

EMILIA PETLICKA-RAJ*

REMOVAL OF AMMONIA NITROGEN FROM WASTEWATER THROUGH PRECIPITATION OF MAGNESIUM AMMONIUM PHOSPHATE

Conditions and process performance of ammonia nitrogen removal in the form of magnesium ammonium phosphate are presented. The experiments were conducted using bench scale reactors. As the precipitation reagents two sets of chemicals were applied: $MgCl_2$ with Na_2HPO_4 and MgO with H_3PO_4 . Efficiency of the process depends on pH, excess of precipitating ions, and initial ammonia nitrogen concentration. The described method allows us to achieve effective (78–93%) removal of ammonia nitrogen and can be recommended to wastewater treatment if its concentration exceeds $100 \text{ mg N-NH}_4/\text{dm}^3$.

1. INTRODUCTION

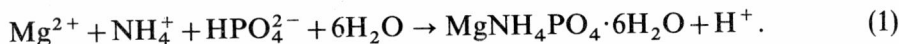
Municipal and industrial wastewater discharge results in an increased concentration of ammonia nitrogen in the surface waters. Its presence in water has a harmful impact on fish and other aquatic organisms and enhances the eutrophication process. Ammonia nitrogen also disturbs the water treatment plant and water system operation due to its corrosivity exerted toward some metals and construction materials. The presence of ammonia nitrogen affects also the efficiency of chlorine disinfection, increasing the required chlorine dosage [5].

The methods, used currently to achieve ammonia nitrogen removal from wastewater are: selective ion exchange, break point chlorination, ammonia stripping, and biological nitrification. Their application at ammonia nitrogen concentrations above $100 \text{ mg}/\text{dm}^3$, however, is very limited; biological nitrification is becoming less effective at such high concentrations, while ammonia stripping requires a significant amount of energy and creates air pollution. Break point chlorination, on the other hand, increases wastewater salinity, while a selective ion exchange process is complex and difficult in operating [3].

*Institute of Meteorology and Water Management, Water Renovation Section, ul. Manifestu Lipcowego 22, 31-109 Kraków, Poland.

The chief advantage of ammonia nitrogen precipitation in a form of magnesium ammonium phosphate is the end product ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) which can be utilized as an excellent fertilizer in agricultural and forested land [1].

Precipitation of poorly soluble salt of MgNH_4PO_4 is described by a chemical reaction:



This reaction is widely used in analytic chemistry to estimate the amount of magnesium and phosphates with ammonium ions present in excess [2].

The purpose of the paper is to describe the process of MgNH_4PO_4 precipitation as a method of ammonia nitrogen removal from wastewater.

2. MATERIALS AND METHODS

The research work was conducted on a laboratory scale in a series of batch tests. Working NH_4Cl solution was used together with two pairs of reagents: 1) MgCl_2 and Na_2HPO_4 , 2) MgO and H_3PO_4 . The experiment took place in a thermostat at 25°C and pH adjustments were done with sodium hydroxide.

The following factors, affecting the precipitation of MgNH_4PO_4 , were analysed: pH (from 8 to 12), excess of precipitating ions: magnesium (from 5 to 300%) and phosphates (from 5 to 50%),

initial concentration of ammonia nitrogen (from 50 mg/dm^3 to 500 mg/dm^3).

Wastewaters from the fertilizer industry have been used to verify the possible application of N- NH_4^+ precipitation as MgNH_4PO_4 in wastewater treatment technology.

3. RESULTS AND DISCUSSION

Because pH has a significant influence on MgNH_4PO_4 precipitation, the conditional solubility product P_s has been analysed with respect to pH. The analysis has been conducted in different ways: 1) using a theoretical method derived by STUMM and MORGAN [4], 2) using the experimental data collected during precipitation of MgNH_4PO_4 from NH_4Cl solution at ammonia nitrogen concentration of 100 mg/dm^3 and different N- $\text{NH}_4^+:\text{PO}_4$:Mg molar ratios (fig. 1).

