

Simultaneous Removal of Ammonium and Phosphate Ions from Wastewaters and Characterization of the resulting Product

A. Negrea, L. Lupa, P. Negrea, M. Ciopec and C. Muntean

Faculty of Industrial Chemistry and Environmental Engineering, University "Politehnica" Timisoara, Piata Victoriei no. 2, 300006 Timisoara, Romania, Phone: +40256404192, e-mail: adina.negrea@chim.upt.ro

Abstract : The compounds of ammonium and phosphate ions are major pollutants, which contribute to the stimulation of aquatic plants growth, microorganism development and eutrophication. This paper presents studies regarding the simultaneous removal of ammonium and phosphate ions from synthetic wastewaters through precipitation with magnesium sulfate. The laboratory research was carried out on four types of synthetic wastewaters with various initial concentrations of ammonium (0.08–1.6 g/L) and phosphate (0.4–8 g/L), at several $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratios (1:1:1 – 2:1:1), and at various values of the pH of the reaction mass (6 – 11). The possibility of simultaneous removal of ammonium and phosphate ions from wastewaters was also studied on a micro-pilot installation, in the operating conditions established at laboratory scale. The resulting solid product (magnesium ammonium phosphate) was characterized in view of capitalize it as fertilizer, through: chemical analysis, thermal analysis and X-ray diffractometry.

Keywords: ammonium, phosphate, simultaneous removal, magnesium ammonium phosphate, fertilizer

1. Introduction

The compounds containing ammonium and phosphate ions are major pollutants. They stimulate the aquatic plant growth, micro-organisms development and contribute to eutrophication in general [1-3].

Wastewaters containing ammonium and phosphate ions result from swine growth industry, tannery industry, dye industry, fertilizers industry, municipal waters, use of detergents with phosphate and ammonium content, agriculture and livestock farms [4-7].

During the precipitation process of ammonium and phosphate ions with magnesium sulfate usually results the magnesium ammonium phosphate (MAP). MAP is a white inorganic crystalline compound which can be used as fertilizer. The crystallization process depends on multiple parameters such as: concentrations of phosphate, ammonium and magnesium, pH value, ionic strength of solutions, N/P ratio [2, 8-13].

MAP appears as crystal-hydrates $MgNH_4PO_4 \cdot nH_2O$ (where $n = 1, 3, 6, 7$). In analytical and technological practice prevails magnesium ammonium phosphate crystallized with one and six moles of water, respectively. MAP is a concentrated complex fertilizer, which contains three nutritive elements: phosphorus, nitrogen and magnesium. MAP can be used as fertilizer as it is, or it can be used to obtain mixed fertilizers. MAP is among the few fertilizers which contain nitrogen under a water insoluble, slowly assimilable form. The efficiency of MAP components in soil is higher than the efficiency of the same components, but bound in other combinations. MAP can be also used as fireproof material in fire extinguisher foam, as ceramic pigment and for metal phosphating [14].

Taking into account the importance of ammonium and phosphate removal from wastewaters for the protection of

the environment, our paper presents studies carried out on synthetic wastewaters, in laboratory and on a micro-pilot installation. The precipitation with magnesium sulfate has the advantage that it simultaneously removes ammonium and phosphate ions, which contribute together to the eutrophication process and are to be found together in different wastewaters. The laboratory studies were carried out on four types of synthetic wastewaters, in view to apply this method for different wastewaters, resulting from different industries. The study on the micro-pilot installation was carried out to establish if this method can be used for the treatment of large amount of wastewaters from different industrial processes. The product resulting in the precipitation process was characterized in view of using it as fertilizer. The method also presents the advantage that the resulting precipitate does not represent a new waste, but it is in fact a useful product.

2. Experimental

The laboratory research was carried out at room temperature using the Jar-Test precipitation method. As precipitation agent a magnesium sulfate solution was used. Four types of synthetic wastewaters with various initial concentrations of ammonium and phosphate ions were used (Table 1). The samples of wastewater were treated with a solution containing 10 g/L Mg^{2+} at several $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratios (1:1:1, 1.2:1:1; 1.4:1:1; 1.6:1:1; 1.8:1:1 and 2:1:1). The pH of the reaction mass was adjusted to various values (6, 7, 8, 9, 10 and 11) using a 10% NaOH solution. All used chemicals were in analytical reagent grade. The pH of the reaction mass has been measured using a Denver Instrument 250 pH-meter / conductivity-meter.

