Magnesium Ammonium Phosphate Crystallization: A Possible Way for Recovery of Phosphorus from Wastewater

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Abstract. There is large quantity of phosphorus in wastewater, which leads to the water eutrophication. Magnesium ammonium phosphate (MAP) crystallization is used to remove and recover phosphorus from wastewater, which can not only restrain the eutrophication, but also realize the sustainable utilization of phosphorus resource. The mechanism of MAP crystallization is introduced, the influencing factors of crystallization are analyzed, and application of MAP crystallization is reviewed. While, the study of MAP crystallization is still at the beginning stage and further research need to be done in China. What’s more, the prospects for future development trend of MAP crystallization are also summarized, which might provide reference for removal and recovery of phosphorus.

1. Introduction

A large number of untreated wastewater discharge caused the nitrogen and phosphorus accumulation in the water body with the rapid development of industry and agriculture, resulting in the eutrophication of water body[1]. However, phosphorus is an important natural resource[2], which is not renewable and limited[3]. Therefore, the removal and recovery of phosphorus in sewage not only can solve the problem of phosphorus pollution, but also realize the sustainable utilization of phosphorus resources[4], making wastewater treatment develop towards resource-recycled, energy regeneration and ecologicalization[5].

The technologies of phosphorus removal from wastewater mainly include biological method, chemical method and crystallization method. The biological method is to store excess phosphorus in the cells by phosphorus accumulating organisms, and finally to discharge the system in the form of phosphorus rich excess sludge, so as to achieve dephosphorization. However, biological treatment is easily affected by environmental factors, and the effect of phosphorus removal is unstable[6]. Chemical precipitation is a method of producing insoluble salts by iron salt or aluminum salt and phosphate ions in water, and it is removed by precipitation or filtration[7]. But the precipitated phosphate is not easy to separate from biological sludge and can not recover phosphorus.

Phosphorus removal by crystallization is that phosphorus in water can be deposited in the form of phosphate crystals by controlling certain reaction conditions, so as to achieve removal and recovery of phosphorus[8]. At present, the main product forms of phosphorus recovery are FePO₄, AlPO₄, MgNH₄PO₄ and Ca₅(PO₄)₃OH. Among them, the content of P₂O₅ in magnesium ammonium phosphate (MAP) is about 58%, which is about 5% higher than that of phosphorus ore. At the same time, MAP is also an excellent slow release fertilizer. Therefore, phosphorus removal by the MAP crystallization has become research hotspot.
2. Mechanism of MAP crystallization

MAP commonly known as struvite, is a colorless or white orthorhombic crystal system. MAP crystal usually contain six crystalline water and the chemical formula is MgNH₄PO₄·6H₂O. The solubility product in water at room temperature is 2.5×10⁻¹³, which has the property of dissolving in acidic solution but not in alkaline solution. When the ion concentration product is greater than the solubility product constant, MAP crystals are produced. The reaction formula is as follows:

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \downarrow
\]

(1)

The MAP crystallization process in sewage can be divided into two stages: nucleation and crystal growth. In the nucleation stage, the crystals precipitate in the water to form the nucleus. At the growth stage, the ions that form the crystals are continuously bonded to the surface of the crystal nucleus, so that the crystals grow and finally reach equilibrium[9].

3. Influence factors of MAP crystallization

In order to improve the harvest rate of MAP crystal, the factors affecting its precipitation must be studied. The crystallization process of MAP is a complex process, involving solid and liquid phase transfer, reaction kinetics, reaction thermodynamics, and some physical and chemical related knowledge. Because of the complexity of sewage components, the main influence factors include pH, ion concentration, seed crystal and ultrasonic enhanced crystallization.

3.1. pH

When pH is less than 7, the crystal is generally not precipitated. When pH is 7.5~10, there will be a large number of MAP crystals. However, the content and purity of MAP decreases with the increase of pH. Liu et al[10] found that the solubility and supersaturation of MAP decreased gradually with the increase of pH, and the crystallization induction period was also shortened. The results showed crystallization process was promoted by increasing pH. Wang et al[11] also found that phosphorus removal rate increased from 52.12% to 96.27% with the increase of pH. Therefore, it was also proved that the high removal rate of phosphorus is feasible by MAP crystallization. However, Hao et al[12] found that the MAP in the precipitate is very few through XRD and microscope images under the condition of high pH (pH>9), and there would be Mg₃(PO₄) and Mg (OH)₂.

3.2. Ion concentration

For the MAP crystallization, NH₄⁺, Mg²⁺ and PO₄³⁻ are removed according to the stoichiometric relationship 1:1:1 theoretically. However, in order to improve phosphorus removal rate, NH₄⁺ and Mg²⁺ need to be excessive. It is found that the phosphorus removal rate increased with the increase of NH₄⁺ concentration. The concentration of ammonia nitrogen in wastewater is generally high, so it is necessary to add Mg²⁺. When dosage is insufficient, the removal of nitrogen and phosphorus in wastewater is not complete. While dosage is excessive, it will not only increase the processing cost, but also cause secondary pollution. In order to find the most suitable proportion, scholars at home and abroad have done a lot of experiments. Yuan et al[13] treated simulated swine wastewater and found that the removal rate of phosphorus was above 97% under the high pH condition when molar ratio of Mg²⁺ to PO₄³⁻ was increased to 1.4:1. Further increasing the molar ratio, the removal rate of phosphorus is not obvious. Jaffera[14] found that a mixture of MAP and calcium phosphate would be produced when molar ratio of Mg²⁺ to PO₄³⁻ is lower than 1.05:1.

