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Temperature-programmed pyrolysis of magnesium ammonium phosphate and removal of ammonia-nitrogen by its pyrolysate

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Abstract: In order to achieve the dual goals of complete deamination of magnesium ammonium phosphate (MAP) and ensure the pyrolysate's good removal properties towards ammonia-nitrogen, a temperature-programmed method for the pyrolysis of MAP was studied, as well as the thermodynamic and kinetic processes involved in the removal reaction system between MAP pyrolysate and aqueous ammonium. It was found that the pyrolysis method and pyrolysis final temperature had significant effects on the MAP pyrolysate's removal properties towards aqueous ammonium, and the following conditions were deemed to be more appropriate: pyrolysis final temperature and heating rate at 180 °C and 5 °C/min, respectively, and a pH level of 9.5 for the removal reaction system. The resultant ammonium removal capacity by the MAP pyrolysate was 95.62 mg/g. After 120 min, the removal rate with an initial concentration of 1000 mg/L was 82%. The kinetic and thermodynamic results indicated that the removal of aqueous ammonium by MAP pyrolysate was the exchange process between H^+ and NH_4^+ via MAP precipitation. The kinetics complied with the Lagergren quasi second-order model with an equilibrium time of 120 min, while the isothermal curves complied with the Freundlich model.

Key words: magnesium ammonium phosphate; temperature-programmed heating; pyrolysate; ammonia−nitrogen

1 Introduction

The issue of eutrophication caused by ammonia−nitrogen pollution has become increasingly prominent, burdening environmental workers with the task of finding economical but effective ways to treat ammonia−nitrogen wastewater. The main treatment methods used currently include chemical precipitation [1−3], physical stripping [4,5], and biological method [6]. Among these, the first method is the most popular due to its various advantages, such as the simplicity of its process, being economical and effective, and high treatment efficiency. It has already been applied to actual engineering projects, with many examples available.

The biggest constraint affecting the practical application of the chemical precipitation method is the price of the precipitation agents (soluble phosphate and magnesium salts), which increases the processing costs. Various researchers sought ways to reduce processing costs during the actual application of this method. AHMAD and IDRIS [7] studied the regeneration of $MgNH_4PO_4\cdot 6H_2O$ (MAP) under acidic conditions: $MgNH_4PO_4\cdot 6H_2O(s)+H^+ \rightleftharpoons MgHPO_4\cdot 3H_2O+NH_4^+ + 3H_2O$. HE et al [8] studied the regeneration of MAP under alkaline conditions: $MgNH_4PO_4\cdot 6H_2O(s)+NaOH \rightarrow MgNaPO_4(s)+NH_3+7H_2O$ and $MgNaPO_4(s)+NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4\cdot 6H_2O\ (s) + Na^+$, thereby recycling MAP and solving the cost issue of using precipitating agents. Since acidic regeneration involves the use of ammonium salts to recover ammonia−nitrogen in the wastewater, the recovered liquor inevitably contains small amounts of Mg^{2+} and HPO_4^{2-}, making the discharging of the liquor problematic. On the other hand, although regeneration methods using alkaline conditions can recover ammonia−nitrogen in the form of aqueous ammonia, an equivalent amount of NaOH must be consumed, which is not cost effectively.

The study by BHUIYAN et al [9] showed that after pyrolysis, MAP became a mixture comprising $MgHPO_4$,

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$Mg_3(PO4)_2$, and $Mg_2P_2O_7$. SUGIYAMA and YOKOYAMA [10] found that $MgHPO_4$, followed by $Mg_3(PO_4)_2$, had good removal properties towards NH_4^+, but $Mg_2P_2O_7$ showed no removal effect. RINAUDO et al [11] and ZHAO et al [12] indicated that at a suitable pH value, the exchange reaction between $MgHPO_4$ and NH_4^+ would create MAP. Theoretical calculations further indicated that upon complete pyrolysis of MAP, aqueous ammonia at 13.6% could be obtained. Hence, the controlled pyrolysis of MAP under specific conditions could lead to the recovery of highly-concentrated aqueous ammonia. Furthermore, the pyrolysate could be used as an agent for the treatment of ammonia−nitrogen wastewater. The potential for recycling would also help to address the cost issue of using agents to treat ammonia−nitrogen wastewater.

