

# **Ionic-Molecular Constructions in the Polymer Phase - A New Way to Obtain Different Materials with Selective Properties**

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**ABSTRACT:** It was obtained a lot of composites: AV-17(Cr), AV-17(Fe), Varion-AD(Cr), Varion-AD(Fe) (polymers containing ultra fine particles of jarosite mineral type compounds) and AV-17(Cr-NCS), AV-17(Cr-NCO), AV-17(Fe-NCS), AV-17(Fe-NCO), AV-17(Cr-NCS-Ag), AV-17(Cr-NCO-Ag), AV-17(Fe-NCS-Cu) and AV-17(Fe-NCO-Cu). The composites AV-17(Cr) and Av-17(Cr-NCS-Ag) and also the polymer AV-17(Cl) (for comparison), have been tested in selective sorption of NCS<sup>-</sup> ions from solutions. The isotherms were calculated using Freundlich, Langmuir, Sips and Dubinin-Radushkevich sorption models. There was found that isotherms consist from two parts - one in a low and another part, in a large range of NCS<sup>-</sup> concentration. The IR spectra show that in some composites, the NCS<sup>-</sup> ions are coordinated bidentate with metal and in others – monodentate. The using of polydentate ligands opening up new opportunities for obtaining many composites with selective properties which can be used in environmental protection, catalysis, separation and concentration of substances.

**KEYWORDS:** Cr(III)-containing composites, Strongly basic cross-linked polymers, Chemisorption, Ion exchange, Sorption models, Isothiocyanate ions, Isotherms.

## **I. INTRODUCTION**

Many technologies of concentration, separation and analytical determination of substances, purification of different types of water and gases are unthinkable without using of the ionic cross-linked polymers containing strongly basic groups. The largest quantity of these polymers, a high tonnage product of the chemical industry, is used to water treatment at thermoelectric and nuclear stations. The main function of these polymers is the ion exchange process:



where  $R_4N^+$  is the polymer matrix,  $A^-$  and  $B^-$  are anions. The biggest drawback of ionic crosslinked polymers containing strongly basic groups is the lack of selectivity of sorption of anions, especially the inorganic ones. This occurs because the ions sorption by the polymers is conditioned by Coulomb's electrostatic interactions. The smart technologies require new materials with selective sorption and catalytic properties. The question is whether these polymers could be transformed into materials with selective sorption and catalytic properties. At first glance, such polymers cannot be modified with metal compounds that would significantly change their physical and chemical properties. They do not contain in their matrix negatively charged or electron donor atoms and, theoretically, they are unable to interact with metallic cations. However in our previous studies [1-4], it was shown that in the phase of strongly basic crosslinked ionic polymers can be synthesised inorganic compounds of some metals (M) as  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ,  $Ga^{3+}$ ,  $In^{3+}$ . These compounds can be formed only in sulfate solutions, but not in those of nitrate or chloride. The metal compounds in the polymer phase are in the form of ultrafine particles which are located both inside and on the surface of polymer beads. The inorganic compounds in the polymer phase are in the form of jarosite mineral type:  $R_4N[M_3(OH)_6(SO_4)_2]$ , where  $R_4N^+$  are functional groups of the polymer. Depending on the pH of the solution of

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$M_2(SO_4)_3$ , in the polymer phase also is formed some amount of  $H_3O[M_3(OH)_6(SO_4)_2]$ . On heating in water media ( $t \geq 80^\circ C$ ) synthetic  $Na_3[Fe_3(OH)_6(SO_4)_2]$  is converted into  $\alpha$ -FeOOH [5]. But jarosite type compounds in the polymer phase on boiling in water are converted into  $\beta$ -FeOOH ultradispersed particles in a superparamagnetic state [2]. Using different procedures (carried out several cycles of "Fe(III) sorption - heating in water") the particles sizes and morphology, their repartition on the surface and in the volume of the polymer granule, the composition of the "polymer - inorganic compound" structural units may be modified. With increasing iron content in the polymer phase metallic compounds turn into relatively massive and magnetic ordered particles of  $\beta$ -FeOOH [2,6]. Besides jarosite mineral type compounds in phase of the strongly basic cross-linked ionic polymers can be synthesized  $BiOCl$  and  $Bi_2O_3$  compounds [7,8]. The composites formed by polymeric and metallic compounds are thermally stable up to  $120^\circ C$ , which is important for their application in different technological processes [6,9]. The composites radically changes the physical and chemical properties of strongly basic cross-linked ionic polymers. They can be used in modeling of biochemical mass transfer processes and as models with peculiar magnetic properties [10,11] and be involved in redox processes [12,13]. But most important is that they become adsorbents and catalysts [14] with selective properties. In this paper are presented research results of the functionality modification of strongly basic cross-linked ionic polymers, through the composites synthesis in their phase by ion-molecular constructions.

### II. MATERIALS AND METHODS

**Materials:** The commercial strongly basic cross-linked ionic polymers AV-17 in  $Cl^-$  form (AV-17(Cl)) and Varion-AD in  $Cl^-$  form (Varion-AD(Cl)) have been used. The AV-17 and Varion-AD, containing  $R_4N^+$  functional groups, are gel-type polymers, had a polystyrene-divinylbenzene matrix and full sorption capacity 3.5-4.0 meq./g [15]. Salts  $Fe_2(SO_4)_3 \cdot 9H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $KCr(SO_4)_2 \cdot 12H_2O$ , KNCS, NaNCO, KCl,  $KNO_3$ ,  $AgNO_3$ , hydroxides NaOH,  $NH_4OH$  and acids HCl,  $HNO_3$  have been used.