The theoretical relationship between the conditional solubility product P_s and pH has been calculated from the equation:

$$P_s = \frac{K_{so}}{\alpha_{\text{Mg}^{2+}} \cdot \alpha_{\text{NH}_4^+} \cdot \alpha_{\text{PO}_4^{3-}} \cdot f_{\text{Mg}^{2+}} \cdot f_{\text{NH}_4^+} \cdot f_{\text{PO}_4^{3-}}} \quad (2)$$

where:

K_{so} – thermodynamic solubility product of $MgNH_4PO_4$ ($K_{so} = 7.1 \times 10^{-14}$),
 $f_{Mg^{2+}}$, $f_{NH_4^+}$, $f_{PO_4^{3-}}$ – ion activity coefficients calculated from Güntelberg approximation to the Debye–Hückel theory.

The coefficients $\alpha_{Mg^{2+}}$, $\alpha_{NH_4^+}$, $\alpha_{PO_4^{3-}}$ are calculated as:

$$\alpha_{Mg^{2+}} = \left[1 + \frac{*K_1}{[H^+]} \right]^{-1},$$

$$\alpha_{NH_4^+} = \left[1 + \frac{K_1(NH_4^+)}{[H^+]} \right]^{-1},$$

$$\alpha_{PO_4^{3-}} = \left[1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_1 \cdot K_3} + \frac{[H^+]^3}{K_1 \cdot K_2 \cdot K_3} \right]^{-1}$$

where:

$$*K_1 = 10^{-11.4},$$

$$K_{1(NH_4^+)} = 10^{-9.24},$$

$$K_{1(H_3PO_4)} = 10^{-2.1},$$

$$K_{2(H_2PO_4^-)} = 10^{-7.2},$$

$$K_{3(HPO_4^{2-})} = 10^{-12.3}.$$

The relationship between the conditional solubility product and pH has been determined from the equation:

$$P_s = C_{T,Mg} \cdot C_{T,NH_3} \cdot C_{T,PO_4} \quad (3)$$

where $C_{T,Mg}$, C_{T,NH_3} , and C_{T,PO_4} were magnesium, ammonia nitrogen, and phosphate concentrations expressed as moles/dm³.

It can be seen from fig. 1 that the data plot obtained during the experiment complies well with the theoretical curve. The linear correlation coefficient between those two curves is 0.99. The above results indicate quite clearly that the equation (2) describes the experimental data at the ionic strength values from 0.022 to 0.038 moles/dm³.

Basing on fig. 2, illustrating the concentrations of ammonia nitrogen, magnesium and phosphates vs pH of precipitation reaction, it can be stated that the amount of $N-NH_4^+$, Mg^{2+} and PO_4^{3-} ions in the solution is being reduced sharply at the pH range 8.0–10.0. The minimal ammonia nitrogen concentration (1.4 mmoles/dm³) occurred at pH = 10.5, and was equivalent to 79.7% ammonia removal. Thus, the optimal pH for the magnesium ammonium phosphate precipitation reaction should remain within the pH range from 10.4 to 10.8. The final pH values, corresponding to the optimal pH range, varied from 9.5 to 10.1.

