Research on recovery of phosphorus in high concentrations of phosphorus wastewater by struvite precipitation

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ABSTRACT

Struvite is an efficient slow-release compound fertilizer. Struvite precipitation method can not only remove phosphorus in wastewater, but also can recycle phosphorus in waste water and solve resource shortages problem. This article researches the effect of pH, contact time reaction, three crystal ions structures (Mg²⁺, NH₄⁺, PO₄³⁻) ratio and Ca²⁺ on struvite precipitation and precipitation ingredients. The results show that when the pH was 9.5, the exposure reaction time was 20 min, the molar ratio of Mg²⁺:NH₄⁺:PO₄³⁻ was 1.2:2:1, and the molar ratio of Mg²⁺:Ca²⁺ is 1:0.5 or more, the phosphorus removing and recycling effect on high concentration of phosphorus wastewater is remarkable.

Keywords: influence factors; phosphorus recycling; struvite; wastewater with high concentration of phosphorus

INTRODUCTION

Phosphorus is a valuable resource for its non-renewable, which is also the key factor of leading to eutrophication [1-2]. Struvite is an efficient slow-release compound fertilizer[3]. Struvite precipitation method can not only remove phosphorus in wastewater, but also recycle wastewater phosphorus, solve shortage of resource problem[4]. Therefore, struvite precipitation becomes the research focus of removal and recovery phosphorus in wastewater.

There are adsorption, biological, struvite precipitation methods, and etc to remove and recover phosphorus in wastewater currently [5]. The adsorbent requires regular replacement because the adsorbent soon reaches adsorption saturation on treating high concentrations of wastewater, which results higher processing cost. So it is not appropriate for treating high concentrations wastewater[6]. High concentrations of nitrogen and phosphorus wastewater are unsuitable for adopting biological methods, because high concentrations of ammonia nitrogen and phosphorus will produce inhibition to the activity of microbial. And biological treatment would discharge large amounts of excess sludge [7]. Though struvite precipitation[8,9] needs a lot of chemicals, high cost, however it can be used as pretreatment of biotechnology to reduce the pressure of high concentrations of nitrogen and phosphorus to biological method. At the same time, it can recycle ammonia nitrogen and phosphorus and other elements in wastewater. Struvite precipitation method is simple process, high phosphorus removal efficiency, easy operation and etc. Brisbane, Australia Oxley Creek Wastewater Treatment Plant[7] and UK Slough STW sewage treatment plant[10] and etc are equipped with struvite precipitation device. And the recycled struvite precipitation has been produced into fertilizer and sold on the market. As we can see, struvite precipitation nutrient removal process has broad application prospects. Therefore, it has practical significance to make further research of mechanism, influencing factors and application methods on struvite precipitation.

This article synthesizes existing research and further investigates the effect on pH, contact time reaction, three crystal
ion ratio and Ca$^{2+}$ on the precipitated product ingredients and phosphorus recovery (PRE). This research will provide some basis for the recycling of phosphorus from wastewater with high concentrations of phosphorus.

**EXPERIMENTAL SECTION**

**Materials**

K$_2$HPO$_4$·12H$_2$O, NH$_4$Cl, MgCl$_2$·6H$_2$O, CaCl$_2$ and NaOH were of analytical grade. Simulated wastewater is K$_2$HPO$_4$·12H$_2$O of 80 mg/L, and add a certain amount of NH$_4$Cl and MgCl$_2$·6H$_2$O for close to the actual wastewater pollutants.

**Operation Methods**

(1) Make the reaction ratio (mole ratio, hereinafter the same) of Mg$^{2+}$:NH$_4^+$:PO$_4^{3-}$ to be 1:1:1, and stir for 10 min at the rate of 100 rpm, and add dropwise NaOH of 1 mol/L at the 0.10 ml/s flow to make pH of reaction system from 7.5 to 10.5, and stand for 30 min to completely precipitate. Residual PO$_4^{3-}$ concentration after the reaction in solution was measured. The precipitate filtered baked for 48 h at a temperature of 40°C in drying oven. The composition of crystalline product is tested.

