Studies Regarding the Obtaining Process of Iron (II) -Ammonium Phosphate from Residual Solutions

CLAUDIA MORGOVAN[1]*, ELEONORA MARIAN[2], AUREL IOVI[3], IOAN BRATU[4], GHEORGHE BORODI[4]
[1]University of Oradea, Faculty of Electrical Engineering and Information Technology, 1 Universitatii Str.,410087, Oradea, Romania
[2]University of Oradea, Faculty of Medicine and Farmacy, 29 Nicolae Jiga Str., 410028, Oradea, Romania
[3] Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Piata Victoriei, 300006, Timisoara, Romania
[4]National Institute for R&D of Isotopic and Molecular Technologies, 71-103 Donath Str., Cluj-Napoca, Romania

This paper presents the extraction of iron ions from waste, and their revaluation in mineral fertilizer, as iron(II)-ammonium phosphate. In order to obtain the iron(II) -ammonium phosphate, we used waste solutions, resulted from galvanic industry. To obtain the iron(II)-ammonium phosphate, we used diammonia phosphate and ammonia solution 25%. We studied the separation degree of iron depending on the variation of the pH of the reaction mass according to the added volume of ammonia solution, and temperature. After the analysis of the obtained products, we determined the optimum conditions of the obtaining process of iron(II)-ammonium phosphates, who determined a maximum separation degree of iron from solution. The phosphate was characterized by FTIR and X-ray powder diffraction analysis.

Keywords: waste solutions, micronutrient fertilizer, metal-ammonium phosphate, iron(II)-ammonium phosphate

All around the world, a special attention is being payed to the development and modernization of the mineral fertilizer industry. The agricultural sector especially needs concentrated and complex, solid and liquid fertilizer assortments and micronutrient fertilizers, respectively.

The iron(II)-ammonium phosphate may be used as a primary complex fertilizer with iron as microelement, in obtaining solid fertilizers with iron as microelement and as a technical phosphate [1].

The iron(II)-ammonium phosphate contains iron linked with the macro elements nitrogen and phosphorus, determining an increased efficiency of the assimilation process of fertilizers by plants. In order to obtain the iron(II)-ammonium phosphate, industrial waste or residual solutions may be used as a source of iron.

Today, in the world, there is the tendency of improving the existing technologies and to promote new technologies, so called „clean technologies", without production of wastes or with possibility of waste recycling [2].

In this paperwork, we followed the extraction of ferrous ions from waste solutions resulted from galvanic industry, and their revaluation as micronutrients fertilizers, as metal-ammonium phosphates.

Experimental part

To a previously established volume of waste solution, wich contents ferrous sulphate with 390 g/L Fe^{2+} concentration, with permanent stirring up, we added the diammonia phosphate saturated solution, in order to achieve a molar report of $(NH_4)_2HPO_4:Fe^{2+} = 1.02:1$. The reaction mass was neutralized with ammonia (25% solution) [3]. All the chemical regents used in this work were of analytical grade with purity higher than 99.99% , obtained from Reactivul Bucuresti.

The pH of the reaction mass was determined to different reports $NH_3:Fe^{2+}$, taking into account the ammonia added. In order to determine the *p*H of the reaction mass, the analyser PH/ion METTLER TOLEDO Switzerland was used. The precipitate product, separated by filtration, was dried in the drying oven, at 70°.

In the filtrate, the content of residual iron was determined, and the solid products were subject to chemical analysis [4].

The content of iron from the filtrate and the final product was determined through spectrophotometry of atomic absorption, using the spectrophotometer of atomic absorption VARIAN SPECTR AA 110.

The content of ammonium nitrogen and phosphorus pentoxide from the final product was determined using the spectrophotometer VARIAN CARY 50 Probe.

X-ray powder diffraction measurements were performed with SHIMADZU - 6000 diffractometer using CuKα radiation.

FTIR spectroscopic investigations were performed with a JASCO 6100 spectrometer in the 4000-400 cm^{-1} spectral domain with a resolution of 2 cm^{-1} using the KBr pellet technique.