**Analysis:** The content of  $Fe^{2+}$  and  $Fe^{3+}$  ions was determined photocolometrically using  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ , 1.10 phenanthroline,  $NH_2OH \cdot HCl$  and  $CH_3COOH + CH_3COONa$  buffer solution [16]. The  $NCS^-$  ions were determined according to the Ref. [17]. The  $Cr^{3+}$ ,  $Cu^{2+}$  and  $Ag^+$  ions also were determined fotocolometrically [16].

**Obtaining of primary composites:** A 5 g sample of the dried AV-17(Cl) was put in contact with 0.5 L of solution of  $KCr(SO_4)_2 \cdot 12H_2O$ , containing 2 g Cr/L at  $55^\circ C$  for 10 h. The system "polymer-solution of Cr(III) salt" pH value was adjusted periodically to 4.2 using KOH solution. Thus was obtained composite **AV-17 (Cr)**. In the same way was obtained and composite **Varion-AD (Cr)**. The  $Cr^{3+}$  content in the AV-17(Cr) and Varion-AD(Cr) phase was 20.1 and 35,7 mg/g respectively. Composites **AV-17(Fe)** and **Varion-AD(Fe)** were obtained by contacting of 5 g polymers samples with 0.5 L of solution, containing 7 g  $Fe_2(SO_4)_3 \cdot 9H_2O/L$  for 8 h at  $50 \pm 1^\circ C$ . The system "polymer-solution" had  $pH 2.0 \pm 0.1$ . The  $Fe^{3+}$  content in the AV-17(Fe) and Varion-AD(Fe) phase was 19,6 and 21,9 mg/g respectively.

**FT-IR spectroscopy:** The FT-IR spectra of the composites samples were recorded at 300 K in the range of 400-4000  $m^{-1}$  on the Bruker Vertex 70 spectrometer. The composites samples were in the Vaseline-oil medium.

**Scanning Electron Microscopy (SEM):** For SEM analysis a Vega II ISH Tescan Company with acceleration voltage of 30 kV was used to examine the morphology of the compounds on the surface and in the volume of polymer granules. The solid samples were attached to aluminum holders using a silver based adhesive. Samples conductivity was achieved by sputter coating with a 15 nm layer of gold.

### III. RESULTS AND DISCUSSION

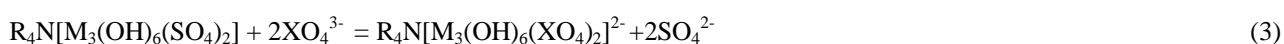
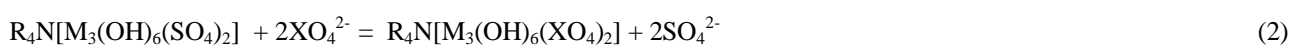
In the polymer phase, ultra dispersed particles of the jarosite type compounds of  $R_4N[Cr_3(OH)_6(SO_4)_2]$  and a small part of  $H_3O[Cr_3(OH)_6(SO_4)_2]$ , of  $R_4N[Fe_3(OH)_6(SO_4)_2]$  and a part of  $H_3O[Fe_3(OH)_6(SO_4)_2]$  were synthesized. As is shown in Fig.1, the metal compounds in the phase of composites have a very low crystallinity, that was confirmed and by X-ray diffraction analysis. The jarosite mineral type compounds are formed as layers of 3 or 6 octahedral cycles [18]. The OH groups are located in the equatorial plane, forming a bridge between metal ions, but  $SO_4^{2-}$  groups are located in

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axial position, each coordinate with 3 metal cations of 3 octahedra. Between the jarosite polymer layers there are mobile  $R_4N^+$  and  $H_3O^+$  and other cations retained by electrostatic interactions. In fact, the  $R_4N^+$  groups are linked by the organic polymer chains and their mobility is limited by the chains flexibility. This, together with the different degree of hydration of mobile ions, causes the formation in the polymer phase of jarosite type compounds with almost absence of crystallinity. The natural jarosites have a high degree of crystallinity. The selective sorption properties of the composites are due to the  $SO_4^{2-}$  groups that may be substituted by tetrahedral anions such  $XO_4^{2-}$  or  $XO_4^{3-}$  ( $CrO_4^{2-}$ ,  $VO_4^{2-}$ ,  $WO_4^{2-}$ ,  $AsO_4^{3-}$ ,  $PO_4^{3-}$  and other) according to Equation (2) and (3):



The anions  $XO_4^{2-}$  and  $XO_4^{3-}$  can also be adsorbed by the polymer according to Equation (4) and (5):