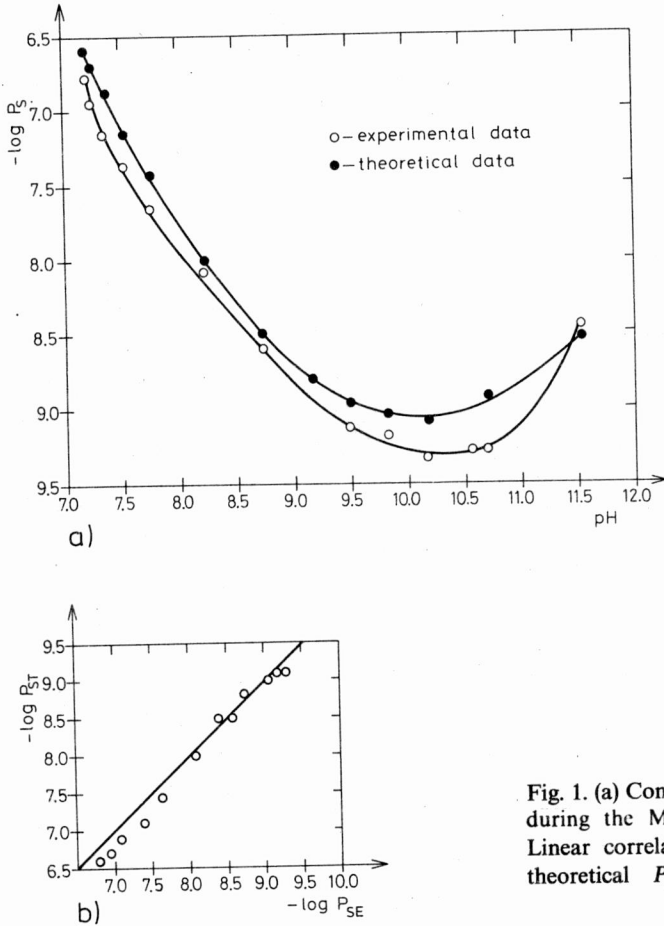


Fig. 1. (a) Conditional product solubility vs final pH during the $MgNH_4PO_4$ precipitation process, (b) Linear correlation between experimental P_{SE} and theoretical P_{ST} conditional product solubility, $R = 0.99$

In order to control the common ion effect and its influence on the reduction of the final $N-NH_4^+$ concentration in the solution, observations of the precipitating ions excess were conducted.

Concurrently occurring excess of Mg^{2+} and PO_4^{3-} ions resulted in increased precipitation of $N-NH_4^+$. The removal of $N-NH_4^+$ at molar ratio $N-NH_4^+ : PO_4^{3-} : Mg = 1:1:1$ was 79.7%, while at the ratio $N-NH_4^+ : PO_4^{3-} : Mg = 1:1.5:1.2$ it reached 91.5% (fig. 3). Additional dosage of magnesium in 20% excess and phosphates in 50% excess resulted in a drop of $N-NH_4^+$ concentration in the solution from 19.5 to 8.2 mg $N-NH_4^+ / dm^3$.

The effectiveness of ammonia nitrogen precipitation with MgO and H_3PO_4 depended upon the excess of magnesium oxide used (fig. 4). At the initial ammonia nitrogen concentration of 100 mg/dm³ and molar ratio $Mg:N = 1$, the lowest final concentration of ammonia nitrogen was 32 mg/dm³; additional dosage of Mg^{2+} ions

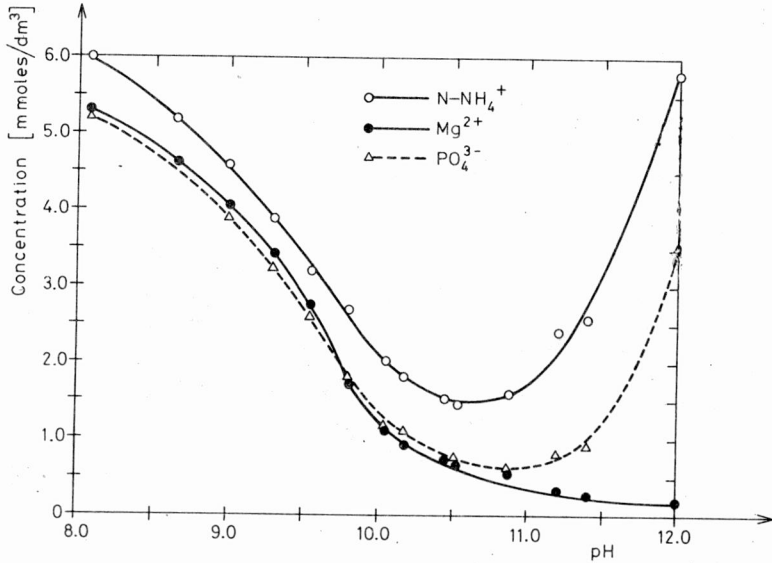


Fig. 2. Final concentration of N-NH_4^+ , PO_4^{3-} , and Mg^{2+} after MgNH_4PO_4 precipitation vs the initial pH