The precipitation agent was added to the water samples in the amount requested to reach the desired $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio, and the pH was adjusted to the desired value. The reaction mass was stirred with 150 rpm for 5 min (blending and reaction time), then with 50 rpm for 10 min (flocculation period). The resulting suspension was immediately filtered and the filtrate was analyzed to determine the residual concentrations of ammonium and phosphate ions.

TABLE 1. Initial concentrations of ammonium and phosphate ions in the studied wastewaters

Water type	Initial concentration of NH_4^+ , g/L	Initial concentration of PO_4^{3-} , g/L
1	0.08	0.4
2	0.4	2
3	0.8	4
4	1.6	8

The concentration of ammonium ions was determined through UV-VIS spectrometry at 425 nm, using double tartrate of sodium and potassium and Nessler reagent [15]. The concentration of phosphate ions was determined through UV-VIS spectrometry, using vanadomolibdate at 460 nm [16]. The absorbance was measured with a Varian Cary 50 spectrophotometer.

The micro-pilot installation used for the studies is presented in Fig. 1.

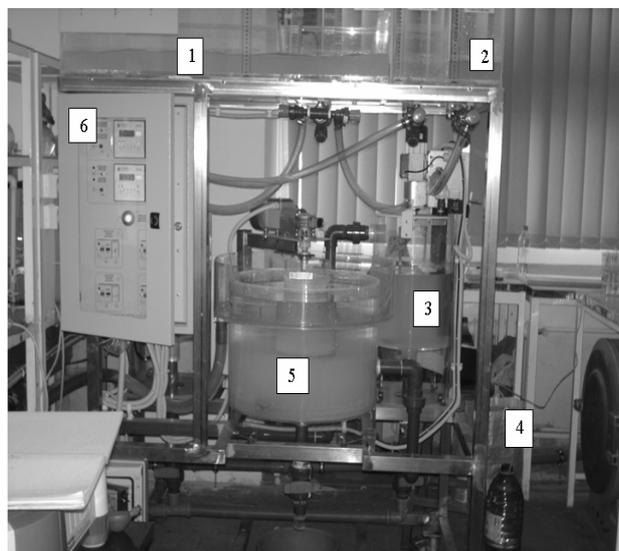


Figure 1. View of the pilot installation

- 1 – feed tank (170 L) containing waste water
- 2 – tank (20 L) with 10% NaOH solution for pH adjustment
- 3 – tank (20 L) for pH adjustment and precipitation, with agitator with impeller (100 rpm)
- 4 – peristaltic pump for $MgSO_4$ solution dosing
- 5 – settling tank (70 L), with agitator with rake blades (2 rpm)
- 6 – control and monitoring electric panel

The pilot installation was operated for 240 min and the pH value was monitored from the control panel. The wastewater to be treated was transferred from feed tank (1) with a flow rate of 10 L/h into precipitation and pH adjustment tank (3). In tank (3) was added the precipitation

agent, a 10 g/L Mg^{2+} solution, with a flow rate of 0.6 L/h. The pH of the reaction mass in tank (3) was adjusted to the desired value using the 10% NaOH solution stored in tank (2). At these flow rates, the reaction mass needed 50 min (contact time) to fill the precipitation tank (3) and to reach the settling tank (5) which separates the water from the sludge: the clarified water going to the discharge pipes comes out from the top of the settler, while the sludge comes out from the bottom through a valve.

Samples of clarified water from settling tank (5) were collected every 15 min and were analyzed in order to determine the residual concentrations of ammonium and phosphate ions.

The sludge resulting in steady-state was dried in open air. The solid product was characterized in order to find out if it can be used as fertilizer. The product was submitted to a complex study: chemical analysis, thermal analysis and X-ray diffractometry.

The TG, DTG and DTA curves were registered using a Perkin Elmer Diamond TG/DTA Analyzer in an Al_2O_3 crucible, with a linear heating rate of $10^\circ C/min$, in dynamic atmosphere (air, 100 mL/min), Al_2O_3 as DTA reference, on a sample of ~8 mg.

The X-Ray powder diffraction pattern was recorded on a Bruker D8 Advance automated powder diffractometer using $Mo K_\alpha$ radiation.

3. Results and Discussion

To establish the optimum conditions for the simultaneous removal of ammonium and phosphate ions from wastewaters, the dependence of the degree of separation of ammonium and phosphate ions on different parameters (pH, $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio and initial concentrations of ammonium and phosphate ions) was studied.

