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Research Article

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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 (Mg^{2+}, NH_4^+, PO_4^{3-}) ratio and Ca^{2+}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 Mg^{2+}:NH_4^+:$PO_4^{3-}$was 1.2:2:1, and the molar ratio of Mg^{2+}:Ca^{2+} 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

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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 regularreplacement because the adsorbent soon reaches adsorption saturation on treating high concentrations of wastewater, which results higher processing cost. So it is not appropriatefor 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

$K_2HPO_4\cdot 12H_2O$, NH_4Cl, $MgCl_2\cdot 6H_2O$, $CaCl_2$ and NaOH were of analytical grade. Simulated wastewater is $K_2HPO_4\cdot 12H_2O$ of 80 mg/L, and add a certain amount of NH_4Cl and $MgC1_2\cdot 6H_2O$ 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 dropwiseNaOH 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 ^oC in dryingoven. 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 dropwise1 mol/LNaOH 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) Adddropwise1 mol/LNaOH 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 (DANALYTICALB.V, Netherlands).

RESULTS AND DISCUSSION

Effect of pH on Struvite precipitation reaction

Studies suggest thatstruvite 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.

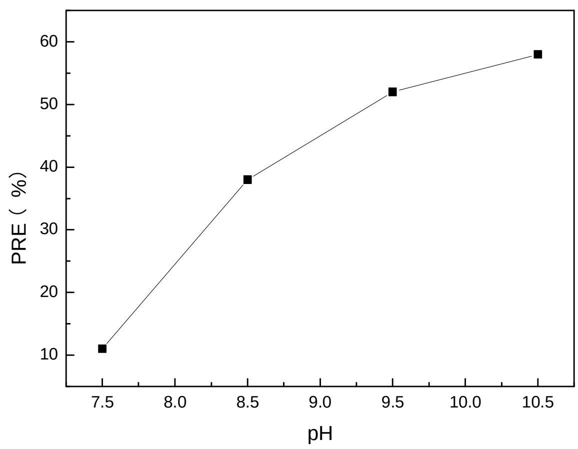


Fig.1 Impact of pH for PRE

Fig. 2, Fig. 3 and Fig. 4 shows X-Ray Diffraction (XRD) pattern of precipitate in different pH. C, D and Ewere the precipitate characteristic diffraction peaks when pH was8.5, 9.5 or10.5, respectively.X is the characteristic diffraction peaks of struvite ($MgNH_4PO_4 \cdot 6H_2O$). Y is the characteristic diffraction peaks of $Mg_3(PO_4)_2 \cdot 22H_2O$. Z is the characteristic diffraction peaks of $Mg(OH)_2$.

