

## PICKING UP $\text{NO}_2^-$ ANIONS FROM POLLUTTED WATER, AFTER REDUCTION WITH FE (II) SALTS

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### Abstract

This paper presents a cleaning method of the waters rich in  $\text{NO}_2^-$  anions. This is a very dangerous ion for the life, especially of the very little children. These anions provide from the ammonium salt oxidation in the agriculture and farm zones or from chemical fertilizer with nitrite in the agriculture yards. Our method bases on the reduction of the  $\text{NO}_2^-$  anions to NO with Fe (II) salts. Along of the study we propose to find the best reaction condition for a very good rate transformation of the  $\text{NO}_2^-$  anions to NO. We follow the evolution of reaction in time, at different temperature and at different Fe (II) concentrations.

**Key words:** nitrite, pollution, water, iron, reaction condition

### INTRODUCTION

Our days, because the frequency of pollution phenomenon, solving the problem has become more complicate. There are situation in which the water is brought from far distance, more than 100 km or a very high depth, more than 300 meters (Vlaicu., 1996; Rădulescu and. Goicu, 1999,).

As result of different human activities, substances penetrate the water lead to lake the equilibrium in the environment (Shafi, 2005). The water from rural zone, respective farms or collective farms may pollute with ammonium ions from chemical fertilizer or excrement animals (Shiklomanov, 2000). Ammonium cations can be transformed in  $\text{NO}_2^-$  anions after an anaerobic oxidation. This is followed the infiltration of this anions in the river waters and in the wells waters using in many families for cooking and drinking (Gârban, 2000).

In conclusion, these waters become importance contaminating sources, dangerous for our healthy. In the case of the very young children the presence of  $\text{NO}_2^-$  anions in great concentration in water can be fatal (Burtică et al., 2005).

The transformation of  $\text{NO}_2$  into strong acid takes place even at the contact between surface water and air, so called acid rain (Manahan, 2000). Therefore, because the acidity increase, pH becomes low, it takes place the change of nitrite ions. The acceleration of heavy metal compounds dissociation, the release and growth of their ions mobility is the result of a low pH (Ciarnău., 2000).

The method chosen and applied by us in this work it is one very easy and efficiently, because Fe (II) ions reduce easily  $\text{NO}_2^-$  to NO in picking bath at acid pH. Therefore the medium is suitable. In addition, the temperature is high enough to development a chemical reaction and influences the progress of the reaction with a good rate.

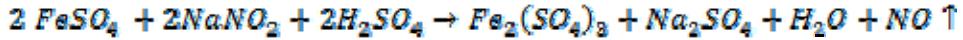
The efficiency of this method is caused by the cheap reagent used, the easily methods for pick up from water of the secondary nontoxic ions ( $\text{SO}_4^{2-}$  and Fe (III)).

## MATERIAL AND METHODS

All chemicals were commercially available, of reagent grade quality and used as received. In all synthesis and studies distilled water was used.

Quantitative determination of the  $\text{NO}_2^-$  made with a photocolorimetric method in the last of reaction with sulphanylic acid and  $\alpha$ -naphthylamide, measured with a Spekol apparatus at 540 nm (Legea nr. 459/2002, Ray and Yang, 2001).

At the foundation of our method is the next chemical reaction:



$\text{FeSO}_4$  reduces  $\text{NO}_2^-$  ( $\text{NaNO}_2$ ) to NO in weak acid solution ( $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{C-COOH}$ ) and gives an unstable brown colour combination  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  by addition  $\text{FeSO}_4$  in excess.

For obtained the best rate of this reaction we proposed to do a kinetic study of this. Our study included three steps, described one by one below:

### I. The influence of the chemical reaction progress

0,01M  $\text{FeSO}_4$  solution were melted in the same quantity with a 0,01M  $\text{NaNO}_2$  solution and their mixture was lived on magnetic agitator, at the room temperature, for different time periods. Iron cations were taken off quantitative from solution, after precipitation with 5M  $\text{NaOH}$ , at  $\text{pH}=8$ , when they were been transformed in  $\text{Fe(OH)}_3$ . The filtrate volume was adjusted at 50 ml with distilled water. The nitrite quantity from filtrate was determinate with photocolorimetric method (Legea nr. 459/2002), remembered before.

