

Nitrite ions sorption on strongly basic anion exchanger Purolite A-400 modified with Cr(III)-containing compounds

Vasile Gutsanu*, Elena Tutovan, Ludmila Cotsofana, Vladimir Bulicanu

Moldova State University, Inorganic and Physical Chemistry Department, 60 A. Mateevici str., MD 2009, Chişinău, Moldova, e-mail: gutsanu@gmail.com

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ABSTRACT

It is shown that in the same conditions the sorption of nitrite ions on strongly basic anion exchanger Purolite A-400 modified with Cr(III)-containing compounds, especially from solution with $\text{pH} > 4$, is much higher as on Purolite A-400(Cl). Sorption on Purolite A-400 (Cl) essentially depends on solution pH and on Purolite A-400(Cr) almost does not depend on solution pH. Nitrite ions sorption isotherm on Purolite A-400 (Cl) may be described by Langmuir sorption model, but on Purolite A-400 (Cr) – by the type III isotherms of the BET classification. The influence of NaNO_2 , KCl, K_2SO_4 concentration, pH, temperature and duration of Purolite A-400 (Cr) contacting with solution on NO_2^- removal has been studied using method of statistical mathematics. Optimizing of NO_2^- ions removal has been studied too. It is shown that NO_2^- ions removal from solution by Cr(III)-containing compounds polymer takes place through the three processes: ion exchange, NO_2^- coordinate with Cr^{3+} in the polymer phase and NO_2^- decomposition (in a low-acid medium). Modified with Cr(III)-containing compounds strongly basic anion exchanger becomes a selective sorbent for NO_2^- ions sorption.

Keywords: ion exchange, nitrite ions sorption, method of statistical mathematics, Cr(III)-containing compounds, FT-IR spectroscopy.

INTRODUCTION

Water pollution with nitrite ions is a serious problem for many countries, especially with developed agro-industrial sphere. Excess of these ions in water and in food is dangerous for human and animal species health. Removal of NO_2^- ions from liquids is a rather actual problem.

The application of the anion exchangers for nitrite ions removal, especially strongly basic exchangers, is not reasonable. Sorption of anions, including NO_2^- , as a result of anion exchange, practically, 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. Some publications^{1,2} contain data on the sorption of nitrite ion by anion exchangers containing secondary amine groups. In fact the NO_2^- ions removal was done not as a result of anion exchange which is a physical process, but in the result of a chemical process, which most likely be decomposition of anions in the polymer phase ($\text{R}_2\text{NH}_2^+ \leftrightarrow \text{R}_2\text{NH} + \text{H}^+$; $\text{H}^+ + \text{NO}_2^- \leftrightarrow \dots$).

This process of decomposition of NO_2^- ions in the polymer phase is confirmed in the Ref.². The polymer containing secondary amine groups cannot have sorption capacity of 3.1 g NO_2^- /g, as is shown in the article². In neutral and alkaline medium degree of protonation of amine groups decreases and tends to zero. Because of this, and ion exchange capacity of the polymer decreases and tends to zero.

Being modified with metallic compounds, strongly basic anion exchangers became selective sorbents for some anions and molecules in function of the metal nature. So, modified with Fe(III)-containing compounds, strongly basic anion exchangers become selective sorbents for CN^- , NCS^- , NCO^- ions³. 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 studies⁴⁻⁶, it was shown that strongly basic cross-linked ionic polymers in certain conditions are able to retain metallic cations from $\text{M}_2(\text{SO}_4)_3$ solutions, where $\text{M} = \text{Fe}^{3+}, \text{Cr}^{3+}$ or Al^{3+} . From MCl_3 or $\text{M}(\text{NO}_3)_3$ solutions sorption of cations do not takes place. The sorption of metallic cations from sulphate solutions takes place through the formation in the