The degree of separation of ammonium and phosphate ions was calculated using the relation:

$$\alpha = \frac{n_i - n_f}{n_i} 100 \quad (1)$$

where n_i is the amount of ammonium or phosphate present in the treated water, and n_f represents the amount of ammonium or phosphate remained in the solution resulting after the separation of the precipitate.

The optimum conditions of the process are those which ensure a maximum degree of separation of ammonium and phosphate ions from the wastewaters.

3.1. Laboratory research

The experimental data regarding the dependence of the degree of separation of ammonium and phosphate ions, respectively, on the pH of the reaction mass and on the $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio for all four types of waters we studied, are presented in Figs. 2 and 3.

From the experimental data in Fig. 2 one may notice that the degree of separation of ammonium ions increases with the increase of the pH of the reaction mass and with

the increase of the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio. Although we noticed that the degrees of separation at $\text{pH} = 11$ are somehow higher than the ones reached at $\text{pH} = 10$, it is possible that this increase is not due to the separation of ammonium in the precipitate, but to the transformation of ammonium in ammonia, which takes place at pH values higher than 9.25 (pK_a). Therefore, a pH value higher than 10 is not recommended since a fraction of ammonium is lost in the atmosphere, also causing pollution.

The increase of the degree of separation of ammonium with the increase of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio is insignificant for $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratios $> 1.2:1:1$. Therefore is not worthy using the precipitation agent MgSO_4 in excess. Besides, higher $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratios lead to higher amounts of unreacted Mg^{2+} and therefore to higher residual concentrations of magnesium.

One can also observe that the degree of separation of ammonium ions increases as the ammonium ions initial concentration increases. Obviously, the residual concentration of the ammonium ions also increases, and is recommended to choose the conditions which ensure residual concentrations lower than the values permitted by the legislation for the discharge of wastewaters.

From Fig. 3 one can notice that the degree of separation of phosphate ions increases with the pH of the

reaction mass. The increase of the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio has not an important influence on the increase of the degree of separation of phosphate ions, therefore is not worthy using the precipitation agent MgSO_4 in excess. We consider as optimum a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 1.2:1:1. One may also notice that the degree of separation of phosphate ions increases with the increase of the initial concentration of the phosphate ions, but consequently the residual concentration of phosphate also increases.

The residual concentration of magnesium ions also increases with the increase of the initial concentrations of phosphate and ammonium ions, because to maintain the optimum $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 1.2:1:1, as the amount of ammonium and phosphate in the water increases, the required amount of precipitation agent also increases.

Taking into account the results of the laboratory studies, we consider that the optimum conditions for the process of simultaneous removal of ammonium and phosphate ions from the wastewaters we studied are: a pH of the reaction mass of ~ 10 and a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 1.2:1:1. Table 2 presents the degrees of separation reached in these conditions for ammonium and phosphate ions, for the synthetic wastewaters we studied.

