



# Thermal decomposition of magnesium ammonium phosphate and adsorption properties of its pyrolysis products toward ammonia nitrogen

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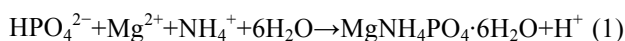
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**Abstract:** High-purity magnesium ammonium phosphate (MAP) was precipitated by controlling pH value of the reaction system of 9.0–9.5. The thermal decomposition behavior of MAP and the adsorption properties of its pyrolysis products toward ammonia–nitrogen were also studied by XRD, SEM, TGA-DTA and FT-IR methods. The results indicated that high-purity MAP was obtained at pH value of 9.0–9.5. Upon heating to 100–120 °C for 120 min, MAP was thermally decomposed, losing water and ammonia concomitantly with a reduction in grain size and crystallinity. The capacity of pyrolysis products for ammonia nitrogen adsorption reached 72.5 mg/g, with a removal rate of up to 95% from an 800 mg/L solution. The characteristic diffraction peaks corresponding to MAP mainly appeared in their XRD patterns after adsorption of ammonia nitrogen. The pyrolysis products of MAP at 100–120 °C could be recycling-used as the chemical treatment reagents of ammonia nitrogen in the practical application.

**Key words:** magnesium ammonium phosphate; magnesium hydrogen phosphate; thermal decomposition; ammonia nitrogen; adsorption properties

## 1 Introduction

Ammonia nitrogen is a common pollutant that causes eutrophication and environmental damage. In nearly all of China's contaminated water, ammonia nitrogen is one of the major pollutants at present. The effective and economical treatment of ammonia nitrogen in wastewater is an important objective of environmental research. Frequently used methods for treating ammoniated wastewater include air stripping [1], adsorption and ion exchange [2], biological treatment [3], and chemical sedimentation [4–6]. The latter method is typically simple, using various treatment reagents to produce sediments which are used as fertilizers. Some of these processes have already found application [7,8]. Chemical sedimentation for the removal of ammonia nitrogen from wastewater is based on the following reaction:



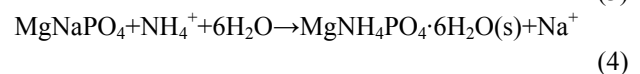
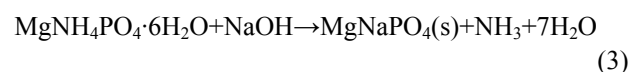
The major limitation for employing the chemical

sedimentation of magnesium ammonium phosphate (MAP,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is the expense of the precipitants (soluble phosphate and magnesium salts), which raises the processing cost. For example, the cost of applying the MAP method to the remediation of landfill leachate was up to 22.9 \$/m<sup>3</sup> [9].

To solve the cost problems associated with the practical application of MAP chemical sedimentation methods, AHMAD and IDRIS [10] studied the acid regeneration of MAP:



HE et al [11] developed a MAP regeneration method under alkaline conditions:



which allowed recycling of the MAP and solved the problem of the precipitating agent cost. However, the acid regeneration method recovered ammonia nitrogen in

the form of an ammonium salt from the wastewater, and the recovered solution inevitably contains a small amount of  $Mg^{2+}$  and  $HPO_4^{2-}$  which complicate its discharge. MAP regeneration under alkaline conditions consumes equimolar amount of NaOH, which is economically unsatisfactory, although ammonia nitrogen is recycled in the form of aqueous ammonia from the wastewater.

The use of an ammonia neutralizer generally produces highly concentrated ammonia nitrogen wastewater in the chemical industry, metallurgy, electroplating and other industries. If the ammonia nitrogen pollutant is recovered in the form of aqueous ammonia, it can be directly reused, finally forming ammonia to close the circuit. This process should be regarded as the best solution for ammonia nitrogen wastewater treatment.