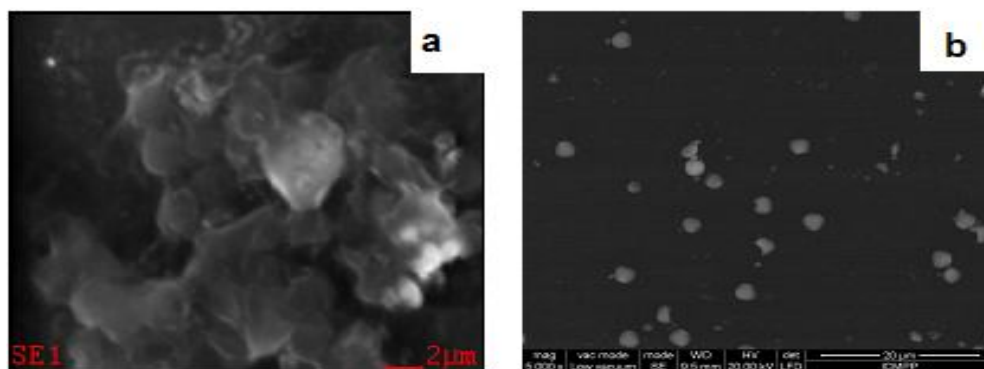
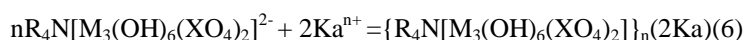


Fig.1.SEM images of the Cr(III) –containing (a) and Fe(III)-containing (b) compounds particles on the surface of polymer AV-17 granule.



But anions sorption according to Equation (4) and (5) is not selective because is conditioned by Coulomb's electrostatic interactions, while the sorption according to Equation (2) and (3) is selective because is conditioned by chemical donor-acceptor interactions. It should be noted that as a result of sorption of anions according to Equation (3), the composite changes its functionality - he becomes able to adsorb cations ( $Ka^{n+}$ ) according to Equation (6):



The researches [19] have shown that the composites, based on the polymer and the jarosite type compounds, are able to adsorb not only the tetrahedral anions, but and anions of different configurations, such as  $NO_2^-$ , for example.

Investigation of selective adsorption of ions that can coordinate bidentate presents not only applied interest, but also a way to change functionality of the composites. We prove this by researching  $NCS^-$  ions interactions with composite AV-17(Cr) and, for comparison, with AV-17(Cl). The sorption value of  $NCS^-$  ions was calculated using Equation (7):

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$$S = \frac{(C_0 - C_e)V}{m} \tag{7}$$

where S is sorption value (mg NCS<sup>-</sup>/g), C<sub>0</sub> and C<sub>e</sub> are initial and respectively the equilibrium concentration of NCS<sup>-</sup> ions (mg NCS<sup>-</sup>/mL), V is the solution volume in contact with sorbent sample (mL), m is the mass of sorbent sample (g).

There were obtained sorption isotherms of NCS<sup>-</sup> ions from KNCS solutions, containing 0.01 mol./L KNO<sub>3</sub>, on the composites AV-17(Cr) and AV-17(Cr-NCS-Ag). For comparison the sorption isotherm of NCS<sup>-</sup> ions from KNCS solution on the AV-17(Cl) has also been obtained. Sorption took place at temperature of 22 °C. The isotherms were calculated according to different sorption models.

### a) Langmuir sorption model.

The nonlinear form of the Langmuir isotherm [20] is described by Equation (8):

$$S = S_L \frac{K_L * C_e}{1 + K_L * C_e} \tag{8}$$

where S is the sorption value at equilibrium (mg NCS<sup>-</sup>/g); S<sub>L</sub> is the monolayer capacity of the sorbent (mg NCS<sup>-</sup>/g); K<sub>L</sub> is the Langmuir isotherm constant (L/mg), C<sub>e</sub> is the NCS<sup>-</sup> concentration at sorption equilibrium (mg NCS<sup>-</sup>/L). The constants S<sub>L</sub> and K<sub>L</sub> were calculated by the graph of the linear Langmuir isotherm expressed by Equation (9):

$$\frac{C_e}{S} = \frac{1}{S_L * K_L} + \frac{C_e}{S_L} \tag{9}$$

### b) Freundlich sorption model.

The nonlinear form of the Freundlich isotherm [21] is described by Equation (10):

$$S = K_F * C_e^{1/n} \tag{10}$$

where S is the same as in Equation (8), K<sub>F</sub> is the Freundlich isotherm constant, which predict the quantity of the NCS<sup>-</sup> ion per gram of sorbent at the equilibrium concentration C<sub>e</sub>=1 mg/L (mg/g), 1/n is a measure of the nature and strength of the adsorption process and of the distribution of active sites. If 1/n > 1, bond energies increase with the surface density; if 1/n < 1, bond energies decrease with the surface density; and when 1/n = 1, all surface sites are equivalent. The constants 1/n and K<sub>F</sub> were calculated by the graph of the linear Freundlich isotherm Equation (11):

$$\ln S = \ln K_F + (1/n) \ln C_e \tag{11}$$

### c) Sips sorption model.

The Sips isotherm is a combination of Langmuir and Freundlich sorption models [22,23]. At low concentration of sorbate, it reduces to a Freundlich sorption model, while at high of sorbate concentration; it predicts a monolayer adsorption capacity characteristic to the Langmuir sorption model. The nonlinear form of the Sips isotherm is expressed by Equation (12):

$$S = \frac{S_s * K_s * C_e^{1/n}}{1 + K_s * C_e^{1/n}} \tag{12}$$

where S and C<sub>e</sub> have the same meaning as in Equation (8) and (10), and K<sub>s</sub> is the Sips constant related to the energy of sorption and S<sub>s</sub> is the monolayer sorption capacity.