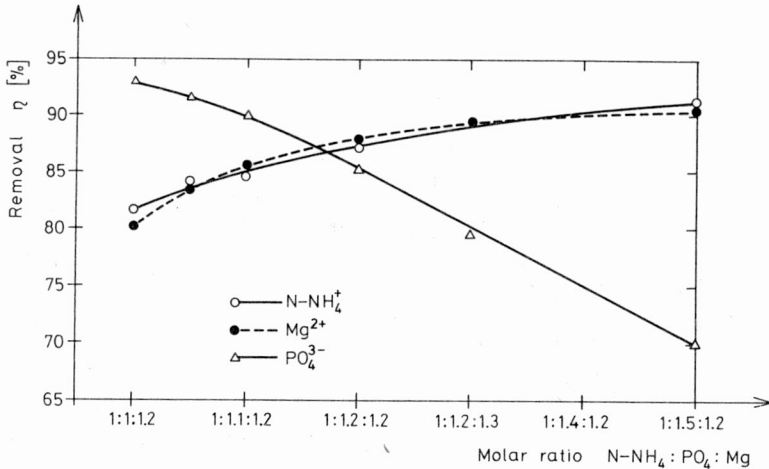


Fig. 3. Effect of the concurrent PO_4^{3-} and Mg^{2+} ions excess on N-NH_4^+ , PO_4^{3-} , and Mg^{2+} precipitation

(as MgO) in 100% excess reduced this value to 22 mg/dm^3 . Excess of MgO affected also the optimum reaction pH causing its shift toward the lower pH values along with the increase of the $\text{Mg}:\text{N}$ molar ratio. Therefore, during precipitation of MgNH_4PO_4 with MgO and H_3PO_4 , conducted in NH_4Cl solution ($\text{N-NH}_4^+ = 100 \text{ mg/dm}^3$), the best ammonia nitrogen removal (78%) was achieved at $\text{pH} = 9.5$ and the molar ratio $\text{N-NH}_4^+:\text{PO}_4^{3-}:\text{Mg} = 1:1:2$. At the same time, a decrease of the phosphate concentration in the solution was observed.

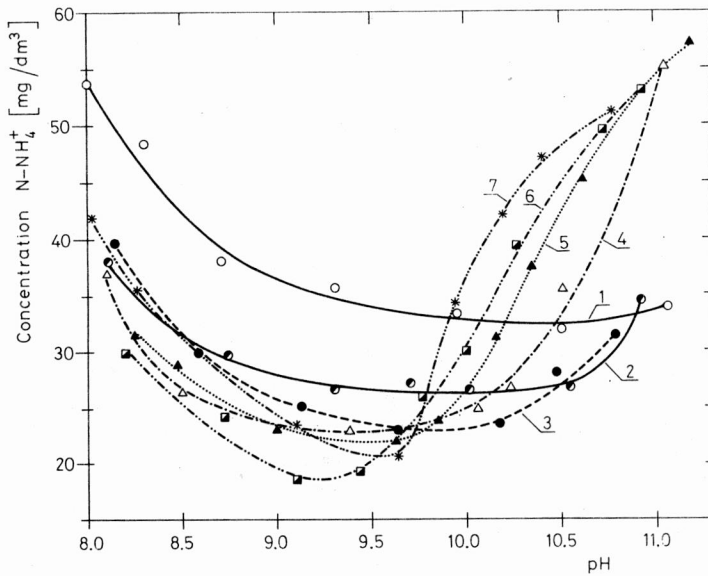


Fig. 4. Concentration of N-NH_4^+ ions after MgNH_4PO_4 precipitation as a function of pH
 Mg:N relative molar ratio for precipitation of N-NH_4^+ as MgNH_4PO_4 with MgO and H_3PO_4 as process reagents. 1 - 1.0, 2 - 1.25, 3 - 1.5, 4 - 1.75, 5 - 2.0, 6 - 2.5, 7 - 3.0