The study of BHUIYAN et al [12] showed that MAP can be thermally decomposed into a mixture of  $MgHPO_4$ ,  $Mg_3(PO_4)_2$  and  $Mg_2P_2O_7$ . SUGIYAMA et al [13] indicated that the thermal decomposition product of struvite had adsorption capabilities; the adsorption properties of  $MgHPO_4$  for  $NH_4^+$  were better than those of  $Mg_3(PO_4)_2$ , whereas  $Mg_2P_2O_7$  hardly adsorbed  $NH_4^+$ . MAP could be employed as an advanced material for the removal/recovery of ammonium. ZHAO et al [14] investigated the formation of MAP from MHP and  $NH_4^+$  by an exchange reaction under suitable pH conditions. Highly concentrated ammonia solutions could be recovered and the MHP adsorbent could be easily regenerated by heat decomposition of the MAP. This process is an effective method that recycles not only the ammonia but also the MHP. Theoretically, the steam released from the pyrolysis of MAP can generate 13.6% aqueous ammonia (mass fraction), which can fully meet the requirements of industrial processes. It is suggested that the thermal decomposition of MAP under certain conditions can produce highly concentrated aqueous ammonia, but also pyrolysis products that may be used to treat ammonia nitrogen wastewater. This would allow recycling and reduce the costs of the ammonia nitrogen wastewater treatment agent.

The thermal decomposition of MAP can be conducted stepwise, and the temperature determines the composition of the pyrolysis products, thereby affecting their  $NH_4^+$  adsorption properties. In this work, the thermal decomposition process of MAP and the adsorption properties of its pyrolysis products toward ammonia nitrogen were investigated.

## 2 Experimental

### 2.1 Preparation of MAP

Ammonia-containing simulated wastewater (2000 mg/L, 200 mL) was prepared in a 250 mL conical flask.

Sufficient  $Na_2HPO_4 \cdot 12H_2O$  and  $MgCl_2 \cdot 6H_2O$  were added sequentially to achieve a N/P/Mg molar ratio of 1: 1: 1. The solution was stirred with a temperature-controlled magnetic stirrer, and the pH value was adjusted with 5 mol/L NaOH. The resulting precipitates were filtered after 20 min. The filtrate was analyzed for the remaining ammonia nitrogen and total phosphorus content, and the MAP sediments after washing were dried in a thermostatted blast oven at 40 °C for 48 h.

### 2.2 Thermal decomposition of MAP

The prepared MAP was placed in a tubular resistance furnace and pyrolyzed at 100 °C (unless otherwise stated) for 120 min. The pyrolysis products were finely ground and then sealed for later use.

### 2.3 Adsorption of ammonia nitrogen

Ammonia-containing simulated wastewater (800 mg/L, 200 mL) was prepared with  $NH_4Cl$  (AR). The MAP pyrolysis product (4 g) was added, and the mixture was magnetically stirred at room temperature for 40 min after adjusting the pH value to ~10 with 5 mol/L NaOH. After the reaction was completed, the mixture was separated using a Hitachi CR22G high-speed refrigerated centrifuge. The supernatant was used to analyze the ammonia nitrogen concentration, and the solid precipitate was treated as described in Section 2.1.

### 2.4 Testing and characterization

The ammonia nitrogen concentration was analyzed by Nessler's reagent spectrophotometry. Phosphate concentration was determined by ammonium molybdate spectrophotometry. Atomic absorption spectrophotometry was used to analyze Mg concentration (Shimadzu AA-6300F). Thermogravimetric-differential thermal analysis (TGA-DTA) studies were conducted by a TGA-DTA 6200 analyzer for a sample with mass of 27.5 mg, at a heating rate of 10 °C/min, and a 100 mL/min of air flow. Infrared spectroscopy was analyzed by a Shimadzu FTIR-8400S Fourier transform infrared spectrophotometer, and KBr tablet method was used for measuring absorption spectrum. Powder morphology analysis was conducted by scanning electron microscopy (SEM, JEOL JSM-6700F). A Panalytical Pert Pro X-ray diffractometer was used to obtain X-ray diffraction (XRD) patterns at room temperature, using a Cu  $K_\alpha$  source at 40 kV and 40 mA. Particle sizes were determined with a Microtrac S3500 laser particle size analyzer (Microtrac, USA).

## 3 Results and discussion

### 3.1 Preparation and characterization of MAP

The recovery of MAP by the chemical

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