### II. The influence of the temperature

We were worked with the same mixture like in first step. All the samples were kept in reaction for ten minutes but at different temperature from room temperature to boiling temperature. The filtrate with  $\text{NO}_2^-$  remained were separated and analysed like before.

### III. The influence of the Fe (II) excess

In these experiments, we prepared mixtures between 0,01M  $\text{FeSO}_4$  solution and 0,01M  $\text{NaNO}_2$  solution at room temperature. These mixtures were melting on the magnetic agitator for ten minutes. Different 0,01M  $\text{FeSO}_4$  excess volumes were introduced in every sample. For the  $\text{NO}_2^-$  remained determination we were used the remembered methods in anterior steps.

## RESULTS AND DISSCUSION

### I. The influence of the chemical reaction progress

The results of the evolution of reaction in time show in the next table and graphic:

Table I

Remaining  $\text{NO}_2^-$  concentration (mg/l) in solution after different reaction times

Det. No.	Time (min)	V <sub>FeSO<sub>4</sub></sub> (ml)	V <sub>NaNO<sub>2</sub></sub> (ml)	Concentration of $\text{NO}_2^-$ remained in solution (mg/l)
1	1	10	10	0,124
2	5	10	10	0,204
3	10	10	10	0,260
4	20	10	10	0,350
5	30	10	10	0,470
6	60	10	10	0,280
7	1200	10	10	0,038

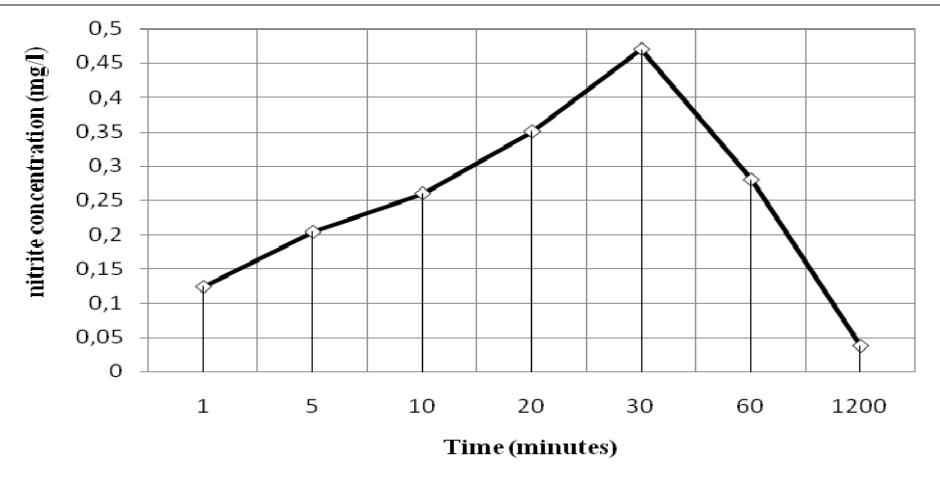


Fig. 1. Evolution of resting  $\text{NO}_2^-$  concentrations after different reaction times

Processing the dates of the table 1 with the initial  $\text{NO}_2^-$  concentration, it was obtained the next rates values showed in Table 2 and Fig. 2.