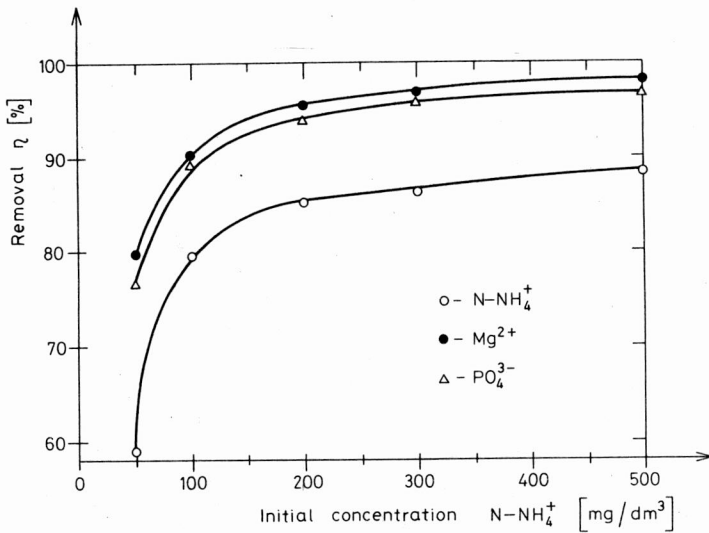


Fig. 5. Effect of the initial N-NH_4^+ concentration on N-NH_4^+ , PO_4^{3-} , and Mg^{2+} precipitation at the molar ratio $\text{N-NH}_4^+:\text{PO}_4^{3-}:\text{Mg} = 1:1:1$

The increase of the initial ammonia nitrogen concentration enhanced the intensity of the precipitation (fig. 5). Ammonia nitrogen removal increased from 59% to 88% for the initial concentrations of 50 mg/dm³ and 500 mg/dm³, respectively. It has been also observed that magnesium and phosphate precipitation intensified during the process. Because ammonia nitrogen removal, at the initial concentration of 50 mg/dm³, reaches only 59%, the precipitation method is recommended for the initial concentrations of at least 100 mg/dm³.

The experiments conducted on the wastewater generated during ammonium sulfate production confirmed the results obtained in the previous experiments on pure NH₄Cl solutions. Precipitation of magnesium ammonium phosphate with MgCl₂ and Na₂HPO₄ at the initial N-NH₄⁺ concentrations ranging from 82 mg/dm³ to 600 mg/dm³ resulted in the ammonia nitrogen removal from 46% to 94%, respectively. The removal effect improved with the increase of the initial N-NH₄⁺ concentration; the final ammonia nitrogen concentrations observed varied from 34 to 44 mg/dm³.

When MgO and H₃PO₄ were used as the reagents, the ammonia nitrogen removal was from 61% to 89% and showed an increasing tendency along with Mg:N molar ratio.

The amount of ammonia nitrogen that has been left in the wastewater ranged from 30 mg/dm³ to 640 mg/dm³ (tab. 1), and was a function of the initial N-NH₄⁺ concentration and precipitation conditions. At the equal molar ratios of N-NH₄⁺ to Mg and PO₄, the remaining phosphate concentration in the wastewater ranged from 92 mg/dm³ to 212 mg/dm³. As the amount of Mg²⁺ ions was increased up to 50% excess, the final phosphate concentration fell down to the values ranging from 1 mg/dm³ to 35 mg/dm³.

Table 1

Removal of N-NH₄⁺ through MgNH₄PO₄ precipitation from the wastewater generated during ammonium sulfate production (pH = 9.5; reagents used: MgO and H₃PO₄)

Run	Parameters	Raw wastewater concentration mg/dm ³	Treated effluent concentration at various N-NH ₄ ⁺ :PO ₄ :Mg molar ratios mg/dm ³		
			1:1:1	1:1:1.5	1:1:2
I	N-NH ₄ ⁺	185.0	57.0	40.0	30.0
	PO ₄ ³⁻	0.2	212.0	35.0	8.4
II	N-NH ₄ ⁺	580.0	205.0	76.0	63.0
	PO ₄ ³⁻	0.5	121.5	3.5	2.6
III	N-NH ₄ ⁺	2000.0	640.0	330.0	280.0
	PO ₄ ³⁻	0.5	92.0	1.0	0.9

Comparing the ammonia nitrogen precipitation with either MgCl_2 and Na_2HPO_4 or MgO and H_3PO_4 it can be stated that the latter gives both a lower N-NH_4^+ removal and a higher final N-NH_4^+ concentration in the wastewater (tab. 2). On the other hand, though using MgO and H_3PO_4 as reagents in a precipitation reaction undesirable chloride ions are eliminated, reducing the conductivity level below the one found in raw wastewater. Furthermore, excess of MgO decreases the final phosphate concentration in the wastewater.