Results and discussions

The process of obtaining the iron(II)-ammonium phosphate, by processing the solutions of waste solution, conteining ferrous sulphate [5], with diammonia phosphate and ammonia, has as basis the reaction:

$$\begin{aligned} &FeSO_4 + (NH_4)_2HPO_4 + NH_3 + H_2O = \\ &=FeNH_4PO_4\cdot H_2O + (NH_4)_2SO_4 \end{aligned} \qquad (1)$$

The lab research intended to establish the optimal conditions of the process of obtaining the iron(II)-ammonium phosphate, in order to achieve a maximum degree of separation of the iron from the solution.

pH of the reaction mass

Because the *p*H of the reaction mass represents the control parameter of the process of neutralization with ammonia, the dependence of the *p*H from the molar report and the mass report NH_3: Fe^{2+} were determined. The experimental data obtained are presented in figure 1.

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* email: cmorgovan@yahoo.com

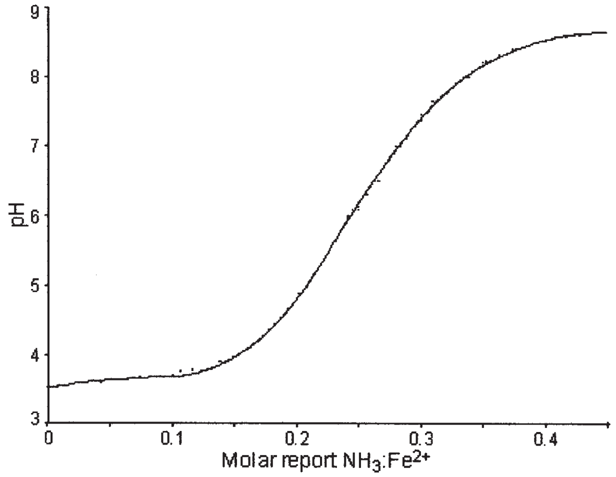

Fig. 1. The dependence of the reaction mass's *p*H from the molar report NH_3: Fe^{2+}, for a solution with a content of 390 g/L Fe^{2+}, at a molar ratio $(NH_4)_2HPO_4$:Fe^{2+} = 1,02:1, at 25°

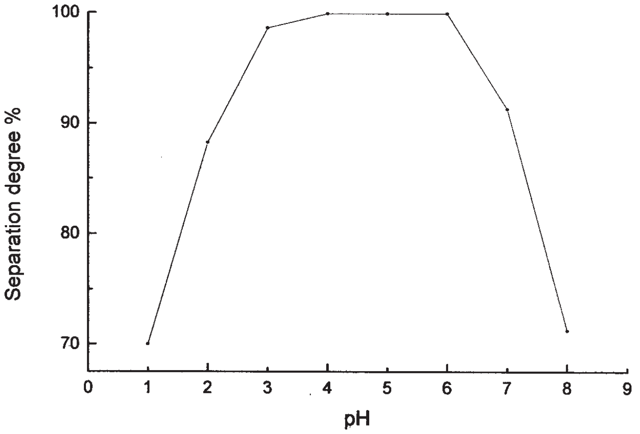

Fig. 2. The dependence of the separation degree (α) of the iron from the solution from the *p*H of the reaction mass, for a solution with a content of 390 g/L Fe^{2+}, at a molar ratio $(NH_4)_2HPO_4$: Fe^{2+} = 1,02:1, at 25°.

After adding the diammonia phosphate, the reaction mass has the *p*H = 3.56. This represents the starting point of the neutralization process with ammonia of the reaction mass.

The experimental data proves that between the reaction mass *p*H and the report NH_3: Fe^{2+}, there is a well defined difference. The curve traced indicates three fields: the first field, until a molar report NH_3: Fe^{2+}= 0.16:1, corresponds to a slow increase of the *p*H (*p*H = 3.56-3.96); the second field, corresponding to a molar report NH_3: Fe^{2+} between (0.16 – 0.33):1, determines a sudden increase of the *p*H (*p*H = 3.96 – 8.01); the last field, corresponding to a molar report NH_3: Fe^{2+} higher than 0.33:1, the *p*H slowly increases to a constant value. In this field, the partial pressure of the ammonia over the system increases, leading to ammonium loss.

Separation degree of the iron in the solution

In order to establish the best conditions of the process of obtaining the iron(II)-ammonium phosphate from ferrous sulphate solutions, by processing with diammonia phosphate and ammonia, the influence of certain parameters was analyzed (the final *p*H of the reaction mass, temperature, concentration of the ferrous sulphate, duration of the process) over the separation degree of iron [6].

*p*H of the reaction mass

The experimental data regarding the influence of the reaction mass *p*H over the separation degree of the iron from the solution are presented in figure 2. The separation degree of the iron from the solution, after adding the diammonia phosphate (saturated solution) is α = 70%.