Table 2

Rates variation of the  $\text{NO}_2^-$  reduction with Fe (II) at different reaction times

Det. No	Reaction time (min.)	$m_{\text{initial}} \text{NaNO}_2$ (mg)	$m_{\text{remain}} \text{NaNO}_2$ (mg)	$m_{\text{reaction}} \text{NaNO}_2$ (mg)	Rate (%)
1	1	6,9	0,0062	6,8938	99,9120
2	5	6,9	0,0102	6,8898	99,8523
3	10	6,9	0,0130	6,8870	99,8115
4	20	6,9	0,0175	6,8825	99,7463
5	30	6,9	0,0235	6,8765	99,6594
6	60	6,9	0,0140	6,8860	99,7971
7	1200	6,9	0,0019	6,8981	99,9724

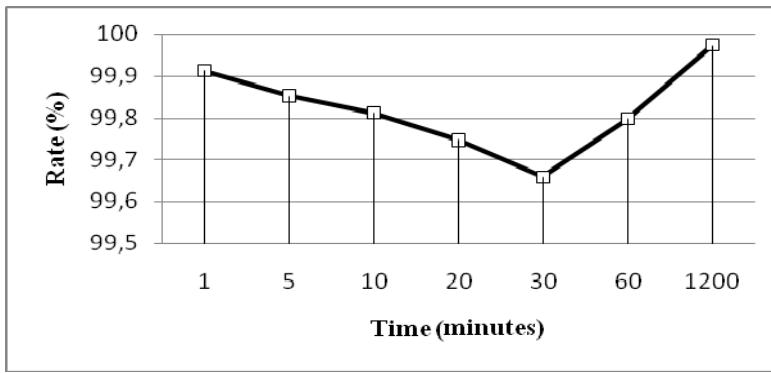


Fig. 2. Curve of the rates variation with the progress reaction in time

## II. The influence of the temperature

All the samples reacted for ten minutes but at different temperature.

After reading at Spekol the concentration values of  $\text{NO}_2^-$  remained were recorded in the table 3 and the reaction evolution were drown in fig.3.

*Tabel 3*

Remaining  $\text{NO}_2^-$  concentration (mg/l) in solution at different temperature

Det. No.	Temperature (°C)	$V_{\text{FeSO}_4}$ (ml)	$V_{\text{NaNO}_2}$ (ml)	Concentration of $\text{NO}_2^-$ remained in solution (mg/l)
1	25	10	10	0,260
2	40	10	10	0,228
3	60	10	10	0,216
4	80	10	10	0,060
5	100	10	10	0,054

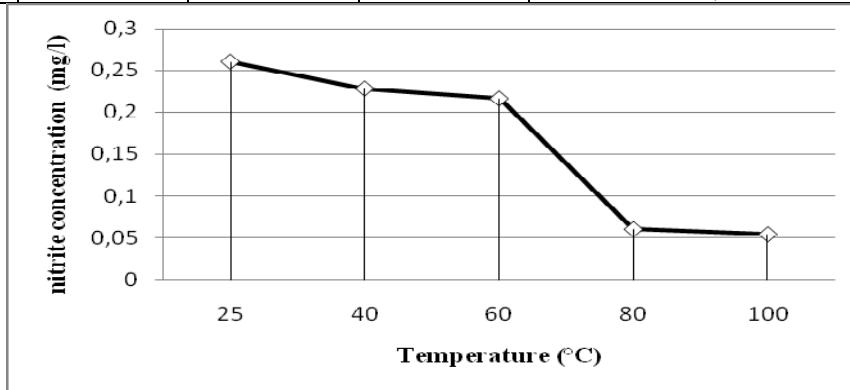


Fig.3. Variation of remaining  $\text{NO}_2^-$  concentration (mg/l) with temperature

The rates values of reduction reaction were calculated from processing of the initial and remained  $\text{NO}_2^-$  quantity. The data obtained are exposed in Table 4 and Fig. 4.

