

Crystallization and phosphorus removal from anaerobic effluent in A/O alternant biofilters

Hongtao Cheng^{1,a}, Liping Qiu^{1,b*}, Shoubin Zhang^{1,c}, Jiabin Wang^{1,d}, Kang Xie^{1,e}

¹School of Civil Engineering and Architecture, University of Jinan, No.336. West Road of Nan Xinzhuang. Jinan250022, PR China

1206384223@qq.com, cea_qiulp@ujn.edu.cn, cea_zhangsb@ujn.edu.cn,
cea_wangjb@ujn.edu.cn, cea_xiek@ujn.edu.cn,

*Corresponding Author

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Abstract: In order to reveal the influence of reaction conditions on the phosphorus crystallization to recover phosphorus from wastewater with low P concentration, an alternate A/O biofiltration system for simulated domestic wastewater treatment was carried out and the effluent from anaerobic filter was considered as the reaction liquid for P crystallization, as well as the influences of phosphorus by beginning phosphorus concentration, pH, Mg/P molar ratio and reaction time on the MAP crystallization and P removal were test systemlly. The results showed that the pH is the main influence factor on the crystallization time, and the higher pH value, the shorter crystallization time. Under the condition of the low P concentration, the key factor of the crystallization phosphorus removal rate is the Mg/P. Improve the Mg/P molar ratio mghit increase the phosphorus removal rate greatly. In addation, when the Mg/P molar ratio is 1:1 and the reaction time is 10 minutes, the lowest crystallization concentration is 18mg/L.

Introduction

In recent years, a large number of nitrogen and phosphorus of other plant nutrients waste water discharged into surface water, which brings a serious eutrophication problem, in which the effect of phosphorus on the growth of algae is much greater than that of nitrogen^[1]. Research shows that the discharge of 1g phosphorus to the sewage will lead to 950g (dry weight) algae growth, therefore, the restriction of phosphorus emissions is more and more stringent from around the world. At the same time, phosphorus is a kind of irreplaceable and limited resources^[2] because of excessive exploitation and use, is gradually facing the depletion. Mining at the current exploitation rate, high grade phosphate rock in the earth's crust ($P_2O_5 > 15\%$) will be exhausted in 100 years^[3], therefore, phosphorus recovery from wastewater is extremely has the prospects for the development of wastewater treatment technology. The crystallization method is the only one that can remove phosphorus from wastewater and the phosphorus removal technology^[2]. At present, there is less research on the crystallization of MAP with low concentration of phosphorus in domestic wastewater. But the total amount of sewage accounted for a large amount of sewage, if it can be a waste of life in the phosphorus in the form of MAP crystal, will produce greater social value. This paper mainly aimed at the low phosphorus wastewater sewage concentration, on the crystallization of MAP removal.

Test materials and methods

Test reagents and instruments

Reagents: KH_2PO_4 , NH_4Cl , $MgSO_4$, etc., all of the reagents are analytical pure.

Instrument: 85-2 constant temperature magnetic stirrer, PB-10 meter, laser power receiver, spectrum analysis of ultraviolet visible spectrophotometer.

Test water quality

This experiment mainly uses synthetic wastewater, sewage water quality characteristics of simulation, study under such conditions map of phosphorus crystallization effect, the specific composition and the corresponding concentration is as follows in Table 1 below.

Table 1 Water quality of test

Project	COD mg/L	Ammonia nitrogen mg/L	Phosphorus mg/L	pH
concentration range	260~350	35~40	9~11	6.8~7.5

Table 1 illustrates the content of phosphorus is low, and magnesium ammonium phosphate standard solubility product is relatively large, under the condition of water quality is difficult to form magnesium ammonium phosphate crystallization. Therefore, the crystallization experiment of sewage from the simulated domestic sewage after A/O alternating BAF anaerobic effluent. After anaerobic treatment of sewage, the concentration of phosphorus will be relatively elevated, ammonia nitrogen concentration will not have a big change, so as to form a favorable condition for the formation of MAP crystals.

In this test, the cycle of alternating BAF of A/O is 48h (in the 48h, 1 reaction column is anaerobic tank, 2 column is aerobic tank, the simulated sewage is influent by 1 reaction column, and the water is discharged from reactor 2. After 48h, the 1 column is aerobic column, 2 column is anaerobic column, at this time the simulation of sewage water from the first 2 columns, and then by the 1 column water. , the filter material for the independent research and development of the new filter material. Anaerobic effluent water quality indicators are as follows: ammonia nitrogen 35mg/L, phosphorus 8 ~29.5mg/L, pH7.4~ 7.9.