(2) Make the reaction ratio of Mg$^{2+}$:NH$_4^+$:PO$_4^{3-}$ to be 1:1:1, and add dropwise 1 mol/L NaOH to keep the pH of reaction system to be 9.5. Stir respectively for 10 min, 20 min and 30 min at the rate of 100 rpm, and stand for 30 min to complete precipitation. Residual concentration of Mg$^{2+}$, NH$_4^+$, PO$_4^{3-}$ in solution are measured after the reaction. The composition of crystalline product is tested.

(3) Add dropwise 1 mol/L NaOH to keep the pH of reaction system to be 9.5. Stir for 20 min at the rate of 100 rpm. Make the reaction ratio of Mg$^{2+}$:NH$_4^+$:PO$_4^{3-}$ to be 1:1:1, 1.2:1:1, 1.4:1:1, 1:2:1, 1.2:2:1, 1.4:2:1 to test the effect of the reaction ratio of Mg$^{2+}$:NH$_4^+$:PO$_4^{3-}$ on the removal of Mg$^{2+}$, NH$_4^+$, PO$_4^{3-}$. 

(4) Make the reaction ratio of Mg$^{2+}$:NH$_4^+$:PO$_4^{3-}$ to be 1.2:2:1. Stir for 10 min at the rate of 100 rpm. Adding dropwise 1 mol/L NaOH to keep the pH of reaction system to be 9.5. Making the reaction ratio of Mg$^{2+}$:Ca$^{2+}$ to be 1:0.2, 1:0.5, 1:0.8, 1:1 to test the effect of the reaction ratio of Mg$^{2+}$:Ca$^{2+}$ on the removal of PO$_4^{3-}$.

**Analysis methods**

The concentration of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ were measured by the standard methods [11]. pH was measured by a sensION378 meter (Hach, USA). The composition of crystalline product was measured by PW040/60 X-ray diffraction (DANALYTICAL BV, Netherlands).

**RESULTS AND DISCUSSION**

**Effect of pH on Struvite precipitation reaction**

Studies suggest that struvite is most likely precipitation when the pH is 8–10, and the pH is gradually reduced during reaction process of struvite precipitation[12]. Fig. 1 shows the PRE changes in different pH. Fig. 1 shows that the recovery of phosphorus increases significantly. The recovery is 11% when the pH is 7.5, and it is 38% when the pH is 8.5. The recovery is 52% when the pH is 9.5, and it is 58% when the pH is 8.5. The reaction gradually stabilized when pH is about 9.5 and it is insignificant to improve PRE by adding NaOH. There is certain significance in improving economic efficiency, to reduce the harm caused by excessive use of chemical terms.

![Fig.1 Impact of pH for PRE](image-url)
Fig. 2. Fig. 3 and Fig. 4 shows X-Ray Diffraction (XRD) pattern of precipitate in different pH. C, D and E were the precipitate characteristic diffraction peaks when pH was 8.5, 9.5 or 10.5, respectively. X is the characteristic diffraction peaks of struvite (MgNH$_4$PO$_4$·6H$_2$O). Y is the characteristic diffraction peaks of Mg$_3$(PO$_4$)$_2$·22H$_2$O. Z is the characteristic diffraction peaks of Mg(OH)$_2$.

Fig. 2 Precipitate XRD picture when pH is 8.5

Fig. 3 Precipitate XRD picture when pH is 9.5

Fig. 4 Precipitate XRD picture when pH is 10.5

Fig. 2 shows that the resultant composition is almost entirely struvite when pH is 8.5, and almost precipitated in 10 min. But the production amount is small. Fig. 3 shows that the most product is MgNH$_4$PO$_4$·6H$_2$O with a little Mg$_3$(PO$_4$)$_2$·22H$_2$O. Fig. 4 shows that the precipitate component is a mixture of MgNH$_4$PO$_4$·6H$_2$O, Mg$_3$(PO$_4$)$_2$ and Mg(OH)$_2$. From the above analysis we can conclude when pH is 8.5, though the react is much faster and the product is much purer, the reaction is not complete and phosphorus in wastewater cannot be effectively removed. When pH is 10.5, the product is more and the reaction is complete. However, the purity of struvite recovery is poor. In short, pH=9.5 is the most suitable condition for removing and recovering phosphorus from wastewater.
Influence of contact time to struvite precipitation