The constants S<sub>s</sub> and K<sub>s</sub> were calculated by the graph of the linear Sips isotherm Equation (13):

$$\frac{C_e^{1/n}}{S} = \frac{1}{S_s * K_s} + \frac{C_e^{1/n}}{S_s} \tag{13}$$

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### d) Dubinin-Radushkevich (D-R) sorption model

The Dubinin-Radushkevich nonlinear isotherm [22,23] is expressed by Equation (14):

$$S = S_{D-R} * \exp \left\{ -K_{D-R} \left[ RT * \ln \left( 1 + 1/C_e \right) \right]^2 \right\}, \quad (14)$$

where S is the amount of adsorbed ions (mg/g),  $S_{D-R}$  is the maximum adsorption capacity of the ions (mg/g),  $K_{D-R}$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2/\text{kJ}^2$ ),  $C_e$  is the equilibrium concentration of ions (mg/L), R is the constant (8.314 J/mol·K), T is the absolute temperature (K). The Dubinin-Radushkevich isotherm constant,  $K_{D-R}$ , is related to the mean free energy of adsorption, (kJ/mol), defined as the free energy when one mol of cations is transferred from infinity in solution to the surface of solid sorbent and computed using the Equation (15):

$$E = \frac{1}{(2K_{D-R})^2} \quad (15)$$

The value of E is used to estimate the type of adsorption. When E is 1-8 kJ/mol, the sorption is determined by physical forces. The values of E between 9 and 16 kJ/mol are characteristic for ion exchange processes, and the E more than 16 kJ/mol - for chemisorption. The constants  $S_{D-R}$  and  $K_{D-R}$  were calculated by the graf of the linear Dubinin-Radushkevich isotherm, Equation (16):

$$\ln S = \ln S_{D-R} - K_{D-R} \left[ RT * \ln \left( 1 + 1/C_e \right) \right]^2 \quad (16)$$

Beside the correlation coefficient of determination ( $R^2$ ), the statistical analysis of errors was performed by the non-linear Chi-square test ( $\chi^2$ ) using Equation (17) [24]:

$$\chi^2 = \frac{\sum (S_{\text{exp}} - S_{\text{calc}})^2}{S_{\text{calc}}} \quad (17)$$

The experimental isotherm of NCS<sup>-</sup> anions sorption on AV-17(Cl), obtained at the contact of the sorbent with solution for 24 hours, is shown in Fig.2(curve 1). As shown in Fig.2, in a large range of NCS<sup>-</sup> ions concentration, on sorption isotherm appears a plateau.

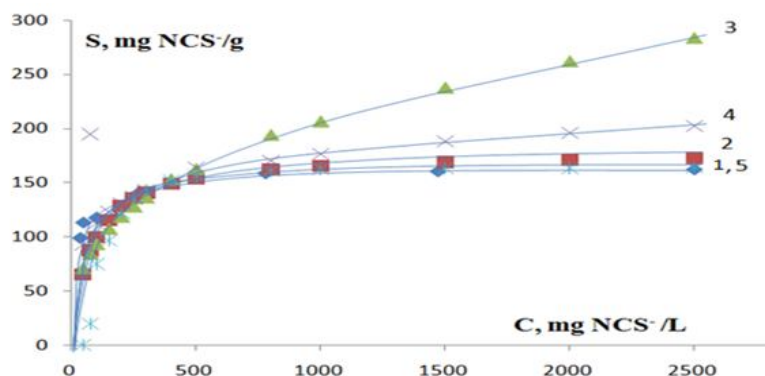


Fig.2. Equilibrium sorption isotherms of NCS<sup>-</sup> ions on AV-17(Cl) in a large range of NCS<sup>-</sup> concentration: obtained experimentally (1), calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models. This is clearly seen in Fig. 4. Perhaps in the systems with a great concentration of NCS<sup>-</sup> ions occur photo catalytic processes with formation of the compounds of different species, in particular (NCS)<sub>2</sub>[25]. Because of this, the isotherm of Fig.2 in the low range of concentrations of NCS<sup>-</sup> ions was also examined (Fig.3). Both isotherms were constructed

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and calculated with the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models. The isotherms parameters and the value of  $R^2$  and  $\chi^2$  are listed in Table 1. The Fig. 2 and Table 1 data, values of  $R^2$  and non-linear Chi-square test  $\chi^2$ , show that the sorption isotherm, obtained in a wide range of the  $\text{NCS}^-$  ions concentration, is best described by Langmuir and Dubinin-Radushkevich (especially at higher than 100 mg  $\text{NCS}^-$  /L concentration), sorption models. But worst the isotherm is described by Freundlich sorption model, especially at high concentrations of  $\text{NCS}^-$

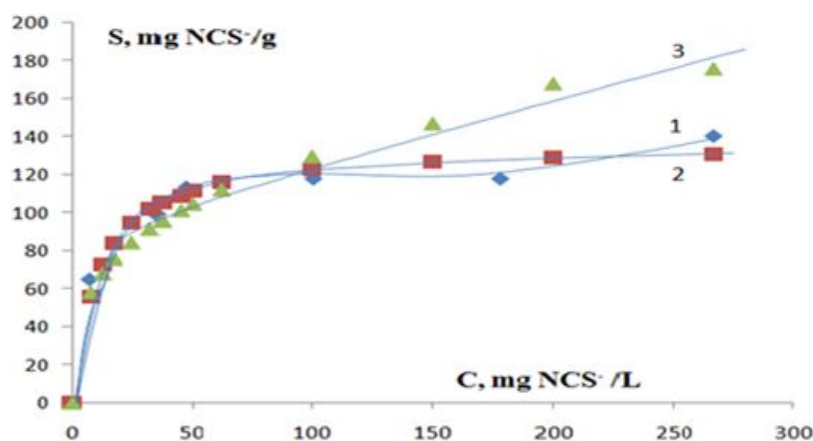


Fig. 3. Equilibrium sorption isotherms of  $\text{NCS}^-$  ions on AV-17(Cl) in a low range of  $\text{NCS}^-$  concentration: obtained experimentally (1), calculated by Langmuir (2) and Freundlich (3) sorption models.