Test method

Crystallization experiments were performed in each group, respectively, to take a certain amount of KH_2PO_4 original solution, deionized water, NH_4Cl solution. And put in a 1000ml beaker. Put the beaker on 85-2 type constant temperature magnetic stirrer, With PB-10 acidity meter for pH and temperature on-line monitoring of the liquid in the beaker. And adjusting the pH of the liquid in the beaker with 1.2mol / L HCl and 1.0mol / L NaOH. Finally, according to the molar ratio of Mg / P, take a certain amount of MgSO_4 solution in a 1000ml beaker, the HCl and NaOH solution regulation the pH value to reach the setting value. At this time the volume of the liquid in the beaker is 1000ml, starting the reaction. At that time the temperature is 20 degrees C, the stirring speed is 250 ~ 300r/min, the reaction time is 10min. In the process of the reaction, the solution is monitored in real time with a laser transmitter and a laser power receiver, and the change time of the receiving power on the laser power device is observed. When the reaction is over, standing 2h. After the supernatant was filtered by 0.45um filter paper, the content of phosphate was determined.

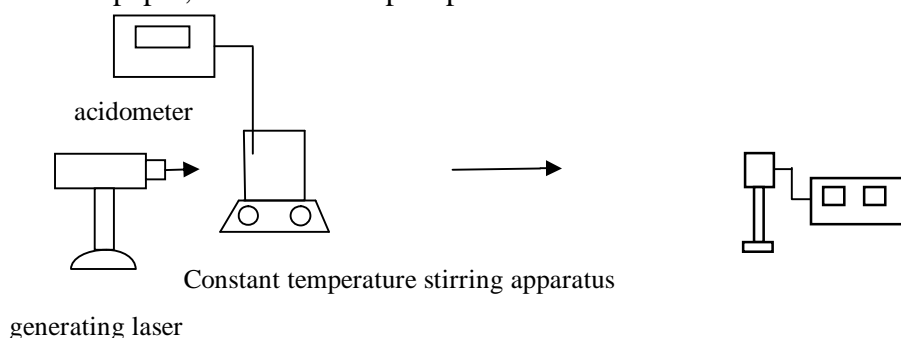


Figure 1 Test device diagram

Results and discussion

Effect of phosphorus concentration on the crystallization of MAP

The concentration of phosphorus in anaerobic effluent was 8 ~ 29.5mg/L, so the concentration of phosphorus in this experiment was 7.5mg/L; 12mg/L; 24mg/L; 18mg/L; 30mg/L. The concentration of ammonia nitrogen in anaerobic effluent was almost the same, so the concentration of ammonia nitrogen in this experiment was 35mg/L. The amount of MgSO_4 in accordance with the molar ratio 1:1 of Mg/P.

Because MAP is soluble in acid solution, the test pH is adjusted to be an alkaline environment. Wang Xiaodan and other^[4] in the study using magnesium ammonium phosphate method to deal with landfill leachate, when pH=9.0 ~ 9.5, the treatment effect is better. When pH is larger, can produce Mg (OH)₂ precipitation, crystallization rate decreases, and so this set of experiments take pH 9.5. As shown in Figure 1 when received laser power instrument showed the received laser power has obvious change, indicating the beaker inside solution phase transition occurs, there are crystal to generate. Recording time, this time is the time to generate a crystal. The reaction time of the whole process is 10mins, when the time is more than 10min, the number of the laser power receiver still does not change, and it shows that 10min cannot form a crystal. Under the condition of different phosphorus concentration, the crystallization time and the removal efficiency of phosphorus are shown in Table 2.

Table 2 Effect of phosphorus concentration on crystallization time and removal rate

Phosphorus concentration (mg/L)	7.5	12	18	24	30
Crystallization time (min)	—	—	10	6.8	6.5
Removal rate (%)	0	0	3	20	40

Table 2 shows that the concentration of phosphorus has a great influence on the crystallization time of MAP, and the removal rate of phosphorus is very high. Visible, in a certain range of concentration of phosphorus is higher for phosphorus removal, so the application of phosphorus removal by crystallization should regard as one of the important factors to influence the initial phosphorus concentration. The concentration of phosphorus in domestic sewage is generally 8 ~ 12mg/L, which can be known from table 2. Under the condition of 10mins, Mg/P molar ratio is MAP, the 1:1 crystal cannot be formed. So the key point is to increase the concentration of phosphorus in wastewater by using the crystallization method to treat domestic sewage.