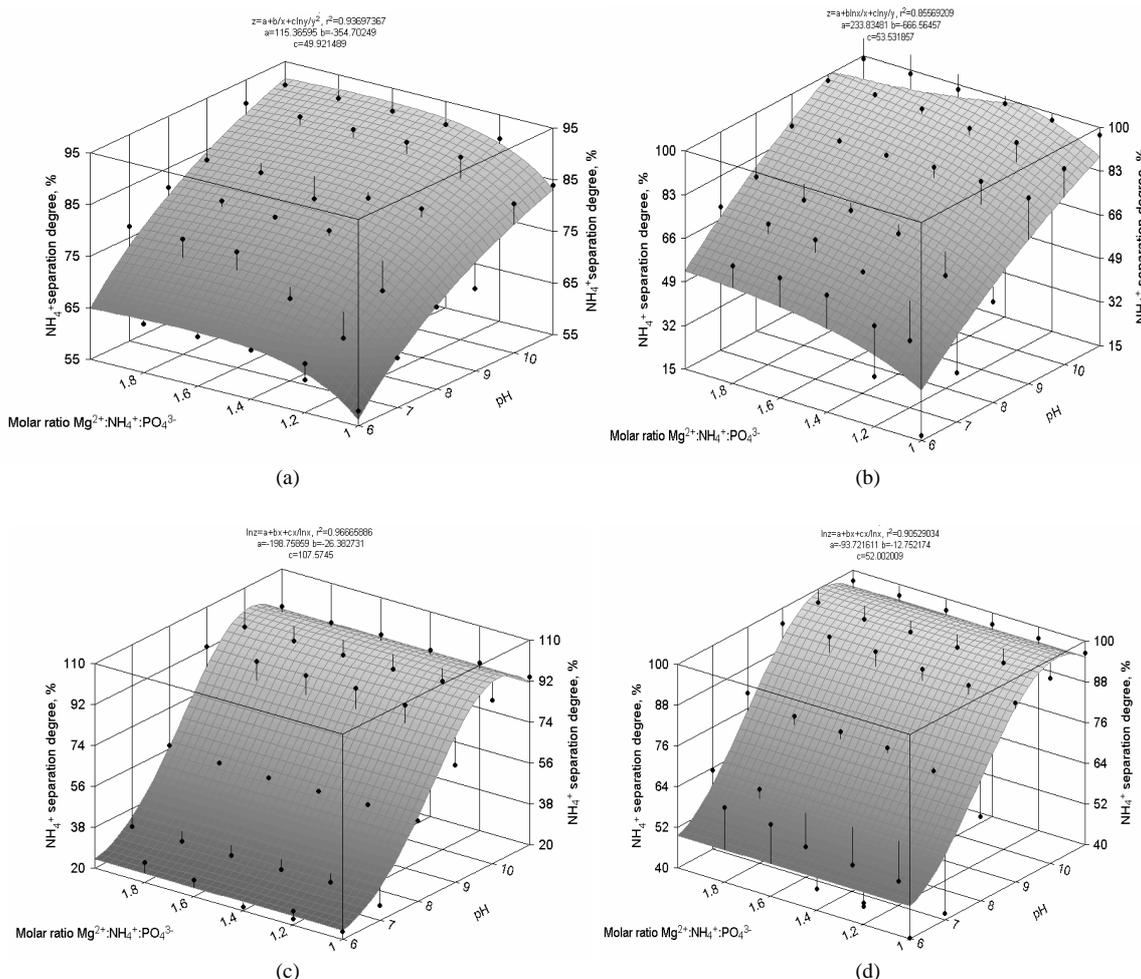


Figure 2. Dependence of the degree of separation of ammonium ions on the pH of the reaction mass and on the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio (a) water type 1; (b) water type 2; (c) water type 3; (d) water type 4.