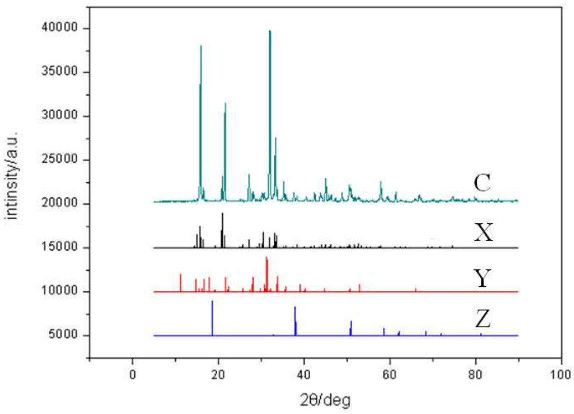


Fig.2 Precipitate XRD picture when pH is 8.5

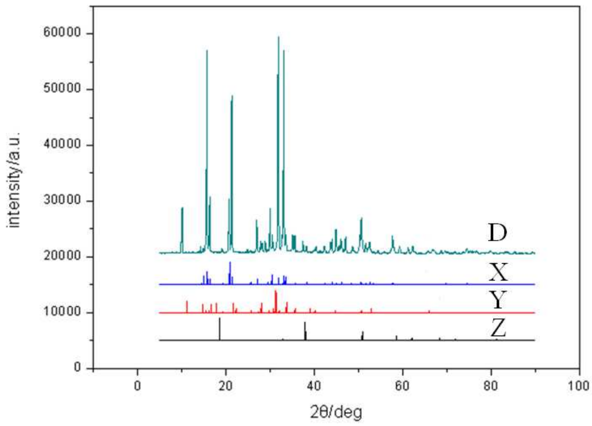


Fig.3 Precipitate XRD picture when pH is 9.5

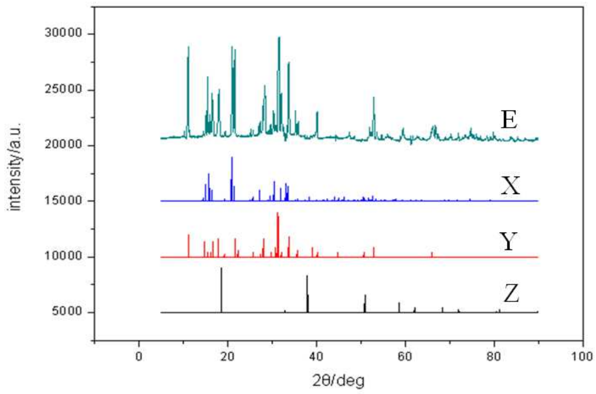


Fig.4 Precipitate XRD picture when pH is 10.5

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 $MgNH_4PO_4 \cdot 6H_2O$ with a little $Mg_3(PO_4)_2 \cdot 22H_2O$. Fig. 4 shows that the precipitate component is a mixture of $MgNH_4PO_4 \cdot 6H_2O$, $Mg_3(PO4)_2$ 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 andphosphorusin 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%.Andwhen the reaction time is 20 min, PO_4^{3-}, Mg^{2+}, NH_4^+ removal rates were increased by49.5%、73.1%、25.6%. It can be seen that 20 min is the best response time for the reaction system.

Table1 The removal rate of the three constituted irons in different reacted times（%）

	10min	20min	30min
PO_4^{3-}	40.9	49.5	51.6
Mg^{2+}	60.9	73.1	77.5
NH_4^+	19.7	25.6	28.4

Fig. 5, Fig. 6 and Fig. 7 shows XRD pattern of precipitate in time of 10min,20min and 30min. 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 ($MgNH_4PO_4 \cdot 6H_2O$). Y is the characteristic diffraction peaks of $Mg_3(PO_4)_2 \cdot 22H_2O$. 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 $Mg_3(PO_4)_2 \cdot 22H_2O$ 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.

