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Research Progress on the Treatment of High-Concentration Nitrogen and Phosphorus Wastewater by Struvite Precipitation

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Abstract: Aiming at the problems of eutrophication of water bodies and the shortage of phosphorus resources, the struvite method for treating high-concentration nitrogen and phosphorus-containing wastewater has been widely used because of its high efficiency and low consumption. This paper summarizes the research progress on the treatment efficiency, influencing factors and stability of high concentration nitrogen and phosphorus mixed wastewater in recent years, and on this basis, the feasibility and development prospect of MAP method in the treatment of high concentration nitrogen and phosphorus wastewater are proposed.

1 Introduction

The 2021 China Environment Bulletin states that eutrophication exists to varying degrees in Taihu Lake , Chaohu Lake and Dianchi Lake[1] .And coupled with the non-renewable nature of phosphorus resources, the recovery of nitrogen and phosphorus in wastewater has become an unavoidable task.Traditional methods of phosphorus removal include adsorption, crystallisa-tion and biological methods; traditional methods of nitrogen removal include air blowing, sel-ective ion exchange and fold point chlorination. The cost and removal effect of traditional nitrogen and phosphorus removal methods and struvite methods to treat high-concentration wastewater are shown in Table 1. However, most of these methods have limitati-ons. The comparison of the advantages and disadvantages of traditional physicochemical method, biological method and struvite precipitation method for nitrogen and phosphorus removal is shown in Table 2.

As a new type of chemical nitrogen and phosphorus remo val method, magnesium ammoni-um phosphate (MAP) p recipitation is not only simple to operate but also has low energy consumption and can remove N and P from waste water, especially for high concentration wastewater. At th e same time, the method is less affected by water quality and temperature, and the resulting precipitation product, magnesium ammonium phosphate, can be used as a slow-release fertiliser, which has some recycling value.

Therefore, this paper reviews the progress of research on the treatment of various types of high concentration nitrogen and phosphorus wastewater by struvite precipitation in recent years. The problems that need to be solved in the practical application of this method are summarised. In order to provide a reference for the research aspect of using struvite precipitation method to treat high concentration nitrogen and phosphorus wastewater.

Table 1 Comparison of traditional physicochemical methods, biological methods and struvite precipitation methods for the treatment of high-concentration wastewater

	Traditional materialization method			Biological method	struvite precipitation method
	Adsorption method	Folding point chlorination method	Air blow-off method		
Construction Costs	/	/	￥40,000	￥550,000	/
Running Costs	/	/	￥0.55/t	￥0.24/t	/
Pharmacy Fee	￥1800-10000/t	￥440/t	/	/	￥230.341/t
Removal rate	60%-90%	90%	80%-95%	60%-85%	95%

Table 2 Comparison of the advantages and disadvantages of nitrogen and phosphorus removal by traditional physical and chemical methods, biological methods and struvite precipitation

		advantages	Disadvantages
	Vapor	High efficiency of over 90% for medium to high	low efficiency of low-temperature denitrification; long stripping

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Traditional physicoche-mical denitrification	extraction	concentration ammonia nitrogen wastewater; low capital and operating costs	time and high energy consumption; secondary pollution by ammonia gas from blow-off
	Ion exchange method	Good effect in treating low concentration wastewater or wastewater containing trace heavy metals	Resin, zeolite and other ion exchange agent dosage, high cost and regeneration difficulties; the existence of secondary pollution
	Folding point chlorination	Treatment effect of 90%-100%; less investment in equipment; rapid and complete reaction, and disinfection effect	High requirements for safe use and storage of liquid chlorine; easy to generate disinfection by-products such as chloramines and chlorinated organics
Traditional physicochemical method to remove phosphorus	Adsorption method	Easy installation and maintenance of the treatment unit, easy material replacement	The preparation of adsorbent is complicated and costly; the amount of adsorbent is large
	Crystallisation	High purity of solids, simple operation, less equipment required	High energy consumption and intermittent operation.
Biological method		Can simultaneously remove N and P; stable operation, and good shock load resistance	phosphorus cannot be truly removed, but only transferr-ed to the sludge; high infra-structure costs
struvite precipitation method		Simple process, fast reaction; can realize wastewater resource recovery by removing N and P at the same time	Large amount of precipitant

2 struvite precipitation method and mechanism of nitrogen and phosphorus removal from wastewater

The basic principle of struvite precipitation method for nitrogen and phosphorus removal is to add magnesium salt to the wastewater containing nitrogen and phosphorus, which should generate insoluble complex salt $MgNH_4PO_4{\cdot}6H_2O$ with NH_4^+ or PO_4^{3-} in the wastewater, and achieve the purpose of nitrogen and phosphorus removal from the wastewater and further recycling of precipitates through solid-liquid separation[2]. The experimental process of removing nitrogen and phosphorus from wastewater by struvite sedimentation is shown in Figure 1.The main chemical reactions that occur during the formation of struvite precipitation are as follows:

$$Mg^{2+} + HPO_4^{2-} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O\downarrow + H^+ \quad (1)$$

$$Mg^{2+} + PO_4^{3-} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O\downarrow \quad (2)$$

$$Mg^{2+} + H_2PO_4^- + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O\downarrow + 2H^+ \quad (3)$$

