

Removal of nitrate/nitrite ions by modified with metal-containing compounds strongly basic exchanger using response surface methodology

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ABSTRACT

The article demonstrates that strongly basic anion exchanger modified with Cr(III)-containing compounds are able to selective removal of nitrate/nitrite ions from liquids. The influencing of NaNO_3 , KCl , Na_2SO_4 and NaHCO_3 concentration, pH and filtration speed on the parameters of nitrate/nitrite removal process was investigated using response surface methodology. Removal of nitrate ions from solution was carried out under dynamic conditions after reduction with metallic Cd. Carboxylic exchanger was used for the selective sorption of Cd^{2+} (and Cr^{3+} ions that could possibly come out of the polymer phase) cations. Were obtained regression equations for sorption capacity until the appearance of nitrites/nitrates ions in the filtrate and total sorption capacity of the sorbent. As a result of optimization, using the method of moving on the gradient, parameters of nitrate ions removing process were improved considerably.

Keywords: strongly basic anion exchanger; nitrate/nitrite ions removal; response surface methodology; Cr(III)-containing polymer

INTRODUCTION

The pollution with nitrate/nitrite ions is a serious problem for many countries, especially with developed agro-industrial complex. Excess of these ions in water and food is dangerous for human and animal species health. Removal of nitrate/nitrite ions from liquids is a very actual problem.

It is known that now nitrate ions are removed either by physicochemical or biological methods. It was investigated [1] the application of catalysts in the removal of nitrate and nitrite ions from drinking water. The nitrate and nitrite ions were reduced with hydrogen on catalysts (noble metal palladium or palladium activated with copper). The products of the reaction are gaseous nitrogen and dissolved ammonia, which is undesired in drinking water.

The application of the anion exchangers, especially strongly basic anion exchangers, for nitrate and nitrite ions removal was also investigated [2-4]. Sorption of anions, including NO_3^- or NO_2^- , on strongly basic anion exchangers is not selective because is conditioned by Coulomb's (electrostatic) interactions and the modern technologies of purification of various categories of fluids and gases, concentration and separation of substances required new selective sorbents.

As selective sorbents can be strongly basic anion exchangers modified with metallic compounds. Strongly basic cross-linked ionic polymers

theoretically are unable to adsorb metallic cations because they do not contain in their matrix negatively charged or electron donor atoms. However in our previous studies [5-7], it was shown that these polymers in certain conditions are able to retain metallic cations from $\text{M}_2(\text{SO}_4)_3$ solutions, where $\text{M} = \text{Cr}^{3+}$, Fe^{3+} or Al^{3+} . The sorption of metallic cations from sulphate solutions takes place through formation in the polymer phase of the jarosite(alunite) mineral type compounds $\text{R}_4\text{N}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]$ and $\text{H}_3\text{O}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]$, where R_4N^+ is a functional group of the polymer.

The R_4N^+ and H_3O^+ ions from jarosite type compounds can be exchanged with different cations and the anions SO_4^{2-} - with different anions or molecules capable to form coordinate bonds with the central metal ions. Thus, selective sorption of ions or molecules on jarosite containing exchangers is due to ligand-ligand exchange process.

In previous study [8] was shown that strongly basic anion exchanger modified with Cr-jarosite type compounds is able to selective sorption of nitrite ions from solution. In this article we investigated the nitrate/nitrite ions removal by Cr-jarosite containing strongly basic anion exchanger.

EXPERIMENTAL

The commercial strongly basic anion exchanger AV-17 (containing $-\text{N}(\text{CH}_3)_3\text{Cl}$ groups) was used. The gel-

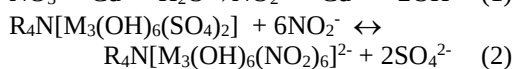
type resin had a polystyrene-divinylbenzene matrix and full exchange capacity 3.4-4.0 meq/g [9]. Before sorption investigation, the polymer was modified with Cr(III)-containing compounds according to the reference [10]. For investigation was used polymer AV-17 containing 35.46 mg Cr/g. The Cr^{3+} content in the polymer phase was determined photocolormetrically [11] after desorption [12].