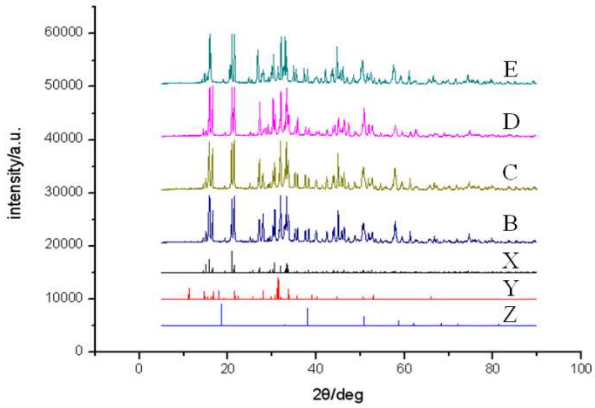


Fig.5 Precipitate XRD picture when time is 10 min

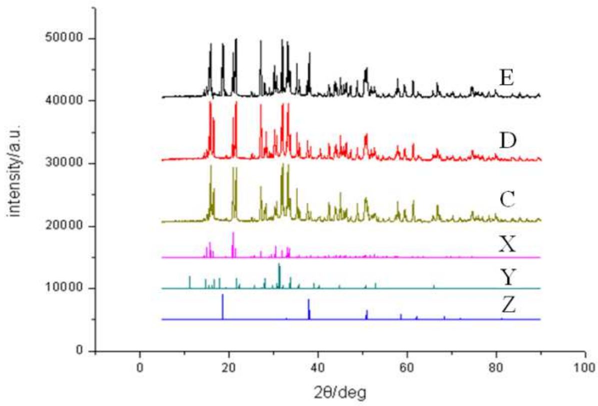


Fig. 6 Precipitate XRD picture when time is 20 min

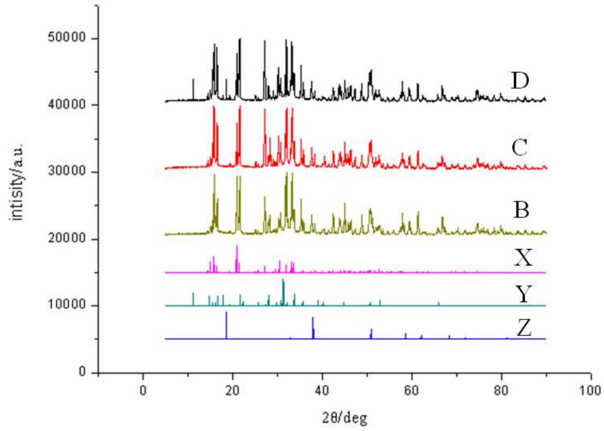


Fig.7 Precipitate XRD picture when time is 30 min

Influence of three configurations crystal ion ratio on the reaction of struvite precipitation

In the formation of struvite, Mg^{2+}:NH_4^+:PO_4^{3-}ratio should be 1:1:1 in theory. Appropriate increase in NH_4^+ and Mg^{2+} can promote the formation of the crystallization product and improve the recovery of phosphorus according to the chemical reaction principle. Table2 shows the changes in the concentration of the three configurations ions crystal when the concentration ratio of Mg^{2+}:NH_4^+:PO_4^{3-} is different. Table 2 shows that the removal rate of Mg^{2+},NH_4^+,PO_4^{3-} increase gradually when keeping the proportional of NH^{4+}:PO_4^{3-} and raising Mg^{2+} gradually. That means the removal efficiency of the three ions can be increased by raising the concentration of Mg^{2+} appropriate. The total Mg^{2+} concentration in the wastewater, however, is still to increase due to the smaller increase in Mg^{2+} removal.Besides resulting in increasing of water salinity, Mg^{2+} can produce $Mg(OH)_2$ precipitate which will mix with $MgNH_4PO_4\cdot 6H_2O$ together when pH is in high, which makes the subsequent processing to be harder[10,12,13].Removal rate of Mg^{2+},NH_4^+,PO_4^{3-} increase gradually when keeping the proportional of Mg^{2+}:PO_4^{3-} and raising NH^{4+}(raise to 2 from 1)gradually. That means that the greater the concentration of wastewater, the greater NH_4^+ removal capacity. The removal rate of PO_4^{3-} increase gradually when keeping the proportion of PO_4^{3-} and raising the proportion ofMg^{2+}:NH^{4+}gradually. Therefore, the best proportion of Mg^{2+}:NH_4^+:PO_4^{3-} is 1.2:2:1. The removal rates of NH_4^+,Mg^{2+} and PO_4^{3-}under the proportion of Mg^{2+}:NH_4^+:PO_4^{3-}=1.2:2:1 were 2.7 times, 1.2 times and 1.3 times than that under the proportion of Mg^{2+}:NH_4^+:PO_4^{3-}=1:1:1.

Table2 Reacted concentration of the three constituted ions in Mg^{2+}:NH_4^+:PO_4^{3-}

Mg^{2+}:NH^{4+}:PO_4^{3-}	NH^{4+} (mmol/L)	Mg^{2+}(mmol /L)	PO_4^{3-} (mmol/L)
1:1:1	0.56	0.68	0.64
1.2:1:1	0.63	0.76	0.77
1.4:1:1	0.67	0.97	0.89
1:2:1	1.49	0.80	0.83
1.2:2:1	1.52	0.84	0.85
1.4:2:1	1.52	1.12	0.90

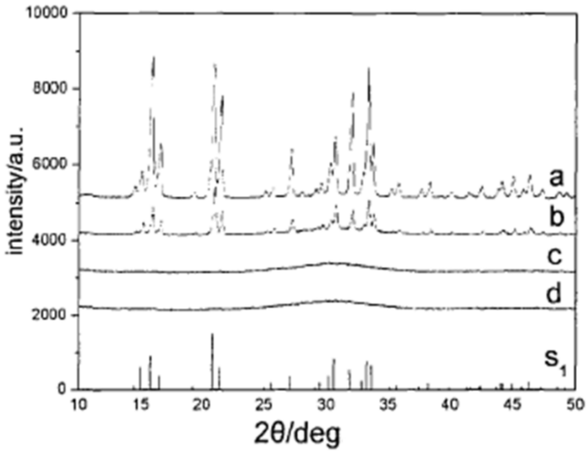
Influence of Ca^{2+} on the reaction of struvite precipitation

Ca^{2+} forming calcium phosphate with 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 Mg^{2+} and Ca^{2+} is different. It shows that PRE does not change significantly and is more than 90% when the ratio of Mg^{2+} and Ca^{2+} is different. It means adding Ca^{2+} has no obvious effect on PRE.