polymer phase of the jarosite(alunite) mineral type compounds: $R_4N[M_3(OH)_6(SO_4)_2]$ and $H_3O[M_3(OH)_6(SO_4)_2]$, where R_4N^+ is a functional group of the polymer. The jarosite mineral type compounds are in form of pseudo-layers of 3 or 6 octahedral cycles⁷. 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. Between the jarosite polymer layers there are mobile R_4N^+ , H_3O^+ and other cations retained by Coulomb's electrostatic interactions. The jarosite mineral type compounds in the polymers phase change essentially their physical-chemical properties. 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 this paper we put in discussion the results of NO_2^- ions sorption investigation on Cr(III) – containing strongly basic anion exchanger Purolite A-400. The choice of the Cr(III) compounds containing polymer as a sorbent is conditioned by the high stability of the metallic compounds in the polymer phase. For comparison, NO_2^- ions sorption has been studied and on Purolite A-400(Cl).

EXPERIMENTAL

Purolite A-400 (Cl), a commercial strongly basic anion exchanger, containing $-N(CH_3)_3Cl$ groups was used. The gel-type resin had a polystyrene-divinylbenzene matrix and full exchange capacity 3.5-4.0 mg.equiv/g⁸. Before sorption investigation polymer was modified with Cr(III)-containing compounds according to reference⁹. For investigation was used Purolite A-400 containing 40 mg Cr/g. The Cr^{3+} content in the polymer phase was determined photocolometrically¹⁰ after desorption¹¹.

Solutions of nitrite ions were prepared using $NaNO_2$. Concentration of NO_2^- ions in solutions was determined photocolometrically using Griess reactive¹². Sorption of NO_2^- ions was calculated using equation (1):

$$S = \frac{(C_0 - C_e) \cdot V}{m}, \quad (1)$$

where S is the sorption value (mg NO_2^- /g), C_0 , C_e – initial and on equilibrium concentration (mg NO_2^- /ml), V – volume of NO_2^- containing solution (ml), m – mass of polymer sample (g).

In wall experiences samples of 0.2 g of polymer were in contacted with 100 ml solution. In

cause of the sorption isotherms obtaining and sorption of NO_2^- as a function of solution pH, polymer samples contact with solution at room temperature during 24 h.

To evaluate the influence of different factors (concentration of $NaNO_2$, KCl and K_2SO_4 , pH and temperature of solution, duration of the polymer contacting with solution) on NO_2^- ions sorption (Tab.1), the method of statistical mathematics was used¹³. The experiences were carried out according to matrix of fractional factorial experiment plan type FFE 2⁷⁻⁴ (Tab.2). There were measured and calculated the following responses of the system as a mean of two parallel experiences: Y_1 – sorption of NO_2^- ions (mg NO_2^- /g) and Y_2 – solution pH at sorption equilibrium. The significance criterion b_{sig} was calculated at a level of significance of 5 % and number of degree of freedom $f=7$ ¹³.

There was carried out optimizing of nitrite ions removal from solution using Cr(III)-containing polymer. In the optimizing experiments, KCl was excluded from the system and pH, temperature and contact duration of polymer with solution were limited corresponding to 3, 20°C and 10 h. The motion steps on the gradient were 0.1 mg NO_2^- /g, 0.1 N K_2SO_4 and 1.0 h.

The FT-IR spectra of the polymer samples were recorded at 300 K in the range of 400 – 4000 cm^{-1} on the Bruker Vertex 70 spectrometer. The polymer samples were in the vaseline-oil medium.

RESULTS AND DISCUSSION

As is seen in Figure 1, sorption of NO_2^- ions on Purolite A-400 (Cl) from $NaNO_2$ solution containing 0.555 mg NO_2^- /ml (initial concentration) at room temperature hardly depends on solution pH, increasing considerable at pH<5. At pH 1.85 the apparent sorption capacity of the polymer is higher than his

theoretical exchange capacity. Sorption of NO_2^- ions on Purolite A-400 (Cl) from solutions with pH>4 takes place mainly due to the ion exchange process (2):



The apparent high sorption of NO_2^- ions from solutions with pH<5 may be explained through the NO_2^- decomposition processes (3) and (4) that takes place in solution and in the polymer phase, in which nitrite ions concentration is higher¹⁴:



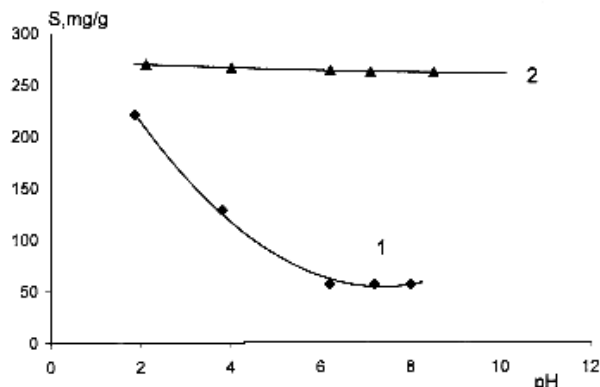
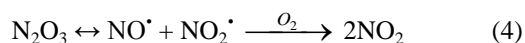
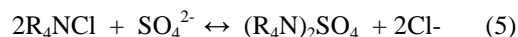


Figure 1. Sorption of the NO_2^- ions on Purolite A-400 (Cl) (1) and on Purolite A-400 (Cr) (2) as a function of pH of the NaNO_2 solution

The IR spectra of the Purolite A-400 (Cl) treated with 0.01 M NaNO_2 solution at different pH confirmed existence of above mentioned processes. As is seen in Figure 2, in IR spectrum of the polymer

treated with NaNO_2 solution at pH 6 appears a large absorption band at 1220 cm^{-1} which belongs to NO_2^- ions. In the IR spectrum of the polymer treated with NaNO_2 solutions at pH 3, this absorption band is almost absent.

In the Purolite A-400 (Cr) – NaNO_2 solution system at the corresponding pH, processes (3), (4) and (6) take place. On the preparing of the Purolite A-400(Cr), some of the R_4N^+ polymer's groups are in the jarosite type compounds, but most of them remain able to anion exchange process according to equation (5) and polymer contain not only jarosite type compounds, but and SO_4^{2-} ions:



Being in contact with NaNO_2 solution, on Purolite A-400(Cr) takes place process (6):

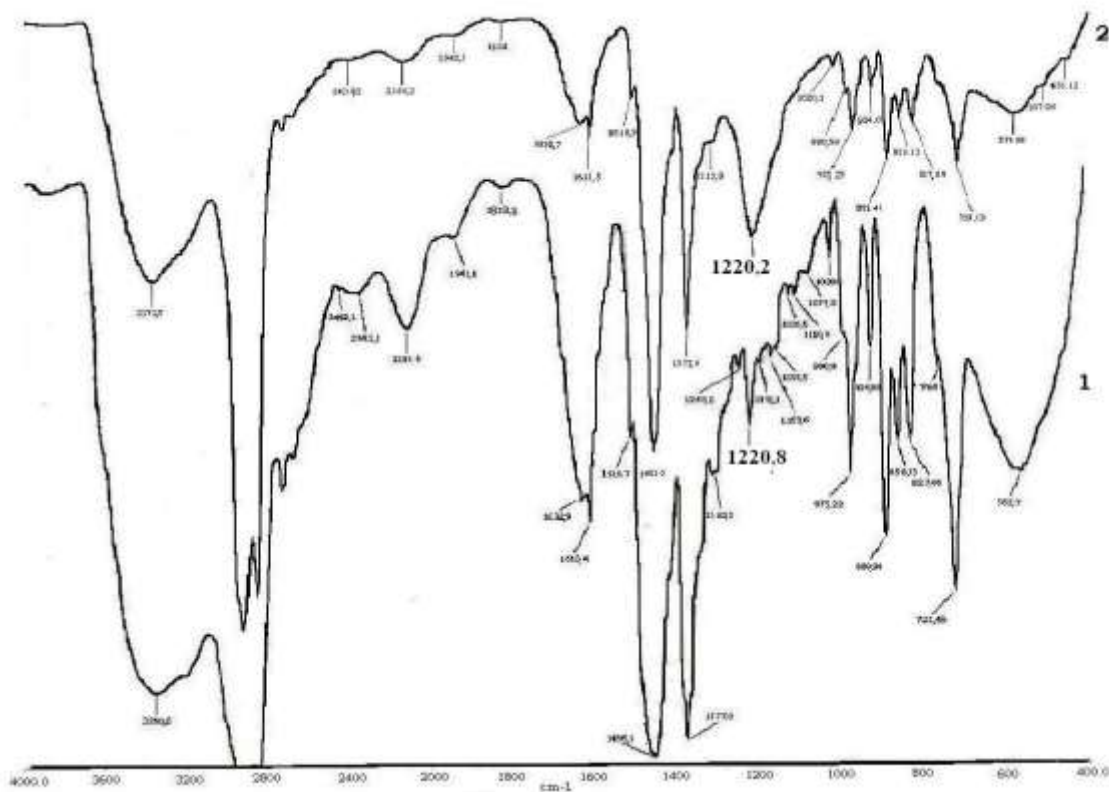
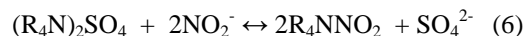