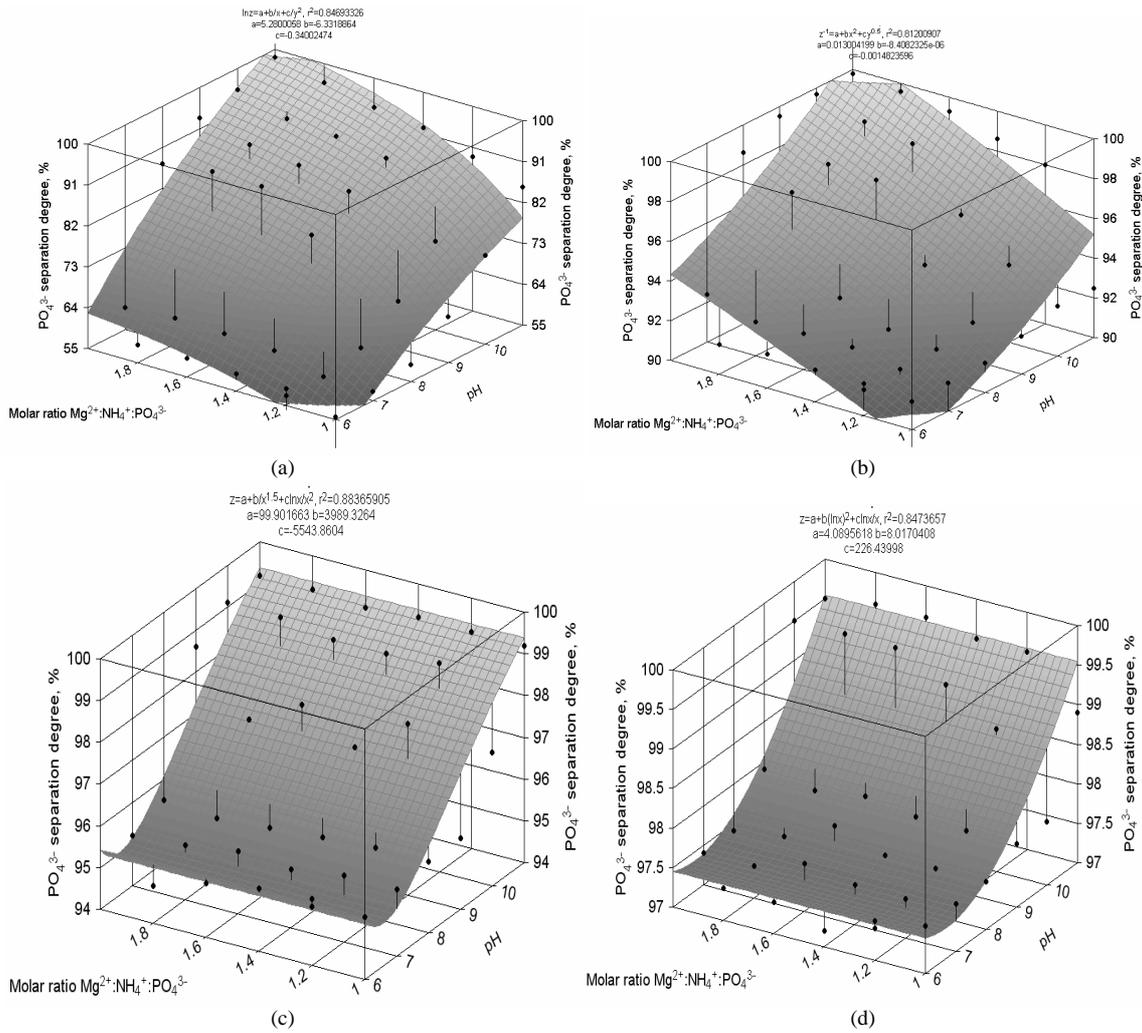


Figure 3. Dependence of the degree of separation of phosphate ions on the pH of the reaction mass and on the Mg²⁺: NH₄⁺: PO₄³⁻ molar ratio (a) water type 1; (b) water type 2; (c) water type 3; (d) water type 4.

TABLE 2. Degrees of separation of ammonium and phosphate ions reached in optimum conditions

Ions	Water type			
	1	2	3	4
Degree of separation, %				
NH ₄ ⁺	90	97	95	95
PO ₄ ³⁻	75	94	99	99

3.1. Research on micro-pilot installation

For the research on micro-pilot installation we decided to use the wastewater of type 2 (containing 2 g/L PO₄³⁻ and 0.4 g/L NH₄⁺). For this water we reached degrees of separation of ammonium and phosphates ions higher than for water of type 1. For wastewaters of types 3 and 4, even the degrees of separation were higher than those reached for the other two types of wastewater, the residual concentrations of ammonium, phosphate and magnesium

ions were also higher. In view of discharge, such residual solutions should be submitted to an advanced purification.

The wastewater and the precipitation agent were mixed in the reaction tank at the molar ratio Mg²⁺:NH₄⁺:PO₄³⁻ = 1.2:1:1. The pH of the reaction mass was maintained from the control panel at ~10, using a 10% NaOH solution. The installation was operated for 240 min.

The experimental data regarding the evolution in time of the degree of separation of the ammonium and phosphate ions and of the pH of the reaction mass are presented in Fig. 4.

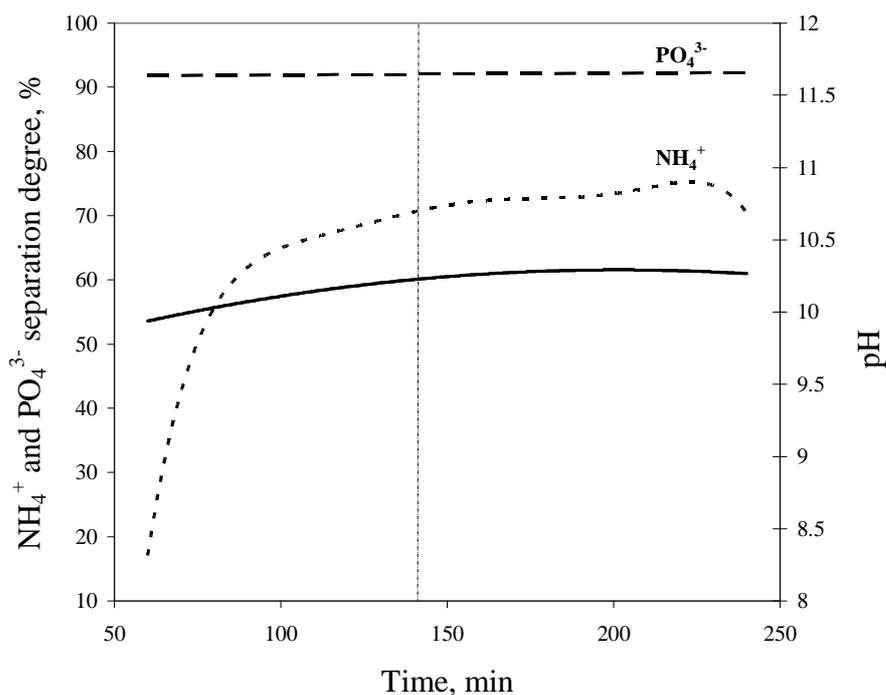


Figure 4. Evolution in time of the degree of separation of ammonium and phosphate ions and of the pH of the reaction mass