Table 1 shows the removal of three crystal ions structures in different reaction time. It shows that with reaction time increasing, the removal rate the crystal structures of three ions increased significantly. When the reaction time range from 10 min to 20 min, PO$_4^{3-}$, Mg$^{2+}$, NH$_4^+$ removal rates were increased by 8.6%, 12.2%, 5.9%. When the reaction time range from 20 min to 30 min, PO$_4^{3-}$, Mg$^{2+}$, NH$_4^+$ removal rates were increased by 2.1%, 4.4%, 2.8%. And when the reaction time is 20 min, PO$_4^{3-}$, Mg$^{2+}$, NH$_4^+$ removal rates were increased by 49.5%, 73.1%, 25.6%. It can be seen that 20 min is the best response time for the reaction system.

Table 1 The removal rate of the three constituted ions in different reacted times (%)

<table>
<thead>
<tr>
<th></th>
<th>10min</th>
<th>20min</th>
<th>30min</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO$_4^{3-}$</td>
<td>40.9</td>
<td>49.5</td>
<td>51.6</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>60.9</td>
<td>73.1</td>
<td>77.5</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>19.7</td>
<td>25.6</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Fig. 5, Fig. 6 and Fig. 7 shows XRD pattern of precipitate in time of 10 min, 20 min and 30 min. B, C, D and E were the precipitate characteristic diffraction peaks when pH was 7.5, 8.5, 9.5 or 10.5, respectively. X is the characteristic diffraction peaks of struvite (MgNH$_4$PO$_4$·6H$_2$O). Y is the characteristic diffraction peaks of Mg$_3$(PO$_4$)$_2$·22H$_2$O. Z is the characteristic diffraction peaks of Mg(OH)$_2$. Fig. 5 shows that all the precipitation were struvite when pH is 7.5, 8.5, 9.5 and 10.5. Fig. 6 shows that it generates high purity struvite when pH is 8.5 and 9.5. And it has a strong Mg(OH)$_2$ diffraction peaks which indicated many Mg(OH)$_2$ were generates under pH of 10.5. Fig. 7 shows that it generates high purity struvite when pH is 7.5 and 8.5, and it is containing a small amount of Mg$_3$(PO$_4$)$_2$·22H$_2$O in the precipitate under pH of 9.5. It means that reaction time of 20 min is the most suitable reaction conditions under the pH of 8.5 or 9.5.
Influence of three configurations crystal ion ratio on the reaction of struvite precipitation

In the formation of struvite, $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio should be 1:1:1 in theory. Appropriate increase in $\text{NH}_4^+$ and $\text{Mg}^{2+}$ can promote the formation of the crystallization product and improve the recovery of phosphorus according to the chemical reaction principle. Table 2 shows the changes in the concentration of the three configurations ions crystal when the concentration ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ is different. Table 2 shows that the removal rate of $\text{Mg}^{2+},\text{NH}_4^+,\text{PO}_4^{3-}$ increase gradually when keeping the proportional of $\text{NH}_4^+:\text{PO}_4^{3-}$ and raising $\text{Mg}^{2+}$ gradually. That means the removal efficiency of the three ions can be increased by raising the concentration of $\text{Mg}^{2+}$ appropriate. The total $\text{Mg}^{2+}$ concentration in the wastewater, however, is still to increase due to the smaller increase in $\text{Mg}^{2+}$ removal. Besides resulting in increasing of water salinity, $\text{Mg}^{2+}$ can produce $\text{Mg(OH)}_2$ precipitate which will mix with $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ together when pH is in high, which makes the subsequent processing to be harder[10,12,13]. Removal rate of $\text{Mg}^{2+},\text{NH}_4^+,\text{PO}_4^{3-}$ increase gradually when keeping the proportional of $\text{Mg}^{2+}:\text{PO}_4^{3-}$ and raising $\text{NH}_4^+$ (raise to 2 from 1) gradually. That means that the greater the concentration of wastewater, the greater $\text{NH}_4^+$ removal capacity. The removal rate of $\text{PO}_4^{3-}$ increase gradually when keeping the proportion of $\text{PO}_4^{3-}$ and raising the proportion of $\text{Mg}^{2+}:\text{NH}_4^+$ gradually. Therefore, the best proportion of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ is 1.2:2:1. The removal rates of $\text{NH}_4^+,\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ under the proportion of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}=1.2:2:1$ were 2.7 times, 1.2 times and 1.3 times than that under the proportion of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}=1:1:1$.