Figure 2. IR spectra of the Purolite A-400 (Cl) treated with 0.01 M NaNO_2 solution with pH 3 (1) and pH 6 (2)

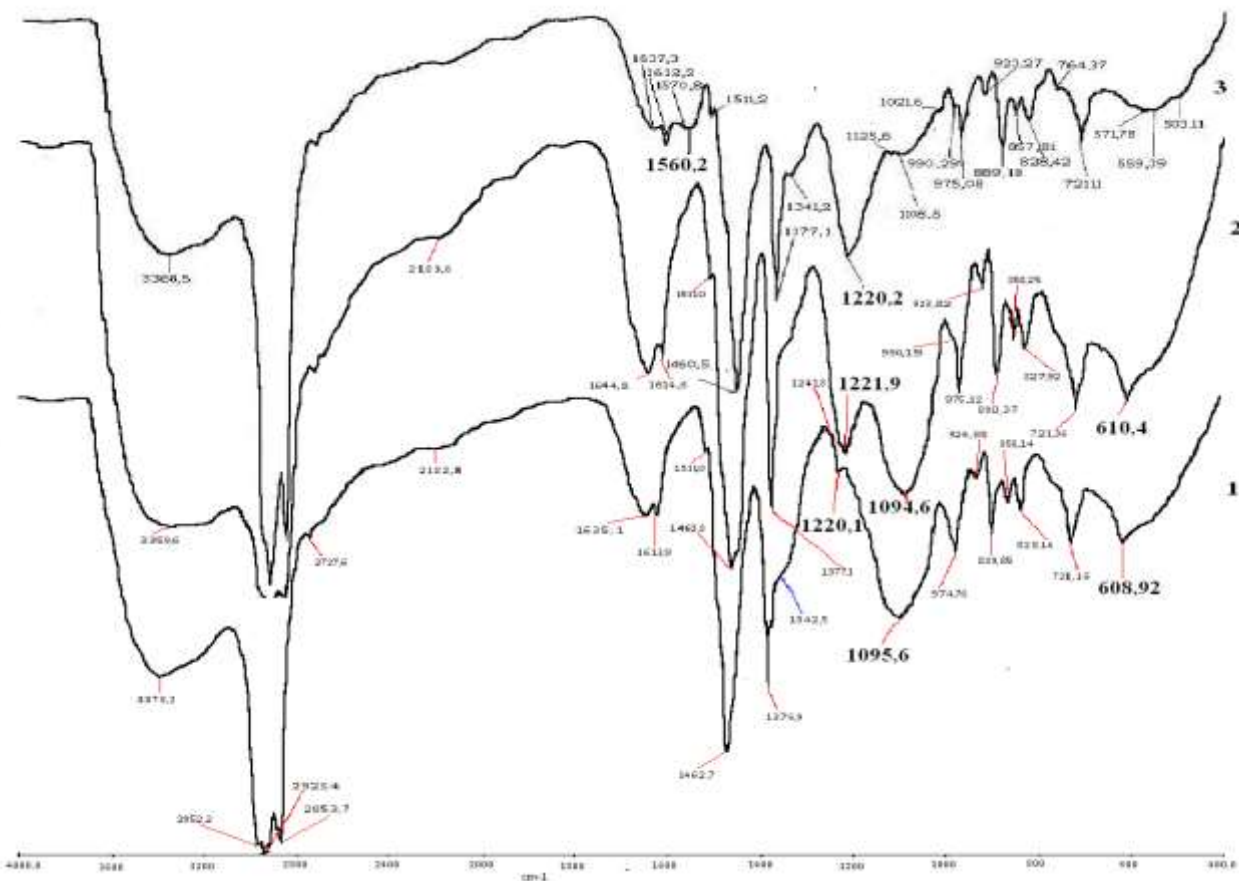
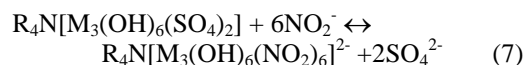