**Table 1.** Parameters of the isotherms, calculated by the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models for sorption of  $\text{NCS}^-$  ions on AV-17(Cl) sorbent.

Langmuir model	$S_L$ , mg/ g	$K_L$ , L/mg	$R^2$	$\chi^2$ (complete isotherm)	$\chi^2$ ( $C_{\text{NCS}^-} > 100$ mg L <sup>-1</sup> )	
Large $\text{NCS}^-$ concentration	177.8	0.013	0.9649	61.52	4,52	
Low $\text{NCS}^-$ concentration	135.9	0.092	0.9507	3.69	--	
Freundlich model	$K_F$	N	$R^2$	$\chi^2$ (complete isotherm)	$\chi^2$ ( $C_{\text{NCS}^-} > 100$ mg L <sup>-1</sup> )	
Large $\text{NCS}^-$ concentration	18.92	0.346	0.9936	131.44	88.9	
Low $\text{NCS}^-$ concentration	31.12	0.31	0.9944	9.61	--	
Sips model	Ss	Ks	1/n	$R^2$	$\chi^2$ (complete isotherm)	$\chi^2$ ( $C_{\text{NCS}^-} > 100$ mg L <sup>-1</sup> )
Large $\text{NCS}^-$ concentration	333.3	0.10	0.346	0.9507	19.61	13.58
Dubinin-Radushkevici model	$S_{D-R}$	$K_{D-R}$	E, kJ mol <sup>-1</sup>	$R^2$	$\chi^2$ (complete isotherm)	$\chi^2$ ( $C_{\text{NCS}^-} > 100$ mg L <sup>-1</sup> )
Large $\text{NCS}^-$ concentration	164.02	0.002	15.82	0.9649	--	0.38

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kJ/mol (Table 1) show that the  $\text{NCS}^-$  ions sorption on polymer AV-17(Cl) is determined mainly by anion exchange process. But a small part of sorption occurs involving chemical forces, especially at low concentration. The experimental isotherm of  $\text{NCS}^-$  anions sorption on AV-17(Cr), obtained at the contact of the sorbent with solution for 24 hours, is shown in Fig. 4. On this isotherm has also appeared a plateau at the low concentrations of the  $\text{NCS}^-$  ions in solution. The data in Fig.4, show that in a similar conditions the sorption of  $\text{NCS}^-$  ions on the composite AV-17(Cr) is less than on the polymer AV-17(Cl). This seems strange at first. As we will see, later sorption on the AV-17(Cr)

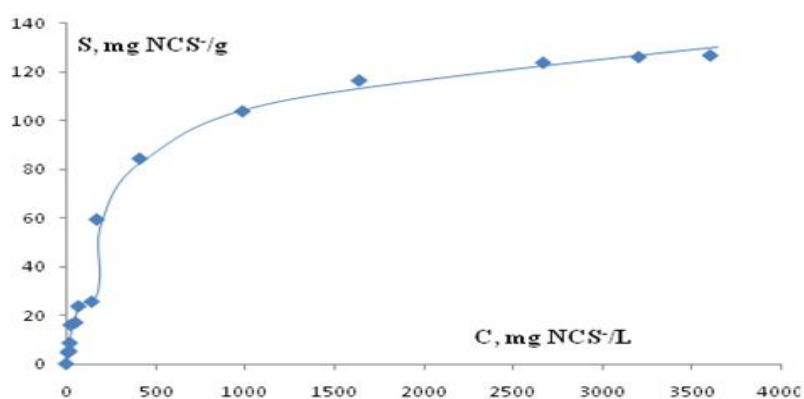


Fig. 4 Nonequilibrium sorption isotherm of  $\text{NCS}^-$  ions on AV-17(Cr).

should be greater than on the AV-17(Cl). This divergence is due to the well known fact that the exchange of ligands (in our case groups  $\text{SO}_4^{2-}$  with  $\text{NCS}^-$  ions) in complexes of chromium (III) takes place rather slowly. The complexes of chromium (III) are kinetically very stable. Sorption of the  $\text{NCS}^-$  ions on the polymer AV-17(Cl) occurs at a relatively fast rate according to the Equation(18):