There are various inorganic or organic impurities in the actual wastewater, and some will affect the production of MAP crystallization, thus affecting the removal efficiency of nitrogen and phosphorus. Calcium ions in the solution affect the formation of MAP by competing with Mg²⁺ for PO₄³⁻ or interfering with the process of MAP crystallization. The effect of calcium ion on MAP crystallization was analyzed by Kristell[15]. It was found that the increase of calcium ion concentration would reduce the size of crystal and inhibit the growth of MAP.
3.3. Crystal species
The size of MAP crystal is small, which is not easy to recycle and use. In the crystallization process of MAP, the introduction of crystal seeds can shorten the nucleation time and reduce the saturation required for crystallization. Battistoni et al. [16] filled with 0.21-0.35mm quartz sand into the fluidized bed, and the removal rate of phosphate was more than 80%. Tao et al.[17] has studied the effect of quartz sand, iron chip and bituminous coal on the removal of phosphorus. It is found that three species can significantly improve the removal rate of phosphorus. The effect of bituminous coal is the best, and the removal rate of phosphate can reach 90%. In order to improve the removal rate of phosphorus in biological sludge, Northern Ireland used bacteria as seeds and combined biological and chemical processes, making bacteria a carrier of phosphorus precipitation[18].

3.4. Ultrasonic
Ultrasonic technology has many functions, such as acoustic cavitation, high temperature pyrolysis, advanced oxidation and supercritical oxidation. Luque et al. [19] have studied the facilitating effect of ultrasound on reducing the crystallization induction period, supersaturation conditions and the width of the metastable zone. And this effect can be achieved by changing the relevant variables of ultrasound, such as frequency, intensity and power. Qiu et al.[20] attained the same results. Therefore, the application of ultrasound has played an important role in strengthening crystallization.

4. Research status of MAP crystallization
In recent years, the international conference on phosphorus recovery has been developed and the price of phosphate ore is rising, which has aroused extensive interest and research on the recovery of phosphorus by magnesium ammonium phosphate crystallization. The MAP crystallization technology started earlier and was relatively mature abroad. At present, many countries have used the method to recover nitrogen and phosphorus[21], which is widely applied to sewage treatment plants or actual sewage treatment[22]. However, the research on the MAP crystallization process is in initial stage in China. It is efficient and simple to remove and recover nitrogen and phosphorus from wastewater by magnesium ammonium phosphate crystallization.

4.1. Application in sludge supernatant treatment
The reflux sludge contains rich phosphorus in wastewater treatment plant, which is refloored to the front end treatment process, increasing the phosphorus load of sewage treatment. The concentration of PO43- is up to 75-300mg/L in the anaerobic digestion juices of the sludge, and the effect of phosphorus recovery from the phosphorus-rich supernatant or the sludge digestion juices in the anaerobic zone is obvious. The process of recovering phosphorus from sludge consists of Anphos and Phospaq processes[23] in Holland, NuReSys process[24] in Germany and Phosnix process in Japan[25]. Li et al.[26] recovered phosphorus from anaerobic phosphorus-rich supernatant by flow induced crystallization, and the treatment efficiency is more than 45%. Tan et al.[27] terated simulated anaerobic supernatant for MAP crystallization, when the phosphate concentration was 63 mg/L and pH was 8.5~9.0, the phosphorus removal efficiency can be over 95 %.

4.2. Application in aquaculture wastewater treatment
Intensive aquaculture is prone to produce a large amount of wastewater, and concentration of total phosphorus is 150-250mg/L, and contains high concentrations of organic matter and ammonia nitrogen. Kim et al.[28] pretreated pig wastewater by MAP method to remove ammonia and phosphorus. When pH is 8~10 and n (Mg2+): n (NH4+): n (PO43-) is 2.8:1:1.4, the removal rate of ammonia nitrogen is 99.2%. Tao et al.[29] recovered nitrogen and phosphorus from pig biogas slurry by continuous flow crystallization reactor. The recovery rate of ammonia nitrogen and PO43- is 74.3% and 99% under optimal operating conditions, respectively. The economic benefit analysis was carried out, and the result showed the treatment cost of MAP crystallization method is lower than that of conventional technology.
4.3. Application in landfill leachate treatment
The landfill leachate with high ammonia nitrogen organic sewage has poor biodegradability. Pretreatment by MAP crystallization method can be used to reduce ammonia nitrogen, and improve the biodegradability of leachate. Lan et al[30] removed the ammonia nitrogen in the leachate by MAP, realizing the significant decrease in the cost of the dosage. Calli et al[31] studied the anaerobic treatment of landfill leachate by MAP crystallization, when n (Mg2+): n (NH4+): n (PO43-) is 1:1:1, 98% of the ammonia nitrogen was precipitated into MAP crystal, and the effluent ammonia nitrogen concentration was below 40mg/L.

5. Conclusions
MAP crystallization is an effective method to alleviate the shortage of phosphorus resources, and is also an important means to protect the water environment, which is in line with the requirements of sustainable development. In summary, MAP crystallization is the most promising method for phosphorus recovery. MAP crystallization method has been widely studied in foreign countries, and has been put into practical application.

The phosphorous content in sewage is low and the cost of recovery is high. The income of phosphorus recovery products can not reach the investment and daily operation cost of the recovery, which limits the development and popularization of the phosphorus recovery technology. In the future research, the development of the crystallization reactor, reducing the operation cost combined with the new biotechnology for phosphorus recovery and further improving the production of MAP will become the focus of the research.

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