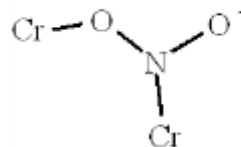
Figure 3. IR spectra of the Purolite A-400 (Cr) treated with 0.01 M NaNO_2 solution with pH 3 (1) and pH 6 (2) and with 0.1 M NaNO_2 solution with pH 6 (3)

Besides these processes in the system also takes place and sorption of NO_2^- ions through the ligand-ligand exchange. On treating of the Purolite A-400 (Cr) (Fig. 3). With increasing of system pH (up to 6 and more), the NO_2^- ions content in the polymer phase increases and SO_4^{2-} decreases (Fig. 3). Considering that NO_2^- ions coordinate monodentate with Cr^{3+} , the ligand-ligand exchange process takes place according to equation (7):

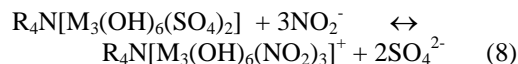


On treating of the Purolite A-400 (Cr) with 0.1 M NaNO_2 solution at pH 6, all SO_4^{2-} ions in the polymer phase are replaced by NO_2^- ions (Fig.3). Besides absorption band at 1220 cm^{-1} , appears a new band at 1560 cm^{-1} . It means that in the polymer phase a part of the NO_2^- ions coordinate with Cr^{3+} forming a bridge between metal ions¹⁵. Taking in to consideration that in the region of $600 - 400\text{ cm}^{-1}$

400 (Cr) with 0.01 M NaNO_2 solution at the pH 3, in the polymer phase there are many SO_4^{2-} ions (bands at 1095 and at about 610 cm^{-1}) and some NO_2^- ions there is a large absorption band (Fig. 3) due to M-O and M-N vibrations, we can conclude that in the polymer phase Cr^{3+} coordinate through the O and N atoms of NO_2^- ions, forming the following coordination centres:



This process can be described by the equation (8):



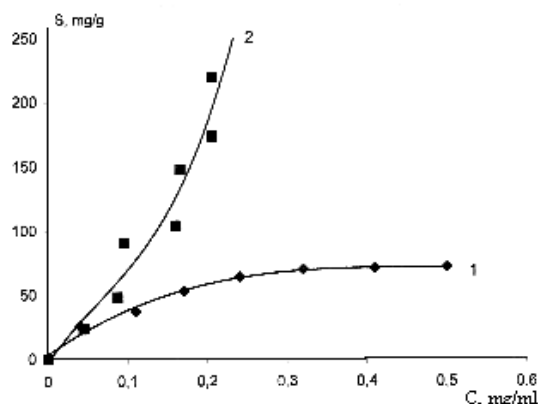


Figure 4. The NO₂⁻ ions sorption isotherms on Purolite A-400 (Cl) (1) and on Purolite A-400 (Cr) (2).