The duration of the AV-17(Cr) composite contact with solution of  $\text{NCS}^-$  during 24 h is not enough to achieve sorption equilibrium. Therefore the isotherm is obtained in non-equilibrium conditions and it will be incorrect to calculate its parameters. The data of the isotherm, obtained at 96 h contact of AV-17(Cr) composite with solution of  $\text{NCS}^-$  (Fig.5, Table 2), have confirmed perfectly the mentioned above assumption. Indeed, at longer contact (96 hours against 48) of the AV-17(Cr) with solutions, containing  $\text{KNCS}$  and  $0.01 \text{ mol L}^{-1} \text{ KNO}_3$ , the sorption of  $\text{NCS}^-$  becomes much higher than had been observed in the examined above cases. The Fig.5 and Table 2 data show that the sorption isotherm, obtained in a wide range of the  $\text{NCS}^-$  concentration, is best described by Langmuir and D-R (especially at higher than  $500 \text{ mg L}^{-1}$ ) sorption models. The Sips sorption model describes slightly inexact, but Freundlich model cannot adequately describe the experimental obtained isotherm, especially at high concentration. The isotherm, obtained at low concentrations of  $\text{NCS}^-$  (Fig.6, Table 2, ), more adequately can be described by the D-R sorption model. The values of E of  $3.1$  and  $57.8 \text{ kJ mol}^{-1}$  confirmed that the  $\text{NCS}^-$  sorption on AV-17(Cr) is determined by physical processes at the large concentration, and chemical - at low concentration of  $\text{NCS}^-$ . The complex interpretation of the isotherms show that they are obtained as a result of several processes, such as ion exchange, involving anions  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and, especially, different coordination modes of  $\text{NCS}^-$  with metal in the composite phase. Already it was mentioned that  $\text{NCS}^-$  can coordinate with the metal via atoms N or S, and can form bridges between metals atoms.

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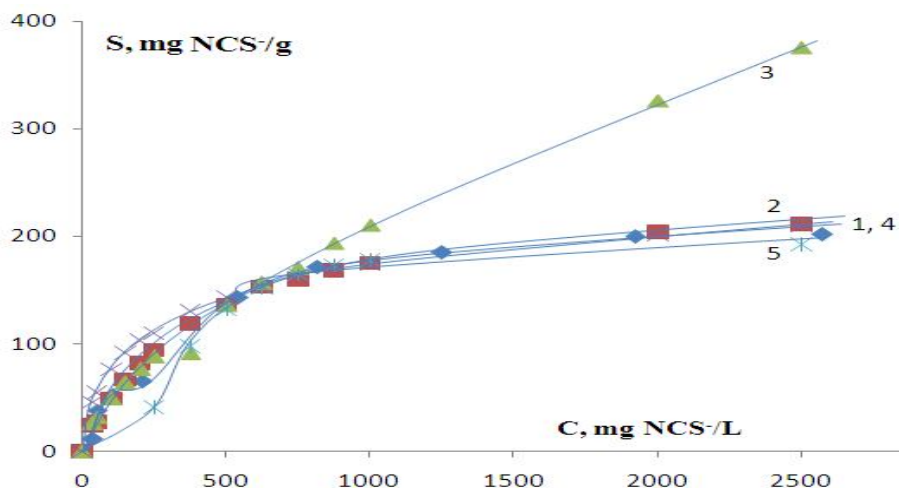


Fig.5. Equilibrium sorption isotherm of  $\text{NCS}^-$  ions on AV-17(Cr) in a large range of  $\text{NCS}^-$  concentration: obtained experimentally (1), calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models.

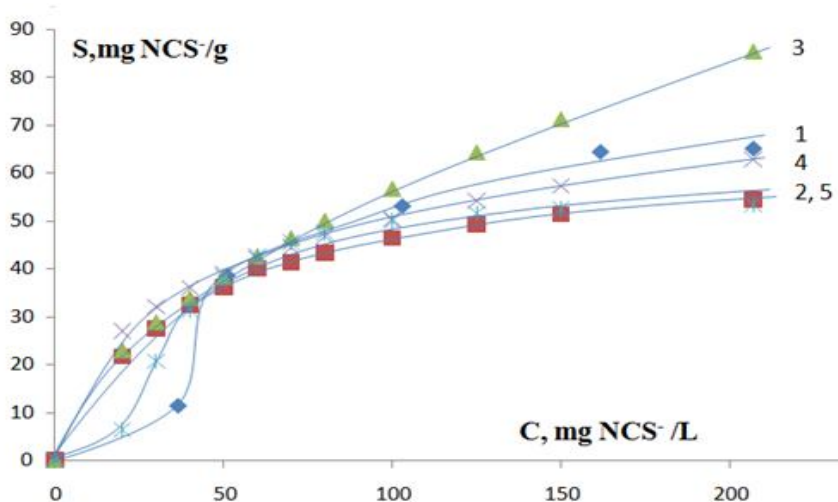


Fig. 6. Equilibrium sorption isotherms of  $\text{NCS}^-$  ions on AV-17(Cr) in a low range of  $\text{NCS}^-$  concentration: obtained experimentally (1), calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich sorption models (5).