*Table 4*

Rates of the  $\text{NO}_2^-$  reduction with Fe (II) at different temperatures

Det. No	Temperature (°C)	$m_{\text{initial}} \text{NaNO}_2$ (mg)	$m_{\text{remain}} \text{NaNO}_2$ (mg)	$m_{\text{reaction}} \text{NaNO}_2$ (mg)	Rate (%)
1	25	6,9	0,013	6,887	99,81
2	40	6,9	0,0114	6,886	99,83
3	60	6,9	0,0108	6,8892	99,84
4	80	6,9	0,0030	6,8970	99,95
5	100	6,9	0,0027	6,8973	99,96

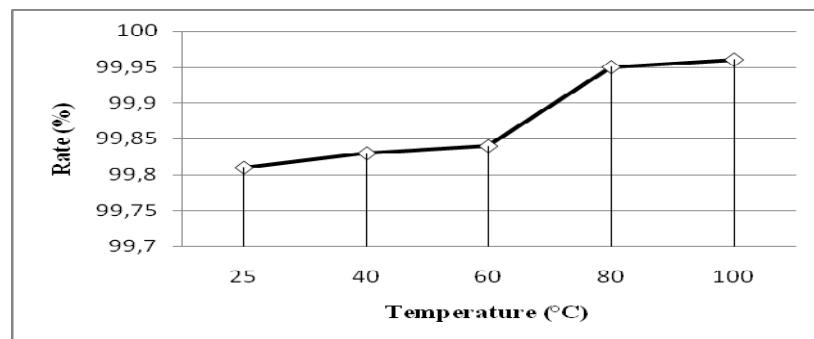


Fig. 4. The rate evolution of the  $\text{NO}_2^-$  reduction with Fe (II) at different temperatures

### III. The influence of the Fe (II) excess

The reaction evolution after adding of different quantity 0,01M FeSO<sub>4</sub> solution was recorded like NO<sub>2</sub><sup>-</sup> consumed. Colorimetric measurements indicated the remaining NO<sub>2</sub><sup>-</sup> concentration. These data are presented in Table 5 and Fig. 5 The FeSO<sub>4</sub> were represented like molar rate - Fe(II)/NO<sub>2</sub><sup>-</sup>.

*Tabel 5*  
Remaining NO<sub>2</sub><sup>-</sup> concentration (mg/l) in solution at different FeSO<sub>4</sub> excesses

Det. No.	0,01 M FeSO <sub>4</sub> excess (ml)	V <sub>FeSO<sub>4</sub></sub> (ml)	V <sub>NaNO<sub>2</sub></sub> (ml)	Molar rate Fe(II)/NO <sub>2</sub> <sup>-</sup>	Concentration of NO <sub>2</sub> <sup>-</sup> remained in solution (mg/l)
1	0	10	10	1	0,260
2	5	10	10	1,5	0,248
3	10	10	10	2	0,132
4	20	10	10	3	0,040
5	50	10	10	6	0,020
6	70	10	10	8	0,015
7	100	10	10	10	0,008

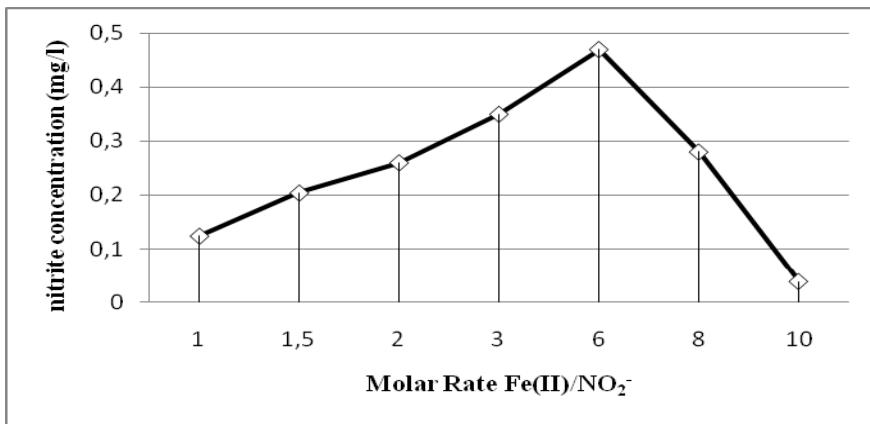


Fig. 5. Variation of the remaining NO<sub>2</sub><sup>-</sup> concentration (mg/l) at different molar rate-Fe(II)/NO<sub>2</sub><sup>-</sup>