Until *p*H = 5.5, the separation degree of the iron from the solution suddenly increases. Between the *p*H = (5.5 – 8.5), the separation degree is maximum, and for *p*H > 8.5, the separation degree suddenly decreases.

Iron concentration

The experimental data concerning the influence of the Fe^{2+} concentration from the solution over the separation degree of iron are detailed in figure 3 [7].

The experimental data shows that, at an optimum *p*H (*p*H ~ 7.5) and a temperature of 35°, the separation degree of the iron from the solution is virtually α = 100%, irrespective of the concentration of iron from the solution (in the limits studied). The residual content of the iron from the solution, after the separation of the precipitate, is under 10 mg/L.

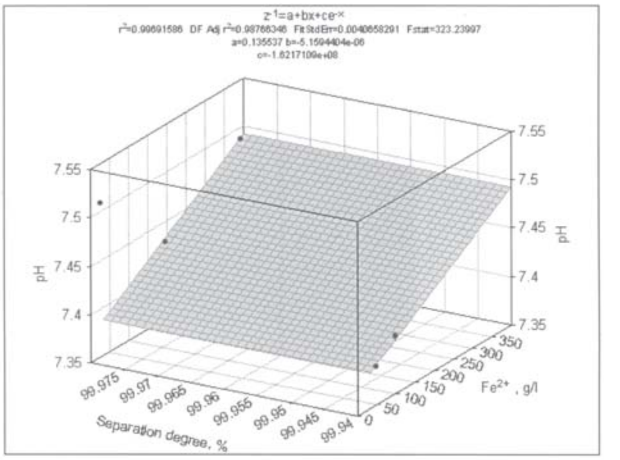

Fig. 3. The dependence of the separation degree (α) of the iron from the solution from the iron concentration, at a molar ratio $(NH_4)_2HPO_4$:Fe^{2+} = 1,02:1, at an optimum *p*H

Temperature

The experimental data regarding the influence of temperature over the degree of separation of iron from the solution are detailed in figure 4 [8].

According to the experimental data, it results that, at an optimum *p*H, the separation degree of the iron is maximum and does not depend on the temperature (within the limits studied). The optimum temperature is considered of 35°, because at this temperature a crystalline precipitate is obtained, precipitate that is easily decanted and filtered.

Duration of the process

The experimental research proved that, in *p*H optimum conditions, in order to obtain a crystalline, easy to filter precipitate, it is necessary that the duration of the process to be about 50-60 min.

The experimental data related to the chemical composition of certain products obtained when treating the ferrous sulphate solution with diammonia phosphate and neutralization with ammonia are presented in table 1.

Table 1

COMPOSITION OF PRODUCTS OBTAINED FROM SOLUTIONS WITH A CONTENT OF 390 g/l Fe^{2+}, AT 35°C, AT A MOLAR RATIO $(NH_4)_2HPO_4:Fe^{2+}$ = 1.02:1 AND VARIOUS VALUES OF REACTION MASS *p*H

Final pH	Composition, %		
	Fe	N	P_2O_5
3,56	29,15	7,03	37,88
4,51	29,05	7,14	37,50
5,64	28,95	7,42	37,43
6,42	27,55	7,45	37,55
7,49	29,50	7,24	37,90
8,26	29,65	7,31	37,78

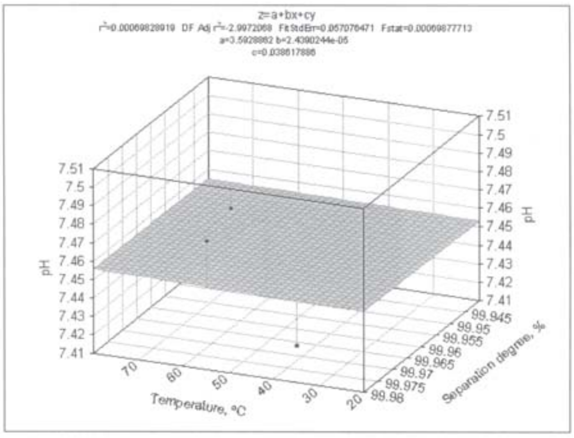

Fig. 4. The dependence of the separation degree (α) of the iron from the solution from the temperature, for a solution with a content of 390 g/L Fe^{2+}, at an optimum *p*H