Table 2

Efficiency of N-NH_4^+ precipitation for two different pairs of reagents: 1) MgCl_2 and Na_2HPO_4 , 2) MgO and H_3PO_4

Parameters	Type of wastewater	MgCl_2 and Na_2HPO_4	MgO and H_3PO_4
		molar ratio $\text{N-NH}_4^+:\text{PO}_4:\text{Mg}$ 1:1:1 pH = 10.5	molar ratio $\text{N-NH}_4^+:\text{PO}_4:\text{Mg}$ 1:1:1.5 pH = 9.5
Ammonia nitrogen mg $\text{N-NH}_4^+/\text{dm}^3$	raw	600.0	580.0
	treated	44.0	76.0
Phosphates mg $\text{PO}_4^{3-}/\text{dm}^3$	raw	0.15	0.5
	treated	49.2	3.5
Magnesium mg $\text{Mg}^{2+}/\text{dm}^3$	raw	2.1	2.6
	treated	47.1	35.6
Conductivity $\mu\text{S}/\text{cm}$	raw	4900	5500
	treated	9800	4100

4. CONCLUSIONS

1. Removal of ammonia nitrogen in a form of MgNH_4PO_4 is a function of pH of the precipitation reaction, excess of precipitating ions, and initial N-NH_4^+ concentration.

2. Precipitation of ammonia nitrogen as MgNH_4PO_4 results in the efficient removal of N-NH_4^+ ranging from 78% to 93%. This method is particularly useful when there is a need to decrease the ammonia nitrogen concentration in the industrial wastewater that has the initial N-NH_4^+ concentration $> 100 \text{ mg}/\text{dm}^3$.

3. Precipitated ammonia nitrogen has a form of MgNH_4PO_4 crystals, which show very good settling and filtration characteristics. It may be utilized as a high-quality fertilizer.

4. Magnesium oxide and phosphoric acid used as the reagents in precipitation reactions do not raise the wastewater salinity. The final phosphate concentration also remains at a low level.

USUWANIE AZOTU AMONOWEGO ZE ŚCIEKÓW METODĄ WYTRĄCANIA FOSFORANU MAGNEZOWO-AMONOWEGO

Ustalono warunki usuwania ze ścieków azotu amonowego w postaci fosforanu magnezowo-amonowego. Badania przeprowadzono w skali laboratoryjnej stosując dwa różne zestawy reagentów: $MgCl_2$ i Na_2PO_4 oraz MgO i H_3PO_4 . Wykazano, że efektywność strącania azotu amonowego zależy od pH, nadmiaru jonów strącających i początkowego stężenia azotu amonowego. Opracowana metoda umożliwia usuwanie azotu amonowego w zakresie 78–93% i może być stosowana do oczyszczania ścieków o stężeniu powyżej $100 \text{ mg N-NH}_4^+/\text{dm}^3$.

УДАЛЕНИЕ АММИАЧНОГО АЗОТА ИЗ СТОЧНЫХ ВОД МЕТОДОМ ОСАЖДЕНИЯ МАГНИЕВО-АММИАЧНОГО ФОСФАТА

Установлены условия удаления из сточных вод аммиачного азота в виде магниево-аммиачного фосфата. Исследования проведены в лабораторном масштабе, применяя два разных состава реагентов: $MgCl_2$ и Na_2HPO_4 , а также MgO и H_3PO_4 . Обнаружено, что эффективность осаждения аммиачного азота зависит от pH, избытка осаждающих ионов и, начально, от концентрации аммиачного азота. Разработанный метод даёт возможность удаления аммиачного азота в пределах 78–93% и может применяться для очистки сточных вод концентрации выше $100 \text{ mg N-NH}_4^+/\text{дм}^3$.

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