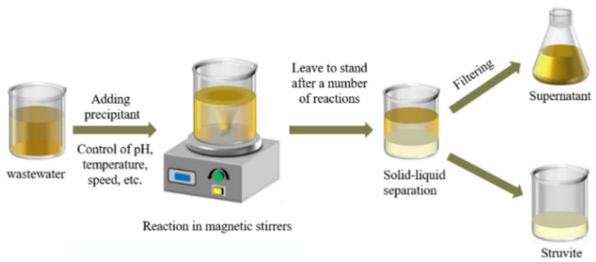

Figure 1 Schematic diagram of the experimental flow of struvite precipitation method to remove nitrogen and phosphorus in wastewater

3 Status of struvite method for treating high concentration nitrogen and phosphorus wastewater

3.1 High concentration ammonia nitrogen wastewater treatment

There have been many studies on the removal of high ammonia nitrogen wastewater by struvite precipitation at home and abroad, such as livestock fermentation methane, waste leachate, coking wastewater, etc. Zhou S[3] applied struvite method to treat high chromium wastewater generated in vanadium industry with an initial ammonia concentration of 2850 mg/L. The optimum conditions obtained were pH=9.16, n(Mg):n(N)=1.3:1, n(N):n(P)=1.165:1, t=20 min and the ammonia removal rate was 98.87% by RSM . The struvite method can not only recover ammonia nitrogen but also remove CODCr from the wastewater when treating high concentrations of ammonia nitrogen. Dekun Yang [4] used struvite method to treat the anaerobically fermented digestate of kitchen waste with an ammonia content of 3382 mg/L.The optimum experimental conditions were pH=9.0, T=28°C, t=90min, Mg:P:N=1.43:1.3:1. The results showed that the ammonia removal rate could reach about 98%, and the carbon to nitrogen ratio of the treated kitchen digestate increased from 5.38 to 43.96. The pretreatment of ammonia nitrogen recovery from wastewater by struvite method can effectively relieve the pressure on the biological treatment system and bring the wastewater to the discharge standard in a simple and efficient way.

3.2 Treatment of wastewater containing high concentrations of phosphorus

The struvite method of phosphorus removal is widely used in industrial wastewater. Kumari Soni et al[5]recovered phosphorus from brewery wastewater in the form of struvite. pH, NH_4^+:PO_4^{3-} and Mg^{2+}: PO_4^{3-} molar ratios were optimised at 9.0, 2.28 and 1.72, respectively, with 95% phosphate removal and struvite yield of 3306 mg/L.Numviyimana C et al[6] recovered phosphorus from a dairy processing wastewater with an initial pH of 4.35 and a phosphate content of 698 mg/L. The optimum conditions for phosphorus removal of 98.6 ± 1.1% were: pH = 8.9, n(Mg): n(N) = 1.21, n(N): n(P) = 2.69, while the struvite precipitation content under these conditions was 85.7 ± 2.5%, with a high nutrient utilisation rate. JABR G. et al[7] used a pilot-scale reactor to treat phosphorus in the anaerobic sludge supernatant, and the phosphorus removal efficiency obtained by operation reached about 77%. Since there is basically no phosphate ore in Europe, struvite crystal phosphorus removal is highly valued, and some sewage plants have introduced this process and achieved good treatment results.For example, the Calahorra wastewater treatment plant in Spain[8]; Esholt sewage treatment plant, Yorkshire, UK [9] install struvite sedimentation units and some of the treatment plant's recycled struvite sediment has been produced into fertiliser for sale on the market. The struvite precipitation products are shown in Figure 2.

Figure 2 struvite sedimentation products

3.3 High concentration nitrogen and phosphorus wastewater treatment

For low-concentration nitrogen and phosphorus wastewater, adsorption method, vertex chlorination method and other methods are more applicable[10]. For high-concentration nitrogen and phosphorus wastewater, researchers use struvite sedimentation method to try the feasibility of recovering high concentrations of nitrogen and phosphorus, and optimize the relevant parameter conditions. Jiannan Ding et al[11]used struvite method to grain fermentation wastewater, the optimum treatment conditions(T=30°C,pH=9.12,n(NH_4^+):n(Mg^{2+}):n(PO_4^{3-})= 1:1.21:0.98, W=100r/ min, t=20min) at 84.99% removal of NH_4^+ and 97.65% removal of phosphorus, and the main component was struvite with 87.19% purity. Thant Zin M et al[12] used mixed wastewater with an initial ammonia nitrogen concentration of 39625±1492mg/L and a phosphate concentration of 843mg/L.At pH = 9.63, molar ratio Mg:N:P = 1:1:1, T = 10 min The removal rate of NH_4^+ was 66.8% and the removal rate of PO_4^{3-} was 99.8% under the conditions of pH=9.63, molar ratio Mg:N:P=1:1:1 and T=10min. Muhmood A et al[13] showed that a pH range of 9.5 to 10.5 was ideal for the removal and recovery of P and N, with a molar ratio of 1:1:1 for Mg:N:P. A mixing rate of 10 min at 150 rpm allowed nutrient recovery with minimal loss of NH_3 (3.32%) through volatilisation, and also gave the best struvite crystal size (50-60 μm). The morphology of struvite crystals under electron microscopy is shown in Figure 3.