In order to elucidate the mode of coordination of the  $\text{NCS}^-$  with  $\text{Cr}^{3+}$  of the AV-17(Cr), were performed investigation using FTIR spectroscopy. To confirm the IR spectra data were also obtained spectra of other composites, namely Varion-AD(Cr), AV-17(Fe) and Varion-AD(Fe). The composite samples were previously washed on the filter with



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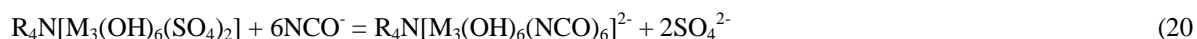
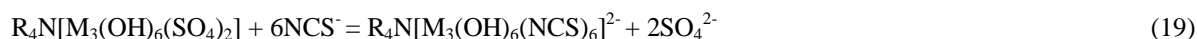
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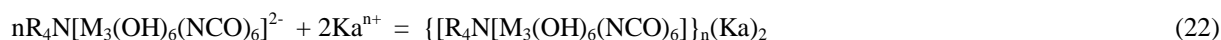
**Table 2.** Parameters of the isotherms, calculated by the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models for sorption of NCS<sup>-</sup> ions on AV-17(Cr) sorbent

<b>Langmuir model</b>	S <sub>L</sub> mg/g	K <sub>L</sub> , L/mg		R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> >100mg/L)
Large NCS <sup>-</sup> concentration	45.1	0.0025		0.9885	9.91	-
Low NCS <sup>-</sup> concentration	64.98	0.025		0.9661	18.3	
<b>Freundlich model</b>	K <sub>F</sub>	1/n		R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> >100mg/L)
Large NCS <sup>-</sup> concentration	2.718	0.63		0.9948	133.88	--
Low NCS <sup>-</sup> concentration	4.263	0.562		0.9944	20.05	
<b>Sips model</b>	S <sub>s</sub>	K <sub>s</sub>	1/n	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> >100mg/L)
Large NCS <sup>-</sup> concentration	285.7	0.02	0.63	0.9885	1265.5	--
Low NCS <sup>-</sup> concentration	123.45	0.052	0.562	0.9507	16.29	--
<b>Dubinin –Radushkevici model</b>	S <sub>D-R</sub>	K <sub>D-R</sub>	E, kJ/mol	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> >500mg/L)
Large NCS <sup>-</sup> concentration	195.39	0.0162	3.1	0.9885	-	1.06
Low NCS <sup>-</sup> concentration	54.6	0.00015	57.8	0.9661	15.88	--

0.1 M KNCS solution. There have also been obtained IR spectra of the composites which were treated with 0.01M solution of NaNCO. The NCO<sup>-</sup> ligand has physico-chemical properties similar to NCS<sup>-</sup> and absorption bands in the same segment of the IR spectrum. Interpretation spectral absorption bands was performed according to Ref.[26]. In the IR spectra of all composites which were treated with solution of KNCS or NaNCO, the absorption bands characteristic to SO<sub>4</sub><sup>2-</sup> (about 1100 and 617 cm<sup>-1</sup>) practically were absent, that show their substitution by other ligands. However, other absorption bands appeared. From the data in Table 3, it follows that NCS<sup>-</sup> and NCO<sup>-</sup> have interacted with the composites through the coordination of the metal with the N atom of the ligand. A small part of NCS<sup>-</sup> have coordinated with Cr<sup>3+</sup> of the AV-17(Cr) through the atom S. In the composites AV-17(Fe) and Varion-AD(Fe) the ligands NCS<sup>-</sup> and NCO<sup>-</sup> have formed bridges (M-NCS -M or M-NCO-M) between the metal atoms. If to take into consideration that each NCS<sup>-</sup> and NCO<sup>-</sup> group with monodentate coordination, substitutes one of the oxygen bound of SO<sub>4</sub><sup>2-</sup> group in jarosite type compound, follows that 2 groups of SO<sub>4</sub><sup>2-</sup> should be substituted by 6NCS<sup>-</sup> or 6NCO<sup>-</sup> ions. Thus, the sorption of NCS<sup>-</sup> and NCO<sup>-</sup> ions by the composites can be expressed by the following Eq.(19) and (20):



As a result of sorption of ligands according to Eq.(19) and (20), the composites changes their functionality - they become cationites and able to adsorb cations (K<sup>n+</sup>) according to Eq.(21) and (22):



Respectively, {[R<sub>4</sub>N[M<sub>3</sub>(OH)<sub>6</sub>(NCS)<sub>6</sub>]}<sub>n</sub>(Ka)<sub>2</sub> and {[R<sub>4</sub>N[M<sub>3</sub>(OH)<sub>6</sub>(NCO)<sub>6</sub>]}<sub>n</sub>(Ka)<sub>2</sub> composites can participate in the cation exchange processes. So, at interaction of AV-17(Cr) or AV-17(Fe) with NCS<sup>-</sup> or NCO<sup>-</sup>, the new AV-17(Cr-NCS), NCS AV-17(Cr-NCO), AV-17(Fe-NCS) and AV-17(Fe-NCO) composites are obtained. In these composites, instead of AV-17 can be any polymer containing strongly basic groups. And that's not all. If ligands NCS<sup>-</sup> and NCO<sup>-</sup> are

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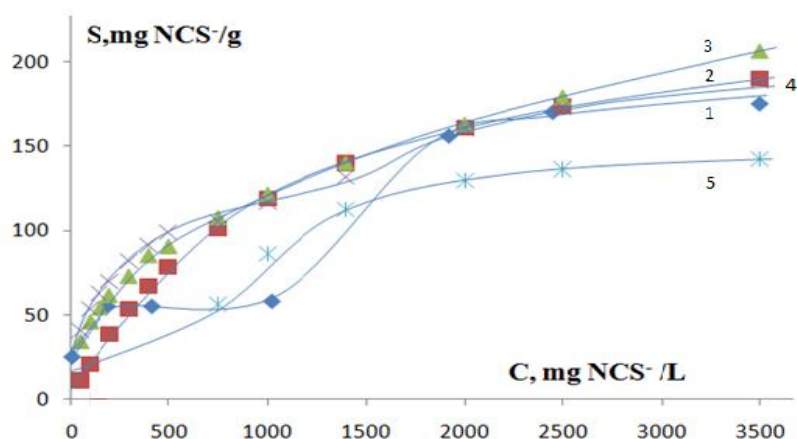
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coordinated monodentate through the atoms N, the S or O atoms are able to form new coordination bonds. Thus, the AV-17(Cr-NCS) and AV-17(Cr-NCO) or AV-17(Fe-NCS) and AV-17(NCO) have become selective sorbents for sorption of heavy metal ( $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and other).