The processing of these data permitted us to find the evolution of the reaction rate with different melting molar rate of the reactants. In the table 6 were found the rate reaction values and in fig. 6 was showed the evolution of reaction rate with molar rate - Fe(II)/NO<sub>2</sub><sup>-</sup>

*Tabel 6*

Reaction rates at different molar rate - Fe(II)/NO<sub>2</sub><sup>-</sup>

Det. No.	0,01 M FeSO <sub>4</sub> excess (ml)	Molar rate Fe(II)/NO <sub>2</sub> <sup>-</sup>	m <sub>initial</sub> NaNO <sub>2</sub> (mg)	m <sub>remain</sub> NaNO <sub>2</sub> (mg)	m <sub>reaction</sub> NaNO <sub>2</sub> (mg)	Rate (%)
1	0	1	6,9	0,013	6,8870	99,811
2	5	1,5	6,9	0,0124	6,8876	99,820
3	10	2	6,9	0,0066	6,8934	99,904
4	20	3	6,9	0,0020	6,8980	99,971
5	50	6	6,9	0,0010	6,8990	99,985
6	70	8	6,9	0,00075	6,89925	99,989
7	100	10	6,9	0,00040	6,8996	99,994

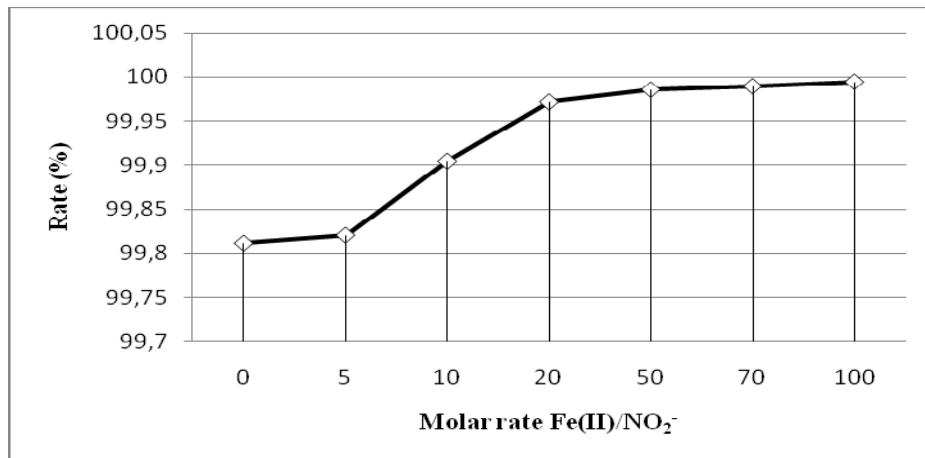


Fig. 6. Evolution of the reaction rate with molar rate -  $\text{Fe(II)}/\text{NO}_2^-$

## CONCLUSIONS

I. From the results of the first study step, we can conclude that a high efficiency of reaction achieved immediately after the start of reaction, at room temperature and more this low progressive in the next half of hour. The minimum value of nitrite concentration was touched after two hours and only this was less than maximum  $\text{NO}_2^-$  concentrate accepted for drinking water ( $< 0,05 \text{ mg/l}$ ).

II. The temperature influence for the  $\text{NO}_2^-$  reduction with Fe (II) were significant after  $80^\circ\text{C}$ , when the NO gas elimination were been more easy and the equilibrium of reaction were driven to the right. An acceptable  $\text{NO}_2^-$  concentration in conformity the normative for drinking water, it was hardly touched only at boiling point.

III. Looking under the results indicated the growing of the Fe (II) quantity were the best solution for  $\text{NO}_2^-$  reduction. It was enough a molar rate  $\text{Fe(II)}/\text{NO}_2^- = 3$ , at room temperature and ten minutes reaction to arrive a  $\text{NO}_2^-$  concentration value under  $0,05 \text{ mg/l}$ , the limited accepted for drinking water.

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