Chem. Bull. "POLITEHNICA" Univ. (Timişoara)

# Studies Regarding the Establishment of the Optimum Conditions of Ammonium and Phosphate Ions Removal from Water

A. Negrea, L. Lupa, M. Ciopec, C. Muntean, P. Negrea, G. Mladin

<sup>\*</sup>University "Politehnica" Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Piața Victoriei, no. 2, 300006 Timişoara, Phone: +40 256 404164, Fax. +40 256 404192, E-mail address: <u>adina.negrea@chim.upt.ro</u>

**Abstract**: Water pollution is considered to be a direct or indirect change of its natural composition, as a result of the human activities. The pollutants cause due to their nature, concentration and their time of action, noxious effects on the health, create discomfort or deteriorate the various uses of the environment. Having in mind the special problem of the pollution of waters with ammonium and phosphate ions, the study of the possibilities of their removal represents a special problem regarding the environmental protection. In this paper we studied the possibilities of ammonium and phosphate removal from waters through precipitation using the Jar-Test method. As precipitation agent it was used the MgSO<sub>4</sub> with a concentration of 100 mg/L. For the establishment of the optimum conditions of ammonium and phosphate removal from water we worked at various initial concentrations of ammonium and phosphate ions from water, at various Mg<sup>2+</sup>:NH<sub>4</sub><sup>+</sup>:PO<sub>4</sub><sup>3-</sup> molar ratios and at various values of the pH of the reaction mass.

Keywords: ammonium ions, phosphate ions, removal, precipitation

#### **1. Introduction**

The environmental protection represents a major problem of the humanity. The pollution is caused, not only by the presence of the toxic substances but also by the presence of some substances (such as compounds with nitrogen and phosphorous) which cause the vegetation development, especially of the aquatic vegetation [1-3].

This phenomenon (eutrophication) is caused not only by the nutritive substances but also by other physicalchemical factors such as flow velocity of the waters, depth, temperature, luminosity etc.). The eutrophication phenomenon can be observed especially in the waters with slow velocity (canals) or ditch water (pool, lakes, barrages etc.). To prevent the eutrophication phenomenon one can take a series of measures such as the reduction of the nutritive substances content, respectively of the compounds with nitrogen and phosphorous [3-7].

The main sources of pollution with ammonium and phosphate ions are: the waters from fertilizers industry, the municipal waters, and the use of detergents containing phosphate and ammonium, the waters resulted from agriculture and animal husbandry etc.

In this purpose trough the laboratory research it was followed the establishment of the optimum conditions of the elimination process through precipitation of the ammonium and phosphate ions from residual waters.

## 2. Experimental

In the view of ammonium and phosphate ions removal from waters it was used the precipitation method Jar-Test. As precipitation agent it was used the  $MgSO_4$  with a concentration of 100 mg/L.

We used 4 types of waters having various initial concentrations of ammonium and phosphate ions as presented in Table 1. A well determined volume of water was treated with MgSO<sub>4</sub> at various molar ratio  $(Mg^{2+}:NH_4^+:PO_4^{3-}=1:1:1, 1.2:1:1; 1.4:1:1; 1.6:1:1; 1.8:1:1; 2:1:1)$ . The pH of the reaction mass was adjusted at various values (6, 7, 8, 9, 10 and 11) using a 10M NaOH solution.

TABLE 1. The initial concentrations of ammonium and phosphate ions from the studied waters

Type of water	NH4 <sup>+</sup> initial concentration, g/L	PO <sub>4</sub> <sup>3-</sup> initial concentration, g/L
1	0.08	0.4
2	0.4	2
3	0.8	4
4	1.6	8

After the adding of the precipitation agent dose and after the pH adjustment the samples were stirred with a higher velocity (~150 rot/min) for 3-5 minutes, which represents the blending and reaction time, then with a lower velocity (~50 rot/min) for 5-10 minutes, which represents the flocculation period. After settling and filtration it was determined the residual concentrations of ammonium, phosphate and magnesium.

The ammonium ions concentration was determined through UV-VIS spectrometry method using the double tartrate of Na and K and Nessler reagents at the wave length of 425 nm. The phosphate ions concentration was determined through UV-VIS spectrophotometry using vanadomolibdate at 460 nm and a Varian Cary 50 spectrophotometer.

The residual concentration of magnesium was determined through atomic absorption spectrometry using an atomic absorption spectrophotometer Varian SpectrAA 110.

### 3. Results and discussion

For the establishment of the optimum conditions of ammonium and phosphate ions removal from waste waters it was determined the dependence of the residual concentration of ammonium and phosphate ions versus the pH of the reaction mass,  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio and initial concentrations of ammonium and phosphate.

The experimental data regarding the dependences of the ammonium ions residual concentration versus the pH of the reaction mass and the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio for all 4 types of studied waters are presented in Figures 1-4.