Effect of pH on the crystallization time and the rate of phosphorus removal

The study shows that pH has a great influence on the solubility of MAP. With the increase of pH, the solubility of MAP will decrease, while the lowest solubility of MAP occurs at^[5] pH=10.3, and the solubility will increase in excess of this value. In the actual treatment of sewage, pH will not exceed this value. It is generally considered^[6] pH above 8.0 can effectively produce MAP crystal. This test is mainly to study the water quality of anaerobic effluent, so pH cannot be too high, if too high, it will affect the activity of microorganisms. Therefore determine the pH value of the test range from 7 to 10, each of the 0.5 units to set a gradient. This part of the test set two groups of experiments, each test, and the concentration of ammonia nitrogen is 35mg/L, one group of tests in the concentration of phosphorus is 24mg/L, the other group of the phosphorus concentration in the test is 30mg/L. In the two groups, the amount of MgSO₄ in accordance with the molar ratio 1:1 of Mg/P. Two groups of tests were all reaction 10mins.

Table 3 Effect of pH on the crystallization time and phosphorus removal rate of MAP (P=24mg/L)

pH	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Crystallization time (min)	—	—	—	—	—	6.8	2.5
Removal rate (%)	0	0	0	0	0	20	35

Table 4 Effect of pH on the crystallization time and phosphorus removal rate of MAP (P=30mg/L)

pH	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Crystallization time (min)	—	—	—	—	—	6.5	2.4
Removal rate (%)	0	0	0	0	0	40	44

The crystallization time and the phosphorus removal rate of the two groups were shown in Table 3 and 4 respectively. From the table, the phosphorus concentration is lower than 24mg/L, pH less than 9, cannot form-crystallization within 10mins. When the concentration of phosphorus is higher than 24mg/L, the crystallization time is almost the same under the same conditions of pH and Mg/P. KH₂PO₄ solution is mainly in the form of PO₄³⁻, HPO₄²⁻, H₂PO₄⁻^[5], and other forms of common H₃PO₄. The proportion relate to pH. While the crystallization reaction, PO₄³⁻ is the effective ion, when pH increases, the ratio is PO₄³⁻. Therefore, it is helpful to increase the crystallization reaction of pH. When the pH is too high, it will form Mg (OH)₂ precipitation, so that the concentration of Mg²⁺ decreased, which affect the amount of MAP crystallization.

The rate of removal effect on MAP crystallization time and the dosage of phosphorus

MAP crystallization is produced by NH_4^+ , Mg^{2+} , and PO_4^{3-} according to the amount of substance 1:1:1 reaction. Under certain conditions, increasing the concentration of ammonia nitrogen and Mg^{2+} can increase the removal rate of phosphorus, and increase the amount of MAP. The effect of dosage (Mg/P molar ratio) on the time of crystallization of MAP and the removal rate of phosphorus was discussed. The experiment mainly in the condition of dosage for 1:1 and 2:1, pH 10.0, ammonia concentration 35mg/L, on MAP crystallization time and phosphorus removal rate, reaction time for 10mins. The test results are shown in Table 5 and table 6.

Table 5 Effect of the dosage of MAP

Crystallization time					
Phosphorus concentration(mg/L)	7.5	12	18	24	30
Mg/P=1:1(min)	—	—	8.6	2.4	2.4
Mg/P=1:2(min)	—	—	0.1	0.1	0.1

Table 6 Dosage on phosphorus removal rate

Phosphorus concentration(mg/L)	7.5	12	18	24	30
Mg/P=1:1(%)	—	—	5	35	44
Mg/P=1:2(%)	—	—	56	68	74

The table 5 results indicated that, coagulant dosage on the crystallization time effect is very obvious, in dosage is 1:1, phosphorus concentrations higher than 24mg / L, the crystallization reaction time 150s, when the dosage is 2:1, reaction crystallization time only need 6S that increase dosage can greatly shorten the crystallization reaction time. The data in Table 6 shows that the water quality in the same conditions, increasing the dosage can greatly increase the removal rate of phosphorus.

Conclusion

From the above experiments, the following conclusions can be drawn:

- (1) when the ammonia concentration is 35mg / L, the dosage of mg / P molar ratio is 1:1, pH = 10, the initial concentration of phosphorus than 18mg / l can form the MAP crystallization;
- (2) Under the same conditions, the initial concentration of phosphorus is higher, while the formation of MAP is shorter, the phosphorus removal rate is greater;
- (3) Under the same conditions, in a certain range, the higher pH, the formation of MAP crystallization time is short, and phosphorus removal rate is high;
- (4) The initial concentration of phosphorus is higher than a certain value. Under the same conditions of water quality, pH is the main factor that influences the crystallization reaction time;
- (5) in a certain range, increasing the dosage can greatly shorten the reaction time of crystallization, and can greatly improve the removal rate of phosphorus.

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