The sorption isotherms of NO₂⁻ ions on Purolite A-400 (Cl) and on Purolite A-400 (Cr) were obtained at 17°C (Fig. 4). Polymer samples were in the contact with solutions with pH=6.2 during 24 h, that was enough for sorption equilibrium establish. Sorption isotherm on Purolite A-400 (Cl) may be described by Langmuir sorption model (9):

$$S = S_{\infty} \frac{kC}{1 + kC}, \quad (9)$$

where $S_{\infty} = 123 \text{ mgNO}_2^-/\text{g}$ and $k = 4.28 \text{ m/mg}$.

On Purolite A-400 (Cr), the sorption isotherm apparently may be approximated with the type III isotherms of the BET classification.

The sorption of NO₂⁻ ions on Cr(III)-containing Purolite A-400 (40 mgCr/g) is influenced by many factors. Influence of various factors on NO₂⁻ ions sorption was studied using the method of statistical mathematics. These factors and their codes are shown in the Table 1. The experiments were carried out according to the matrix of a Fractional Factorial Experiment plan type FFE 2⁷⁻⁴ (Tab.2). There were measured and calculated the following responses of the system: Y₁ – the NO₂⁻ ions sorption value (mgNO₂⁻/g) and Y₂ – the pH of solution at the ending of the experiment. The results are the averages of two independent experiments (Tab.2). The obtained results were used for calculation of the coefficients of the regression equations (10) and (11):

$$Y_1 = 98.85 + 1.58X_1 + 17.26X_2 - 18.36X_3 - 5.46X_4 + 6.37X_5 + 17.29X_6 - 1.49X_2X_3 \\ b_{\text{sign}} = 1.19 \quad (10)$$

$$Y_2 = 4.44 + 0.24X_1 + 0.19X_2 + 0.11X_3 + 0.02X_4 - 0.19X_5 - 0.02X_6 + 0.21X_2X_3 \\ b_{\text{sign}} = 0.03 \quad (11)$$

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

Code	Factor	Lower level (-)	Upper level (+)
X ₁	NO ₂ ⁻ ions concentration, mgNO ₂ ⁻ /ml	0.5	0.8
X ₂	Temperature, °C	19.5	50.0
X ₃	pH	4.0	5.0
X ₄	KCl concentration, N	0.01	0.05
X ₅	K ₂ SO ₄ concentration, N	0.01	0.05
X ₆	Time of contact, h	6.0	8.8
X ₂ ·X ₃	-	-	-

Table 2. Matrix of the Fractional Factorial Experiment plan type FFE 2⁷⁻⁴ and the obtained results

No. of experiment	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₁ ·X ₂	Y ₁	Y ₂
1	+	+	+	+	+	+	+	116.05	5.00
2	-	+	+	-	-	-	+	76.50	4.90
3	+	-	+	-	+	-	-	60.85	4.20
4	-	-	+	+	-	+	-	68.60	4.10
5	+	+	-	+	-	-	-	108.40	4.80
6	-	+	-	-	+	+	-	163.50	3.85
7	+	-	-	-	-	+	+	116.40	4.75
8	-	-	-	+	+	-	+	80.50	3.95

Table 3. Nitrite ions sorption on Purolite A-400 (Cr) optimizing

No. experiment	X ₁	X ₂	X ₃	X ₅	X ₆	Y ₁
1	0.85	25	3.5	0.23	9	245.3
2	0.95	20	3	0.33	10	279.7
3	1.05	20	3	0.43	10	314.1
4	1.15	20	3	0.53	10	348.5
5	1.25	20	3	0.63	10	382.5

All the studied factors, the temperature (X₂) and the duration of polymer contacting with solution (X₆) (equation (10)) being increased have the strongest positive effect on the NO₂⁻ ions sorption. Such strong influence of temperature and contact duration of polymer with solution, confirm once again that NO₂⁻ ions sorption is determined by the chemical process.