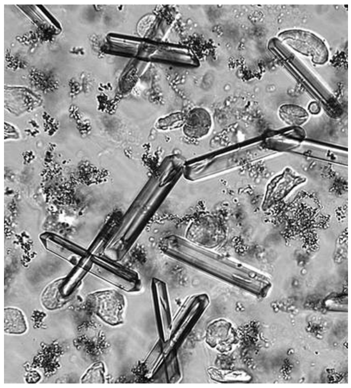

Figure 3 Scanning electron micrograph of struvite crystals

4Existing problems in the treatment of wastewater by struvite sedimentation

4.1 Magnesium source issues

Most domestic and international studies have used $MgCl_2$ and $MgSO_4$ as Mg sources[14], and achieved good nitrogen and phosphorus removal results. This is due to the fact that they are both easily soluble in water, but are expensive. $Mg(OH)_2$ has a higher magnesium content compared to other magnesium compounds and also has the effect of NaOH, which saves the cost of pharmaceuticals to a certain extent cost.However, MgO can effectively increase the pH of the solution and is relatively inexpensive[15], but its solubility is poor. However, its solubility is poor. Some scholars also use brine or seawater as a source of magnesium, salt brine seawater, etc., although inexpensive, but has certain limitations, for areas far from the salt field is not suitable, while other ions contained in seawater such as Ca^{2+} will also have an impact on the MAP method of nitrogen removal and phosphorus removal[16].Astals S et al[17]used struvite technology to recover ammonia nitrogen from pig slurry wastewater. A stabiliser (SA) was synthesised using industrial low-grade magnesium oxide by-product (LG-MgO) and phosphoric acid. Ammonia nitrogen removal rates can reach up to 80%. The choice of Mg salt should facilitate the reaction and save costs, for example by finding inexpensive and efficient combinations of precipitants, any by-products of magnesia production or industrial waste.

4.2 Practical application issues

Although a lot of research has been carried out at home and abroad on the process of nitrogen and phosphorus removal from strutive, most of them are concentrated in the small and pilot stages, and most of the experimental raw water does not have high nitrogen and phosphorus content or is used to simulate wastewater, lacking deeper research. For example, in the treatment of brewery wastewater with strutive, when the concentration of phenol in the wastewater increased from 0 to 9000 mg/L, the phosphate removal rate decreased from 99% to 93%, while the purity of struvite crystals decreased from 96% to 62%[5].

Struvite as a fertilizer is also one of the keys for the method to be valued and widely studied by the academic community, but there are few systematic studies on its real application effects in agriculture, mainly due to the low purity and high cost of struvite obtained from the current experiments, which cannot be applied to agricultural fields as a profitable channel, and future research will continue to be conducted in terms of improving purity and reducing cost. To fundamentally remove highly toxic organic substances and strengthen the research on the effect of organic substances such as benzene and phenols on struvite precipitation.

4.3 Cost issues

Gowd Sarath C [18] analysising resource estimation showed that 17.3 kg of struvite could be generated from 1 million liters per day (MLD) of effluent by chemical precipitation at 80% recovery rate. Xu H et al[19] showed that the economic profit of recovering nitrogen and phosphorus by struvite method is $1.5/ton waste sludge, which is less economical. Qian Ping et al[20] obtained from the cost analysis of pharmaceuticals that the cost of phosphorus salt consumed to treat 1 t of ammonia nitrogen wastewater was 46.9 yuan, the cost of magnesium source was 8.8 yuan, and the resulting struvite recovery could benefit 36.3 yuan. Although the struvite method is simple to operate and less influenced by the external environment, the sedimentation agent and pH adjuster are expensive and the dosage is large, which requires huge cost of chemicals, so the expensive cost is a problem that needs to be solved when it is put into actual production and widely used.

5 Conclusions

Struvite precipitation has great advantages and potential for removing N and P from water, not only removing much of the nitrogen and phosphorus load and reducing pollution, but the resulting precipitation can also be used as a fertiliser. Research into the recovery of nitrogen and phosphorus from wastewater using struvite precipitation has been widely carried out, both in terms of factors affecting the pH, magnesium to phosphorus molar ratio, nitrogen to phosphorus molar ratio, reaction time and reaction temperature of struviteite precipitation and the use of struviteite precipitation as a pre-treatment have all yielded preliminary and mature experimental results. However, apart from a few commercial struvite recovery units in operation at wastewater treatment plants, it is not widely used in actual industry. The main bottleneck is the high cost of chemicals, so the focus of the future application of struvite precipitation should be on finding inexpensive and efficient precipitating agents, designing more reasonable and energy-efficient struvite reactors, and strengthening research on the effectiveness of struvite as a slow-release fertiliser in agriculture.

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