Solutions of nitrate ions were prepared using NaNO_3 . Concentration of nitrate ions was determined photocolormetrically using Griess reactive after their converting into nitrite ions [13]. Continuous flow adsorption studies were conducted in a column made of Pyrex glass tube having inner diameter of 1.2 cm and 25 cm height. The column contained 3 layers - the first layer (upper layer) consisted of granulated metallic Cd, second layer consisted of Cr-jarosite containing AV-17 and third layer consisted of carboxylic cation exchanger (Purolite C-104) in Na-form. In the first layer takes place transformation of nitrate ions into nitrite. In the second layer nitrite ions were selective captured by Cr-jarosite containing AV-17. Carboxylic exchanger was used for the selective sorption of Cd^{2+} (and Cr^{3+} ions that could possibly come out of the polymer phase) cations. As is known, carboxylic exchangers are capable of selective sorption of cations of *d,f*-elements as a result of coordination processes.

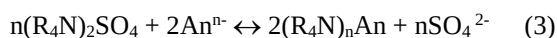
Investigation was carried out using response surface methodology (G.E.P.Box and K.B.Wilson method) [14]. Removal of nitrate ions was carried out at 20°C using modeling solutions similar in composition to natural waters. Influencing factors were concentration of NO_3^- ions, NaHCO_3 , KCl, Na_2SO_4 , solution pH and flow rate of solution through column. In all experiments Cr(III)-containing AV-17 mass was 2.5g, Purolite C-400 mass was 1.5g and of granulated Cd - 2 g. The mass of latest two components was arbitrary. From the experimental data were built breakthrough curves for adsorption of nitrate/nitrite ions and calculated sorption process parameters. The obtained regression equations were used to optimize the removal of nitrate ions process from solutions.

RESULTS AND DISCUSSION

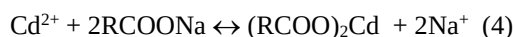
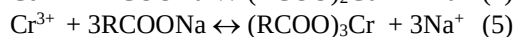
According to the reference [15], the jarosite mineral type compounds $\{\text{R}_4\text{N}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]\}$ and $\text{H}_3\text{O}[\text{M}_3(\text{OH})_6(\text{SO}_4)_2]\}$, are in form of pseudo-layers of 3 or 6 octahedral cycles. The OH^- groups are located in the equatorial plane, and SO_4^{2-} groups are located in an axial position, each coordinate 3 metal ions of 3 octahedrons. Each metal cation of jarosite can coordinate 2 nitrite ions [8]. Removal of nitrate/nitrite ions by Cr(III)-containing AV-17 takes place according to the equations (1) and (2):



Not all of R_4N^+ groups of the polymer are in the jarosite composition. A part of them are in form of $(\text{R}_4\text{N})_2\text{SO}_4$ because the preparation of the Cr(III)-containing polymer occurred in solution of $\text{Cr}_2(\text{SO}_4)_3$. They can participate in the anion exchange processes (3) where An^n is an anion.



If there are Cr^{3+} or Cd^{2+} cations in the system, they are selectively retained by carboxylic cation exchanger, according to the equations (4) and (5):



In case of nitrate/nitrite ions removal from food liquids it is reasonable to use carboxylic exchanger in K-form. The sorption of nitrate/nitrite ions on Cr(III)-containing AV-17 is influenced by many factors. The influencing factors and their codes are shown in the Table 1.

Table 1. Examined factors and their code and levels of variation

Code	Factor	Lower level (-)	Upper level (+)
X ₁	NO_3^- ions concentration, mg NO_3^-/l	50	70
X ₂	pH	6.0	7.0
X ₃	NaHCO_3 concentration, meq./l	2	3
X ₄ (X ₁ X ₂)	KCl concentration, meq./l	2	3
X ₅ (X ₁ X ₃)	Na_2SO_4 concentration, meq./l	2	3
X ₆ (X ₁ X ₂ X ₃)	Filtration speed, ml/min	1	1.8
X ₂ X ₃	-		

There were measured and calculated the following responses of the system:

Y₁- dynamic sorption capacity (DSC- value of sorption until the appearance of the nitrate/nitrite ions into filtrate), mg NO_3^-/g

Y₂- total dynamic sorption capacity (TDSC- sorption value when sorbent was saturated), mg NO_3^-/g .

