. It also showed good selectivity to phosphate in the presence of competing anions commonly present in natural water. Overall, synthesized La\(^{3+}/\)CPAM/Fe\(_3O_4\) is a promising material for the magnetic separation of phosphate, which could change the source-to-sink conversion of P in natural water and prevent the risk of eutrophication.

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References


[38] L. Lai, Q. Xie, L. Chi, W. Gu, D. Wu, Adsorption of phosphate from water by easily separable Fe₃O₄@SiO₂ core/shell magnetic nanoparticles functionalized with hydrolys lanthanum oxide, J. Colloid Interface Sci., 465 (2016) 76–82.