<table>
<thead>
<tr>
<th>$\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$</th>
<th>$\text{NH}_4^+$</th>
<th>$\text{Mg}^{2+}$</th>
<th>$\text{PO}_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:1</td>
<td>0.56</td>
<td>0.68</td>
<td>0.64</td>
</tr>
<tr>
<td>1.2:1:1</td>
<td>0.63</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td>1.4:1:1</td>
<td>0.67</td>
<td>0.97</td>
<td>0.89</td>
</tr>
<tr>
<td>1:2:1</td>
<td>1.49</td>
<td>0.80</td>
<td>0.83</td>
</tr>
<tr>
<td>1.2:2:1</td>
<td>1.52</td>
<td>0.84</td>
<td>0.85</td>
</tr>
<tr>
<td>1.4:2:1</td>
<td>1.52</td>
<td>1.12</td>
<td>0.90</td>
</tr>
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Influence of $\text{Ca}^{2+}$ on the reaction of struvite precipitation

$\text{Ca}^{2+}$ forming calcium phosphate with $\text{PO}_4^{3-}$ or interfering the process of struvite crystals to affect precipitation reaction, which change the nature of struvite[14]. Table 3 shows the PRE change when the ratio of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ is different. It shows that PRE does not change significantly and is more than 90% when the ratio of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ is different. It means adding $\text{Ca}^{2+}$ has no obvious effect on PRE.

<table>
<thead>
<tr>
<th>$\text{Mg}^{2+}:\text{Ca}^{2+}$ molar ratios</th>
<th>PRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.2</td>
<td>93.6%</td>
</tr>
<tr>
<td>1:0.5</td>
<td>94.5%</td>
</tr>
<tr>
<td>1:0.8</td>
<td>92%</td>
</tr>
<tr>
<td>1:1</td>
<td>94.4%</td>
</tr>
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</table>

Increasing $\text{Ca}^{2+}$ in the solution will not have a significant impact on the recovery of phosphorus, but precipitate XRD analysis shows that the $\text{Ca}^{2+}$ in the solution can affect the product composition. Fig. 8 is a precipitated product XRD pattern and standard atlas of $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ when $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ are in different response ratios. In Fig. 8, the main component of the product is precipitated struvite when $\text{Mg}^{2+}:\text{Ca}^{2+}$ is 1:0.2 or 1:0.5. The precipitated product is
amorphous calcium phosphate salt when Mg\textsuperscript{2+}:Ca\textsuperscript{2+} range is from 1:0.2 to 1:1. There is no significant change on the recovery of phosphorus under different proportion of Mg\textsuperscript{2+}:Ca\textsuperscript{2+}, but the composition of precipitated product is different. Ca\textsuperscript{2+} competes with Mg\textsuperscript{2+} to catch phosphate in solution to form amorphous substances and cover the surface of the struvite precipitation, which interferes with the process of struvite precipitation. Therefore, when concentration of Mg\textsuperscript{2+} in solution is at least 2 times of Ca\textsuperscript{2+} concentration in solution, the pure struvite can be obtained.

![Figure 8 XRD of crystallized precipitation in different Mg\textsuperscript{2+}:Ca\textsuperscript{2+} molar ratios and the standard picture of MgNH\textsubscript{4}PO\textsubscript{4}·6H\textsubscript{2}O](image)

**CONCLUSION**

This study suggests that the removal of phosphorus in high concentrations of phosphorus wastewater by struvite precipitation method is significant. When the pH is 9.5, reaction contact time is 20 min, molar ratio of Mg\textsuperscript{2+}:NH\textsubscript{4}+:PO\textsubscript{4}\textsuperscript{3-} is 1.2:2:1 and molar ratio of Mg\textsuperscript{2+} and Ca\textsuperscript{2+} is 1:0.5 or more, purer struvite can be recovered. Meanwhile, this study provides a basis for recycling phosphorus in waste water with high concentrations of phosphorus.

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