Y₃- relative rate of sorption ($W=(\text{DSC}/\text{TDSC})100$), %

The experiments were carried out according to the matrix of a Fractional Factorial Design (Tab.2). The values of Y₁, Y₂ and Y₃ were determined from the breakthrough curves for adsorption of nitrate/nitrite ions (Figures 1 and 2). The results (Tab.2) are the averages of two independent experiments. The obtained results were used for calculation of the coefficients of the regression equations (6)-(8):

$$Y_1 = 11.23 + 0.705X_1 - 0.255X_5 - 0.82X_6 + 0.855X_2X_3 \quad (6)$$

$$b_{\text{sig.}} = 0.210$$

$$Y_2 = 18.32 + 1.848X_1 + 0.434X_4 - 0.432X_5 - 0.886X_6 \quad (7)$$

$$b_{\text{sign.}} = 0.399$$

$$Y_3 = 61.454 + 4.232X_2X_3$$

$$b_{\text{sig}} = 2.163$$

(8)

Table 2. Matrix of the Fractional Factorial Design and the obtained results

Exp. no.	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₂ X ₃	Y ₁	Y ₂	Y ₃
1	+	+	+	+	+	+	+	11.9	19.53	60.92
2	-	+	+	-	-	-	+	12.4	17.60	70.45
3	+	-	+	-	+	-	-	11.2	19.58	57.23
4	-	-	+	+	-	+	-	8.9	15.84	56.40
5	+	+	-	+	-	-	-	12.6	22.25	56.63
6	-	+	-	-	+	+	-	8.8	15.05	58.49
7	+	-	-	-	-	+	+	12.0	19.32	62.41
8	-	-	-	+	+	-	+	12.0	17.40	68.96