From Fig. 4 one can observe that the degree of separation of the ammonium ions increases in time. The degree of separation of the phosphate ions is almost the same during the experimental time. One can also notice that the value of the pH of the reaction mass lies around the established value. The small variations are due to the operating principle of the valve which releases the neutralization agent when the sensor detects a decrease of the pH value.

The sampling has begun after the pilot installation worked for 50 min. This is the period of time required so that the suspension reaches the settling tank, where the samplings were made. The pilot installation reached the steady-state after 140 min of operation. At this moment the degree of separation of ammonium ions was of ~72% and the degree of separation of phosphate ions was of ~93%.

3.3. Characterization of the resulting solid product

The precipitate resulting from the process of simultaneous removal of ammonium and phosphate ions in the micro-pilot installation was analyzed in order to find out if it can be used as fertilizer magnesium ammonium phosphate.

The chemical composition of the product is: NH₄⁺ – 9.1%; PO₄³⁻ – 61.9%; Mg²⁺ – 14.6%. The composition of our product was compared with the theoretical composition of the magnesium ammonium phosphates crystallized with one and six moles of water respectively, which can result during the precipitation process: MgNH₄PO₄·H₂O (NH₄⁺ – 11.6%; PO₄³⁻ – 61.1%; Mg²⁺ – 15.6%) and MgNH₄PO₄·6H₂O (NH₄⁺ – 7.4%; PO₄³⁻ – 38.7%; Mg²⁺ –

9.9%). One can notice that the composition of our product is closer to the theoretical composition of MgNH₄PO₄·H₂O.

The studies on the thermal behavior and stability of the product are significant for obtaining this type of fertilizer in industrial processes. The thermo-analytical curves of the solid product are presented in Fig. 5.

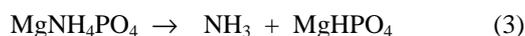
During heating at a constant heating rate of 10°C/min up to ~1100°C, a decomposition process with mass loss takes place in the sample: up to 400°C the sample loses 24.0% in two steps: I – up to 200°C, 17.2% mass loss, with maximum rate at 90°C, and endo-thermal effect at 95°C; II – between 200 and 400°C, 6.8% mass loss, with maximum rate at 225°C. This mass loss is probably due to the loss of moisture, crystallization water and ammonia. Between 400 and 690°C, the sample loses 2.6%. When the temperature increases up to ~1100°C, the mass of the sample remains the same and the residue was of 73.4%. DTA curve shows another two effects: an exo-thermal effect at 700°C and an endo-thermal effect at 1010°C.

During heating of metal ammonium phosphates, several overlapping processes take place [17-20]:

- dehydration of the crystal hydrate:



- removal of ammonia from the resulting anhydrous salt:



- removal of the structural water:



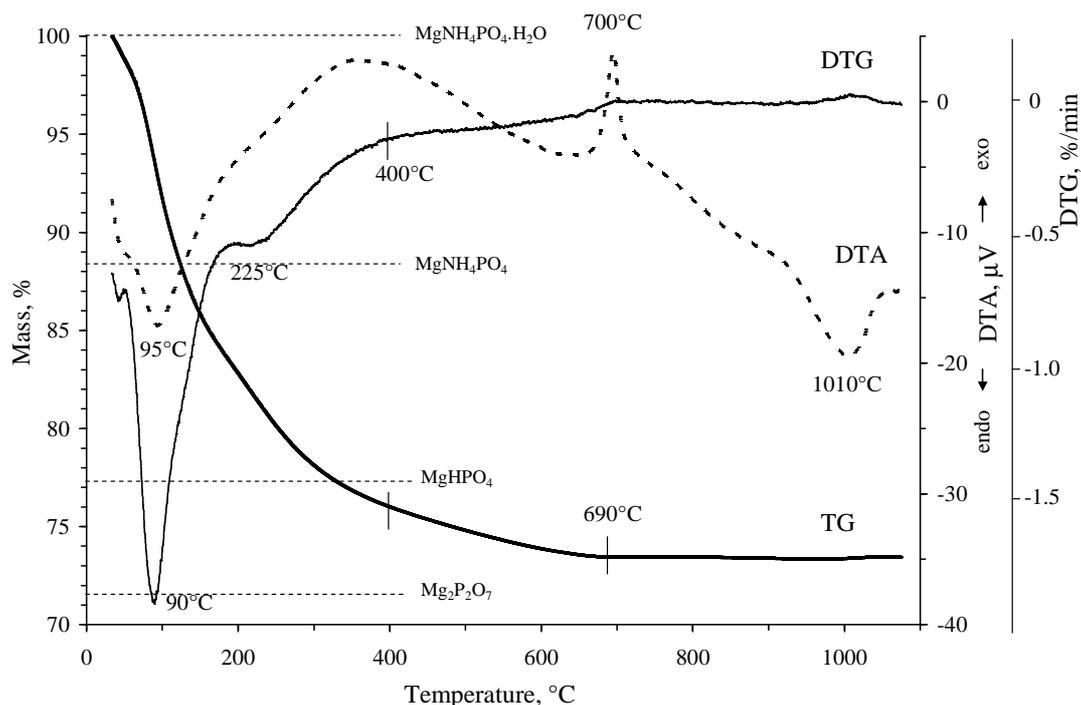


Figure 5. TG, DTG and DTA curves of the resulting solid product

The theoretical mass losses for processes (2)-(4) are: (2) – 11.6%, (3) – 11.0% and (4) – 5.8%. For our sample, the total mass loss of 26.6% (up to ~700°C) is close to the total theoretical mass loss of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ (28.4%). The difference between the theoretical and experimental total mass loss may be due to the fact that besides $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, our product may contain in small proportion other compounds resulting during the precipitation process (such as magnesium hydroxide $\text{Mg}(\text{OH})_2$). From the thermo-gravimetric data one also notice that in the first step of the decomposition process (up to 200°C) the mass loss is of 17.2%, which means that besides the crystallization water, the sample also loses ammonia according to Eq. (3). It is likely that processes (2) and (3) take place together, up to ~400°C. At temperatures higher than 300°C, process (4) overlaps: once formed according to Eq. (3), the magnesium hydrogen phosphate MgHPO_4 begins to lose the structural water (Eq. 4). In Fig. 5 are illustrated the theoretical steps for the decomposition of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$.

The thermal behavior of our product allows us to conclude that if we intend to use it as a fertilizer, in the industrial process, during drying and granulation, the fertilizer does not lose the nutrients phosphorus and magnesium. Depending on the temperature of the process, which is usually of 180-200°C, the fertilizer may lose a fraction of the crystallization water and a fraction of nutrient nitrogen as ammonia. Although the complete removal of the ballast crystallization water represents an advantage, this is not possible without partial loss of ammonia, since processes (2) and (3) overlap.

The X-ray diffraction pattern of the solid product showed that the product is non-crystalline (there are no

lines in the pattern), due to the synthesis conditions. A crystalline magnesium ammonium phosphate monohydrate can be obtained by adding ammonia solution (in drops, under continuous stirring) to a solution containing an 1:1 mixture of MgSO_4 and $(\text{NH}_4)_2\text{HPO}_4$, at 80-100°C [14], but to obtain a crystalline product was not our purpose.

Although the product resulting during the simultaneous removal of ammonium and phosphate ions from the residual water was not crystalline and therefore could not be identified by means of X-ray diffractometry, taking into account the chemical analysis and thermal analysis data, we concluded that this product has as main component the magnesium ammonium phosphate monohydrate $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and it can be used as fertilizer. This type of fertilizer is not hygroscopic, does not lose ammonia during storage, and it is soluble in ammonium citrate and citric acid solution [14].

4. Conclusions

Ammonium and phosphate ions can be simultaneously removed from wastewaters through precipitation with magnesium sulfate. In the present paper were carried out studies in the laboratory and on a micro-pilot installation.

To establish the optimum conditions which ensure a maximum degree of separation of ammonium and phosphate ions, the laboratory research was carried out using four types of synthetic wastewaters with various initial concentrations of ammonium (0.08–1.6 g/L) and phosphate (0.4–8 g/L). The water samples were treated with a MgSO_4 solution at several $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratios (1:1:1 – 2:1:1) and at various values of the pH of the reaction mass (6 – 11).

From the laboratory research we concluded that the ammonium and phosphate removal process was the most efficient for a value of the pH of the reaction mass of 10, a $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio of 1.2:1:1, an initial concentration of phosphate ions of 2 g/L, and an initial concentration of ammonium ions of 0.4 g/L.