Table3 Changes of PRE in different Mg^{2+}:Ca^{2+} molar ratios

Mg^{2+} :Ca^{2+}	PRE
1:0.2	93.6%
1:0.5	94.5%
1:0.8	92%
1:1	94.4%

Increasing Ca^{2+} in the solution will not have a significant impact on the recovery of phosphorus, but precipitate XRD analysis shows that the Ca^{2+} in the solution can affect the product composition. Fig. 8 is a precipitated product XRD pattern and standard atlas of $MgNH_4PO_4\cdot 6H_2O$ when Mg^{2+} and $Ca^{2+}$are in different response ratios. In Fig. 8, the main component of the product is precipitated struvite when Mg^{2+}:Ca^{2+} is 1:0.2 or 1:0.5.The precipitated product is amorphouscalcium phosphatesalt when Mg^{2+}:Ca^{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^{2+}:Ca^{2+}, but the composition of precipitated product is different.Ca^{2+}competes withMg^{2+} to catch phosphatein solution to form amorphous substances and cover the surface of the struvite precipitation, whichinterferes with the process of struvite precipitation. Therefore, when concentration of Mg^{2+} in solution is at least 2 times of Ca^{2+} concentration in solution, thepure struvite can be obtained.



a-Mg^{2+}:Ca^{2+}=1:0.2; b-Mg^{2+}:Ca^{2+}=1:0.5; c-Mg^{2+}:Ca^{2+}=1:0.8; d-Mg^{2+}:Ca^{2+}=1:1;S_1-the standard picture of $MgNH_4PO_4$·$6H_2O$

Fig.8 XRD of crystallized precipitation in different Mg^{2+}:Ca^{2+} molar ratios and the standard picture of $MgNH_4PO_4 \cdot 6H_2O$

CONCLUSION

This study suggests that the removal of phosphorus in high concentrations of phosphorus wastewater by struvite precipitationmethod is significant.When the pH is 9.5, reaction contact time is 20 min, molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} is 1.2:2:1 and molar ratio of Mg^{2+} and Ca^{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.

Acknowledgements

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REFERENCES

[1] NUma Maheswar;GSathiyavani, *J. Chem. Pharm. Res.*,**2012**, 4(8), 4007-4011.
[2] YS Liu;HJHan, *J. Chem. Pharm. Res.*,**2014**, 6(4), 401-405.
[3] K Yetilmezsoy; Z Sapci-Zengin,*J. Hazard. Mater.*,**2009**, 166(1), 260-269.
[4] M Iqbal; H Bhyiyan; DS Mavinic,E*nvironmental Technology*, **2008**, 29(11), 1157-1167.
[5] XJ Yu; YG Chen; GW Gu,*Environmental Science & Technology*, **2008**,31(11),17-19.
[6] QQ Cai; J Liu; Y Jiang; TY Dong,*Environmental Science and Management*,**2008**,33(07),92-94.
[7] EV Münch;K Barr,*Water Res.*, **2001**, 35(01),151-159.
[8] T Zhang;LLDing;HQRen;ZT Guo; J Tan,*J. Hazard. Mater.*, **2010**, 176(1-3),444-450.
[9] JM Ebeling;PL Sibrell;SR Ogden;ST Summerfelt,*Aquacultural Engineering*, **2003**, 29(1-2),23-42.
[10] Y Mitani;Y Sakai;F Mishina;S Ishiduka,*Journal of Water and Environment Technology*,**2003**,1(01),13-18.
[11] APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater, 19th Edition, APHA/AWWA/WEF, Washington DC, **1995**.
[12] QL Zeng; CH Shen,*Environmental Science & Technology*, **2011**, 35(1),80-83.
[13] T Mino;MCMVan Loosdrecht;JJ Heijnen,*Water Res.*, **1998**, 32(11), 3193-3207.
[14] LJ Yuan; XL Zhang,*Environmental Science*, **2004**, 25(6),92-96.