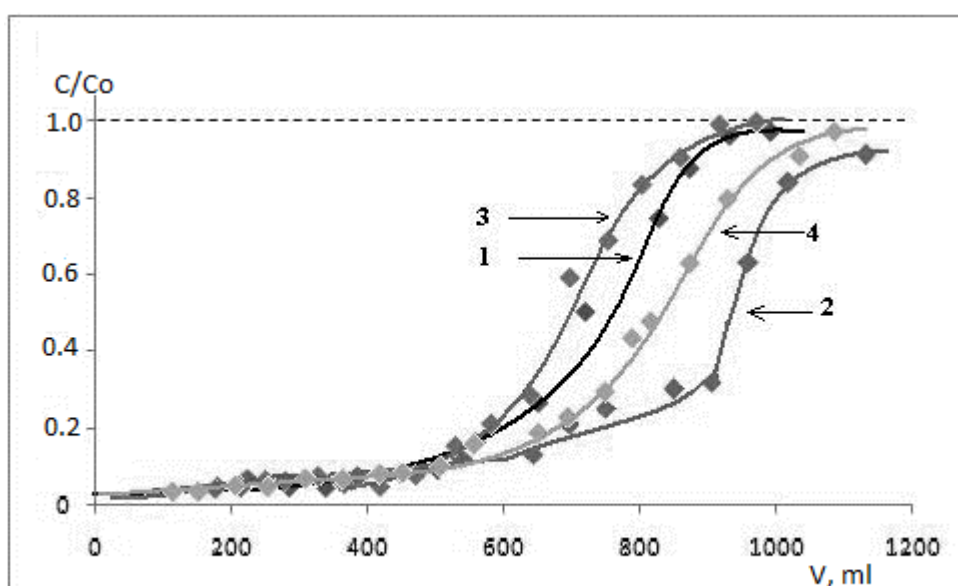
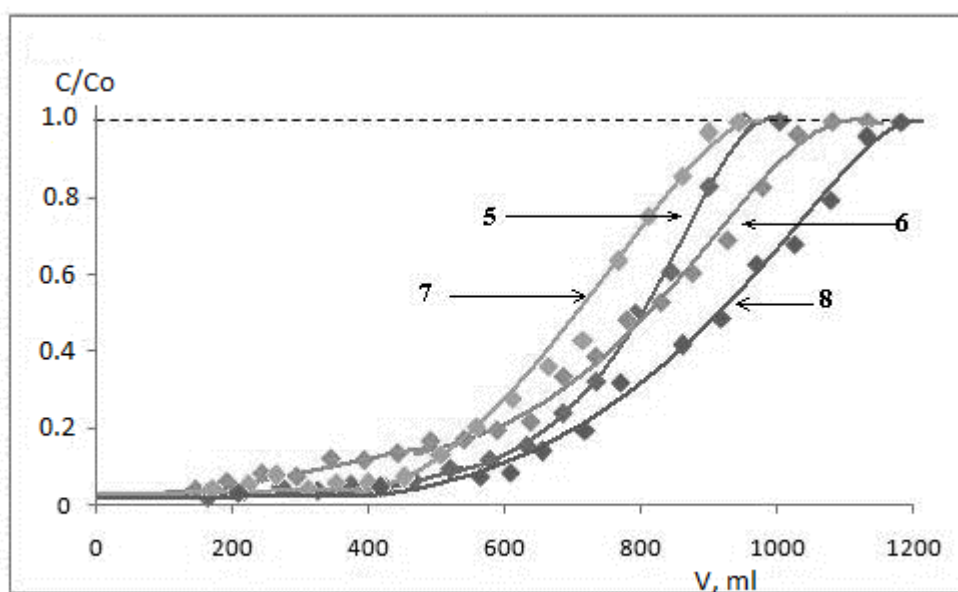
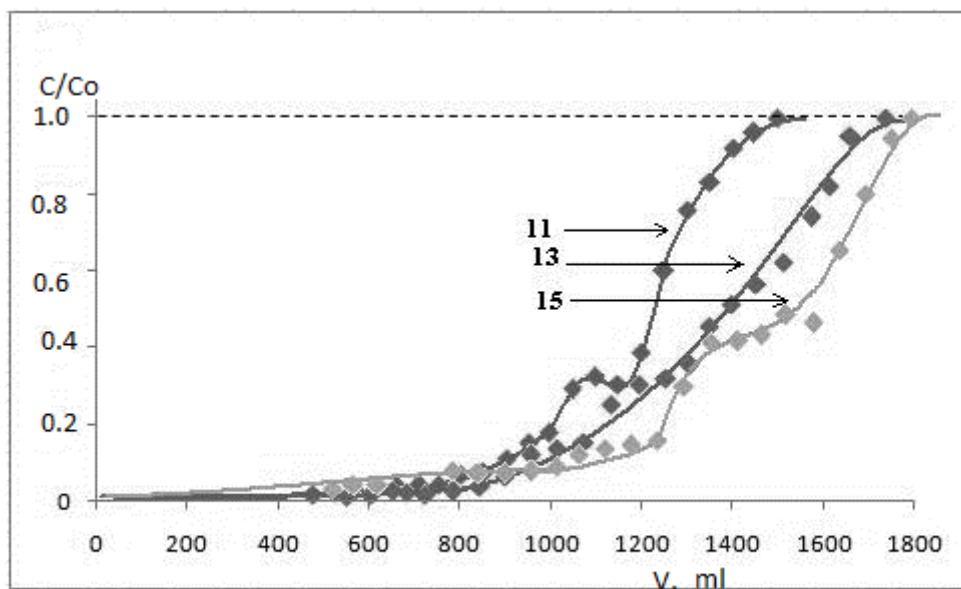
**Figure 1.** Breakthrough curves for adsorption of nitrate/nitrite ions in the experiments 1-4 of the Table 2**Figure 2.** Breakthrough curves for adsorption of nitrate/nitrite ions in the experiments 5-8 of the Table 2.