The process of simultaneous removal of ammonium and phosphate ions in the micro-pilot installation was also very efficient; high degrees of separation were reached for the ions we studied (~72% for ammonium and ~93% for phosphate ions). Consequently, one may conclude that this method can be used for the treatment of large amount of wastewaters from different industrial processes.

The process of simultaneous removal of ammonium and phosphate ions from wastewaters through precipitation with magnesium sulfate presents the advantage that the resulting precipitate does not represent a new waste, but it is in fact a useful product, the magnesium ammonium phosphate. The chemical analysis and thermal analysis data showed that the solid product we obtained is mainly composed of magnesium ammonium phosphate monohydrate. This compound may be used as slow-release fertilizers due to its low solubility in water. This fertilizer contains three nutritive elements: phosphorus, nitrogen and magnesium.

During heating of magnesium ammonium phosphate monohydrate, several overlapping processes take place: dehydration of the crystal hydrate, removal of ammonia from the resulting anhydrous salt and removal of the structural water. In the industrial process, during drying and granulation, the fertilizer does not lose the nutrients phosphorus and magnesium. Depending on the temperature of the process, which is usually of 180-200°C, the fertilizer may lose a fraction of the crystallization water and a fraction of nutrient nitrogen as ammonia. Although the complete removal of the ballast crystallization water represents an advantage, this is not possible without partial loss of ammonia.

REFERENCES

1. Negrea A., Pode V., Negrea P., Iovi A., Lupa L., Ciopec M., and Mosoarca, G., *Rev. Chim. (Bucharest)*, 58, **2007**, 999-1003.
2. Ali M.I., and Schneider P.A., *Chem. Eng. Sci.*, 63, **2008**, 3514-3525.
3. Lupa L., Negrea P., Negrea A., Iovi A., Coheci L., and Mosoarca G., *Braz. J. Chem. Eng.*, 25, **2008**, 9-17.
4. Tunay O., Kabdasli I., Orhon D., and Kolcak S., *Water Sci. Technol.*, 36, **1997**, 225-228.
5. Stratful I., Scrimshaw M. D., and Lester J. N., *Water Res.*, 35, **2001**, 4191-4199.
6. Suzuki K., Tanaka Y., Osada T., and Waki M., *Water Res.*, 36, **2002**, 2991-2998.
7. Chimenos J.M., Fernandez A.I., Villalba G., Segarra M., Urruticoechea A., Artaza B., and Espiell F., *Water Res.*, 37, **2003**, 1601-1607.
8. Sugiyama S., Yokoyama M., Ishizuka H., Sotowa K.-I., Tomida T., and Shigemoto N., *J. Colloid Interface Sci.*, 292, **2005**, 133-138.
9. Wang J., Song Y., Yuan P., Peng J., and Fan M., *Chemosphere*, 65, **2006**, 1182-1187.
10. El Diwani G., El Rafie Sh., El Ibiari N.N., and El-Aila H.I., *Desalination*, 214, **2007**, 200-214.
11. Song Y., Yuan P., Zheng B., Peng J., Yuan F., and Gao Y., *Chemosphere*, 69, **2007**, 319-324.
12. Gunay A., Karadag D., Tosun I., and Ozturk M., *J. Hazard. Mater.*, 156, **2008**, 619-623.
13. Liu Z., Zhao Q., Lee D.-J., and Yang N., *Biores. Technol.*, 99, **2008**, 6488-6493.
14. Iovi A., Iovi C., and Negrea P., *Chemistry and Technology of Complex Fertilizers (in Romanian)*, Politehnica Publishing House, Timisoara, **1999**.
15. Romanian normative – STAS 6328/1985, Determination of ammonia nitrogen in surface waters and wastewaters.
16. Helrich K. (Ed.), *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th Ed., Arlington V.A., USA, 1990.
17. Liptay G., *Atlas of Thermoanalytical Curves*, vol. 4, Akadémiai Kiadó, Budapest, **1974**.
18. Galkova T.N., Pacewska B., Samukevich V.V., Pysiak J., and Shulga N.V., *J. Therm. Anal. Cal.*, 60, **2000**, 1019-1032.
19. Muntean C., Toma D., Iovi C., Iovi A., and Negrea P., *Chem. Bull. "Politehnica" Univ. (Timisoara)*, 47(61), **2002**, 1-6.
20. Muntean C., Marginean G., Iovi A., and Negrea P., *Rev. Chim. (Bucharest)*, 55, **2004**, 81-85.

Received: 17 June 2010

Accepted: 26 November 2010