As is seen in equation (10), increasing of the solution pH has a strongly negative effect on NO₂⁻ ions sorption. This fact and that of the strongest positive effect on the NO₂⁻ ions sorption concentration (more than initial pH influence (X₃) on final pH) on solution pH (X₁ in the equation (10)) indicates that in the polymer-solution system processes (3) and (4) take place. It means that NO₂⁻ ions sorption value is apparently, because a part of NO₂⁻ ions is not retained by polymer, but is removed from the system in form of NO₂. It is in accordance with the form of sorption isotherm of NO₂⁻ ions on Purolite A-400(Cr) (Fig. 4).

The low value of the coefficient at X₄ (equation (10)) also indicate that anion exchange involving NO₂⁻ ions is not a prevalent process in NO₂⁻ ions sorption. The negative influence of increasing of Cl⁻ ions concentrations on NO₂⁻ ions sorption is clear from equation (2).

Unexpected is influence of SO₄²⁻ anions (X₅, equation (10)) on NO₂⁻ sorption. It is known that anion exchangers retain SO₄²⁻ stronger than Cl⁻ ions, SO₄²⁻ influence on NO₂⁻ sorption must be negatively. Moreover, increasing of SO₄²⁻ ions concentration in solution will shift the equilibrium (6) and (7) to the left and coefficient at X₅ in the equation (10) must be negative. The positive influence of the SO₄²⁻ ions concentration on NO₂⁻ ions sorption and negative effect on solution pH indicate that SO₄²⁻ ions are involved not in anion exchange process only. Maybe in the polymer phase, where concentration of SO₄²⁻ is high, the formation of HSO₄⁻ ions takes place, and HSO₄⁻ served a source of protons in process (3).

The obtained results permit us to consider that removal of NO₂⁻ ions from solution using Cr(III)-containing polymer takes place through the processes (3), (4), (6)-(8).

The obtained regression equations provide a means for optimizing responses. We optimized only the removal of the NO₂⁻ ions from solution using Cr(III)-containing polymer. In the optimizing experiments KCl excluded from the system and pH, temperature and contact duration of polymer with solution were limited corresponding to 3, 20°C and 10 h. The steepest-ascent steps were 0.1 mgNO₂⁻/g, 0.1N K₂SO₄ and 1.0 h. The obtained results are presented in the Table 3. As is shown in Table 3, with increasing of NO₂⁻ and SO₄²⁻ ions concentration, removal of nitrite ions from solution rises considerable, but in the limit of these experiments do not reach the maximum. The obtained results showed that experiment plan is true and regression equation described adequate the NO₂⁻ removal process. Continuously increasing of the NO₂⁻ removal in the optimizing experiments confirms that in the polymer-solution system processes (3), (4) take place.

CONCLUSIONS

Sorption of the nitrite ions on strongly basic anion exchanger Purolite A-400 modified with Cr(III)-containing compounds, especially from solution with pH > 4, is much higher as on Purolite A-400(Cl).

The NO₂⁻ ions sorption by Purolite A-400(Cr) almost does not depend on solution pH but by the Purolite A-400(Cl) depends very much. Nitrite ions sorption isotherm on Purolite A-400 (Cl) may be described by Langmuir sorption model, but on Purolite A-400 (Cr) – by the type III isotherms of the BET classification. Using statistical mathematics method the influence degree of the NaNO₂, KCl, Na₂SO₄ concentration, the pH and the contacting duration of the Purolite A-400(Cr) with solution on NO₂⁻ ions sorption was determined. As a result of optimization, the apparent sorption of NO₂⁻ ions on the Purolite A-400(Cr) increases considerable. The apparent sorption of NO₂⁻ ions on Purolite A-400(Cl) occurs as a result of anion exchange process and as a result of NO₂⁻ decomposition (in low-acid medium). On Purolite A-400(Cr), NO₂⁻ ions are retained as a result of anion exchange and of NO₂⁻ coordinate with Cr³⁺ in the polymer phase. In solutions with low concentration, NO₂⁻ ion coordinate monodentate with

Cr³⁺ in the polymer phase, and in the more concentrated solution – bidentate. Important is that the modified with Cr(III)-containing compounds

Purolite A-4000 becomes selective sorbent for NO₂⁻ ions in the presence of Cl⁻, SO₄²⁻ ions.

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