Table 3. Nitrate ions removal optimising

Experiment no.	X ₁	X ₅	X ₆	Y ₁	Y ₂	Y ₃
Step	+5	-0.25	0			
9	65	1.25	1			
10	70	1.0	1			
11	75	0.75	1	22.8	35.9	63.51
12	80	0.50	1			
13	85	0.25	1	28.2	43.2	65.28
14	90	0	1			
15	95	0	1	34.96	56.42	61.96

**Figure 3.** Breakthrough curves for adsorption of nitrate/nitrite ions in the experiments 11, 13 and 15 of the Table 3.

As is seen in equation (6), increasing of the NO_3^- ions concentration (X_1) in solution has a positive effect on DSC. Increasing of the Na_2SO_4 concentration (X_5) and filtration speed (X_6) negatively influences DSC. Concentration of the NaHCO_3 , KCl and pH (X_3 , X_4 and X_2) practically do not influence the value of DSC, though common effect of pH and NaHCO_3 is positive and considerable (X_2X_3).

As it was expected, the increase of NaNO_3 concentration, influences positively, but increasing of Na_2SO_4 concentration and of speed of filtration have a negative effect on total sorption capacity (TDSC) of the Cr(III)- containing AV-17 (equation (7)). The negative influence of the Na_2SO_4 is explained by the shifting of equilibrium (2) to the left. Unexpectedly is the positive and significant influence of KCl (X_4), concentration on value of the TDSC (equation(7)). The influence of KCl, probably, is indirect, through the

process (3). The higher the Cl^- concentration in solution, the higher is content of Cl^- in the Cr(III)-containing polymer phase and the less is the content of SO_4^{2-} ions. The existence of NaHCO_3 in solution and the value of pH in the examined range of variation (Table 1), does not influence the value of TDSC. But, as you will see below, these factors influence the filtrate pH, which varies between 7.7 - 8.3 in the experiments 1-8 (Tab.2).

All investigated factors in part does not influence the relative speed of sorption, but NaHCO_3

and pH in common (X_2X_3), positively influences (equation 8).

The equations (6) and (7) enable planning the optimization of the parameters DSC and TDSC. We have optimized DSC using equation (6). In the

experiments of optimizing the temperature was 20°C, the mass of Cr(III)-containing AV-17 was 2.5 g, the pH of the solution was 6.5. In the NaNO₃ solution not were added KCl and NaHCO₃. The experiments were performed by the moving on the gradient method [14] in the conditions indicated in the Table 3. The obtained breakthrough curves 11, 13 and 15 (Fig.3) for adsorption of nitrate/nitrite ions were obtained according to the conditions corresponding to experiments number (Table 3). The calculated sorption parameters are shown in the Table 3. From the data in Table 3 it can be seen that the maximum value of DSC was not reached.

This occurred because the growth of the NO₃⁻ ions concentration was limited at 95 mg/l. However, the results obtained in the optimization are much higher than those which are obtained in the first phase of the study (Table 2). These results confirm that planning of experiment is entirely correct. It should be noted that in the experiments of optimization the pH of the filtrate has increased gradually up to 9. Increasing pH of the filtrate is due to the process (1) and absence of NaHCO₃ in the system.

CONCLUSION

Strongly basic anion exchangers modified with Cr(III)-containing compounds can be successfully used in selective removing of nitrate ions from liquids after their reduction with metallic Cd. For selective sorption of Cd²⁺ (and Cr³⁺ ions that could possibly come out of the polymer phase) cations, carboxylic exchangers can be used.

The existence of NaHCO₃ in solution does not affect the elimination of nitrate ions, but stabilizes the pH of the filtrate in the range of 7.7 to 8.3. The lack of NaHCO₃ in the system leads to increases of the pH of filtrate to 9. The solution pH also do not influence the removal of the nitrate ions. The increasing of KCl concentration in solution improves the nitrate ions removal, but Na₂SO₄ influences negatively.

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