During the preliminary work of this research [13], the pyrolytic behavior of MAP and the removal properties of its pyrolysate towards ammonia−nitrogen were studied. It was found that ammonia was released when MAP was pyrolyzed under specific conditions, and the pyrolysate could be recycled as an agent for the treatment of ammonia−nitrogen wastewater. However, the results also showed that when the pyrolysis temperature was low, the deamination of MAP was incomplete. Although complete deamination was achieved at high temperatures, the pyrolytic process of MAP produced $Mg_2P_2O_4$, which had no removal effect towards ammonia−nitrogen. This resulted in the deterioration of removal properties of the pyrolysate. As such, we studied a temperature-programmed method for the pyrolysis of MAP, as well as the thermodynamic and kinetic processes involved in the removal reaction system between pyrolysate and aqueous ammonium, thereby achieving the dual goals of implementing the complete deamination of MAP and ensuring that the pyrolysate has good removal properties towards ammonia−nitrogen.

2 Experimental

2.1 Preparation of MAP

NH_4Cl(AR) was used to prepare 1000 mg/L simulated aqueous ammonium wastewater. $Na_2HPO_4\cdot 12H_2O$(AR) and $MgCl_2\cdot 6H_2O$(AR), the precipitating agents, were then added before the MAP was prepared in a magnetic stirring device under constant temperature. The reaction conditions were as follows: the molar ratio of N:P:Mg based on the precipitation agents added was 1:1:1, pH value was 9.5, reaction temperature was room temperature (25 °C), and reaction time was 40 min. After the reaction was completed, the MAP precipitate was filtered, rinsed, and dried in a drying oven at a constant temperature of 40 °C for 48 h. The dried MAP precipitation was placed in a dryer for subsequent use.

2.2 Pyrolysis of MAP

An appropriate amount of MAP was placed inside a tubular resistance furnace and subjected to controlled pyrolysis through a temperature-programmed method. The heating rate was 2, 3, 5, 7, 10, or 20 °C/min from room temperature (25 °C) to the pyrolysis final temperature at 180−240 °C. Unless otherwise specified, the heating rate was 5 °C/min, final pyrolysis temperature was 180 °C, and the holding time at the final pyrolysis temperature was 3 h. The pyrolysate was sealed and stored for subsequent use.

2.3 Acid dissolution experiment

0.1 g of solidified powders (MAP or its pyrolysate) were placed in 200 mL of deionized water. The pH value was adjusted with the addition of 2 mol/L hydrochloric acid solution until the solidified powder was completely dissolved. The concentrations of ammonia−nitrogen, total phosphorus, and magnesium were then analyzed, and the deamination rate of the pyrolysate was calculated.

2.4 Removal experiment

200 mL (1000 mg/L) of aqueous ammonium was prepared inside a conical flask before NaOH and HCl solutions were added to adjust it to a particular pH. Unless otherwise stated, the pH value was controlled at 9.5. Next, 2 g of MAP pyrolysate was added before stirring was done in a constant-temperature magnetic chamber, with the temperature controlled at room temperature (25 °C). During the removal process, tests were done at regular intervals to maintain the reaction system at a constant pH level. Samples were extracted for analysis of ammonia−nitrogen concentration, as well as calculation of the removal capacity of the pyrolysate and the removal rate. Unless otherwise specified, the reaction duration was 120 min.

2.5 Analysis and characterization

Analysis of aqueous ammonium and total phosphorus concentrations was made using the spectrophotometry method. Analysis of Mg^{2+} concentration was done using flame atomic absorption spectrometry. The STA−449−F3 thermal analyzer was used for thermogravimetric and differential thermal analyses, changes in the heating rate were controlled at 2, 3, 5, 7, 10, or 20 °C/min, with the final temperature being 350 °C and air being the reaction atmosphere (20 mL/min). The S−4800 scanning electron microscope (SEM) was used to analyze the microscopic crystal