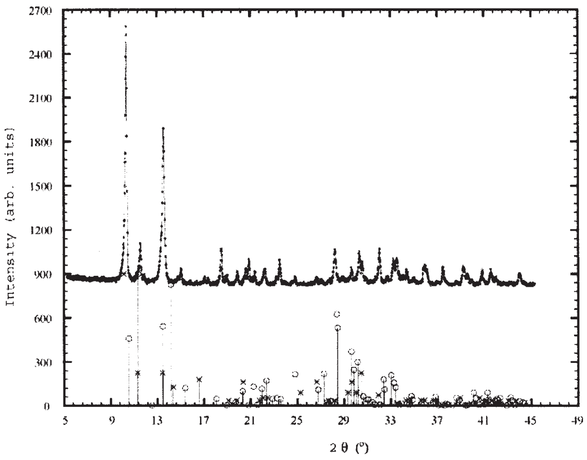

Fig. 5. X-ray powder pattern diffraction for $FeNH_4PO_4{\cdot}H_2O$

According to this experimental data, it results that the products obtained in the processing time of the ferrous sulphate solution with diammoniua phosphate and with ammonia have as basic component the iron(II)-ammonium phosphate $FeNH_4PO_4 \cdot H_2O$.

XRD pattern of the product was shown in figure 5. The pattern matches the standard XRD data for $FeNH_4PO_4{\cdot}H_2O$ of JCPDF 45-0424 [9]. The XRD data indexed as orthorhombic system, with space group: a = 5.660 Å, b = 8.825 Å, c = 4.826 Å , and unit cell volume 241.056 Å^3.

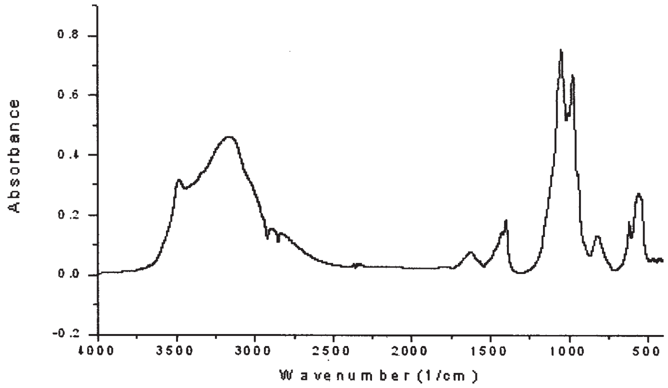

Fig. 6. FT-IR spectrum for $FeNH_4PO_4{\cdot}H_2O$.

The FT-IR spectrum shown in figure 6 reflects characteristic stretching mode of NH_4^+, PO_4^{3-} [10, 11]. Water bonding at 1620 cm^{-1} and O–H stretching broadband centered at 3400–3100 cm^{-1} can be observed implying the presence of crystalline hydrate. Absorption observed at 2897 and 1460-1430 cm^{-1} was attributed to the N–H stretching mode of NH_4^+. The combining of both water stretching and N–H stretching result in the broad peak between 3400 and 2897 cm^{-1}. Absorption peak at 1030 cm^{-1} was attributed to the PO_4^{3-} asymmetric stretching mode and the sharp absorption peak at 970 cm^{-1} was attributed to the PO_4^{3-} symmetric stretching mode. The strong absorption bands at 610–500 cm^{-1} were attributed to PO_4^{3-} bending vibrations mode [12, 13].

Conclusions

The iron(II)-ammonium phosphate may be obtained by processing diammonia phosphate and ammonia with waste solutions of ferrous sulphate. There is a well defined dependence between the report NH_3: Fe^{2+} and the reaction mass *p*H. The experimental research regarding the influence of various parameters over the separation degree of iron from the solution allowed the establishment of optimum conditions of the process of obtaining the iron(II)-ammonium phosphate.

The studies made on the chemical composition and phase, prove that the product obtained in the processing time of the ferrous sulphate solutions with diammonia phosphate and ammonia represents the iron(II)-ammonium phosphate $FeNH_4PO_4{\cdot}H_2O$. The optimum conditions of the processing time of the iron(II)-ammonium phosphate solutions with diammonia phosphate and ammonia, determining a maximum separation degree of the iron ($\alpha \sim 100\%$), respectively the shaping of a crystalline precipitate that is easily decanted and filtered are: molar report $(NH_4)_2HPO_4:Fe^{2+}$ = 1,02:1, reaction mass's *p*H ~ 7.5, temperature 35°, duration of process is of 50-60 min.

Through this process, we can distinguish the element iron(II) from the solutions, respectively residual waters, in the useful product of iron(II)-ammonium phosphate.

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