Figure 1. Ammonium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2^+}$ :  $NH_4^+$ :  $PO_4^{3^-}$  molar ratio in the case of water type 1



Figure 2. Ammonium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 2



Figure 3. Ammonium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 3



Figure 4. Ammonium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 4

From the experimental data it can be observed that the ammonium ions residual concentration decrease with the pH of the reaction mass and with the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio. This influence is insignificant at a reaction mass pH > 10 and at a molar ratio  $Mg^{2+}:NH_4^+:PO_4^{3-} > 1.2:1:1$ . It also can be observed that the residual concentration of ammonium ions increases with the ammonium ions initial concentration.

The experimental data regarding the dependence of the phosphate ions residual concentration versus the pH of the reaction mass and the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio for all 4 types of studied waters are presented in Figures 5-8.



Figure 5. Phosphate ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 1



Figure 6. Phosphate ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2^+}$ :  $NH_4^+$ :  $PO_4^{3^-}$  molar ratio in the case of water type 2



Figure 7. Phosphate ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 3



Figure 8. Phosphate ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 4

From the experimental data it can be observed that the phosphate ions residual concentration decreases with the pH of the reaction mass. The increase of the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio has not an important influence on the decrease of the phosphate ions residual concentration, so is not justified to use in excess the precipitation agent MgSO<sub>4</sub>. The optimum value of the pH of the reaction mass is 10 and the optimum  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio is 1.2:1:1. One may also notice that the phosphate ions residual concentration increases with the initial concentration of the phosphate ions.

The experimental data regarding the dependence of the magnesium ions residual concentration versus the pH of the reaction mass and the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  molar ratio for all 4 types of studied waters are presented in figures 9-12.



Figure 9. Magnesium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 1

Volume 53(67), 1-2, 2008



Figure 10. Magnesium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 2



Figure 11. Magnesium ions residual concentration dependence versus the pH of the reaction mass and the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio in the case of water type 3



Figure 12. Magnesium ions residual concentration dependence versus the pH of the reaction mass and the Mg<sup>2+</sup>: NH<sub>4</sub><sup>+</sup>: PO<sub>4</sub><sup>3-</sup> molar ratio in the case of water type 4

From the experimental data one observes that the magnesium ions residual concentration increases with the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio and with the initial

concentrations of ammonium and phosphate ions. The magnesium ions residual concentration decreases with the pH of the reaction mass.

#### 4. Conclusions

Following the analysis of the experimental data, we concluded that the ammonium and phosphate ions can be removed from waste waters through "Jar Test" precipitation method using MgSO<sub>4</sub> as precipitation agent.

From the experimental data it can be observed that the residual concentrations of the ammonium and phosphate ions decrease with the pH of the reaction mass and with the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio. The residual concentrations of the ammonium and phosphate ions increase with the initial concentrations of ammonium and phosphate ions. The optimum value of the pH of the reaction mass is 10 and the optimum  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio the influence is not so evident so is not justified to use an excess of the precipitation agent  $MgSO_4$ .

It was observed that the magnesium ions residual concentration increases with the  $Mg^{2+}$ :  $NH_4^+$ :  $PO_4^{3-}$  molar ratio and with the initial concentrations of ammonium and phosphate ions. The magnesium ions residual concentration decreases with the pH of the reaction mass.

This method is very efficient to eliminate the ammonium and phosphate ions from waste waters, but the resulted solutions must be submitted to an advanced treatment for ammonium and phosphate ions removal, because the residual concentrations resulted through this method of treatment are higher than the maximum concentration admitted by the legislation.

#### REFERENCES

1. Suzuki K., Tanaka Y., Osada T. and Waki M., Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Research*. **2002**., Vol. 36. Issues 12. pp. 2991-2998.

2. Tunay O., Kabdasli I., Orhon D. and Kolcak, S., Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters. *Water Science and Technology*. **1997**, Vol. 36. Issues 2-3. pp. 225-228.

3. Chimenos J.M., Fernandez A.I., Villalba G., Segarra M., Urruticoechea A., Artaza B. and Espiell F., Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product. *Water Research.* **2003**. Vol. 37. Issue 7. pp. 1601-1607.

4. El Diwani G., El Rafie Sh., El Ibiari N.N. and El-Aila H.I., Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer. *Desalination*. **2007**. Vol. 214. Issues 1-3. pp. 200-214.

5. Song Y., Yuan P., Zheng B., Peng J., Yuan F. and Gao Y., Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine waste water. *Chemosphere*. **2007**. Vol. 69. Issue 2. pp. 319-324.

6. L. Lupa, P. Negrea, A. Negrea, A. Iovi, L. Cocheci, G. Mosoarca, Modeling and automation of the process of phosphate ion removal from waste waters, *Brazilian Journal of Chemical Engineering*. **2008**. Vol. 25. No. 01. pp. 9-17.