**Table 3.** The IR spectroscopic data of the interaction of composites with various ligands and cations.

Composite	Added anion or cation	$\nu(\text{N}\equiv\text{C}), \text{cm}^{-1}$	Chemical bonds
AV-17(Cr)	$\text{NCS}^-$	2040	Cr-NCS
		2090	Cr-SCN
Varion – AD (Cr)	$\text{NCS}^-$	2040	Cr-NCS
AV-17(Fe)	$\text{NCS}^-$	2040	Fe- NCS
		2140	Fe- NCS-Fe
Varion – AD (Fe)	$\text{NCS}^-$	2040	Fe- NCS
AV-17(Fe)	$\text{NCO}^-$	2160	Fe- NCO
		2225	Fe- NCO-Fe
Varion – AD (Fe)	$\text{NCO}^-$	2140	Fe- NCO
		2190	Fe- NCO-Fe
Varion – AD (Cr)	$\text{NCS}^-$ , $\text{Ag}^+$	2081	Cr-NCS
		2146	Cr-NCS-Ag
AV-17(Fe)	$\text{NCS}^-$ , $\text{Ag}^+$	2098	Fe- SCN
		2140	Fe- NCS-Cu
AV-17(Fe)	$\text{NCS}^-$ , $\text{Cu}^{2+}$	2040	Fe- NCS
		2140	Fe- NCS-Cu
Varion – AD (Fe)	$\text{NCS}^-$ , $\text{Ag}^+$	2080	Fe- SCN
		2140	Fe- NCS-Ag



**Fig. 7.** Equilibrium sorption isotherms of  $\text{NCS}^-$  on AV-17(Cr-NCS-Ag) in a large range of  $\text{NCS}^-$  concentration: obtained experimentally (1), calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models.

Indeed, the mentioned above composites, being treated with solutions of  $\text{AgNO}_3$  or  $\text{CuSO}_4$ , retain metal cations according to Equation (23) and (24):

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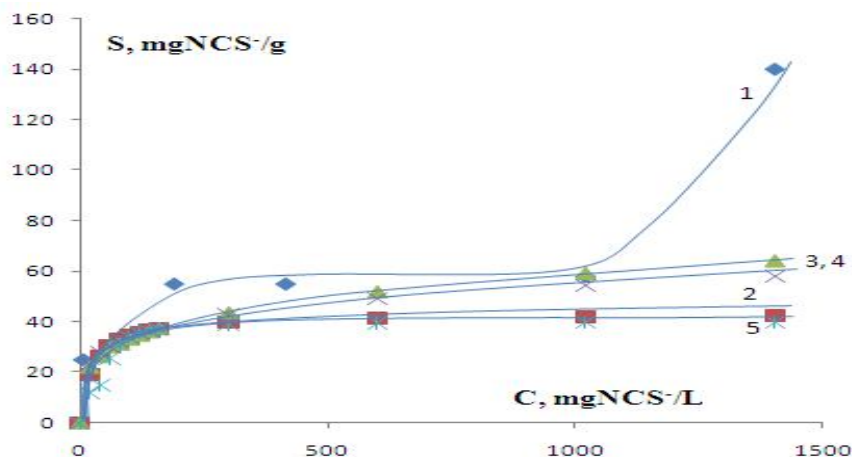
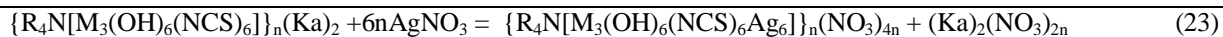


Fig. 8. Equilibrium sorption isotherms of NCS<sup>-</sup> on AV-17(Cr-NCS-Ag) in a low range of NCS<sup>-</sup> concentration: obtained experimentally (1), calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models.

**Table 4.** Parameters of the isotherms, calculated by the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models for sorption of NCS<sup>-</sup> ions on AV-17(Cr-NCS-Ag) sorbent

Langmuir model	S <sub>L</sub> , mg/g	K <sub>L</sub> , L/mg	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> > 1000 mg L <sup>-1</sup> )	
Large NCS <sup>-</sup> concentration	250	0.00091	0.9457	43.08	33.62	
Low NCS <sup>-</sup> concentration	43.1	0.04	0.9285	273	--	
Freundlich model	K <sub>F</sub>	1/n	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> > 1000 mg L <sup>-1</sup> )	
Large NCS <sup>-</sup> concentration	6.55	0.423	0.9457	49.85	39.44	
Low NCS <sup>-</sup> concentration	10.49	0.25	0.9756	101.73	--	
Sips model	S <sub>s</sub>	K <sub>s</sub>	1/n	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> > 1000 mg L <sup>-1</sup> )
Large NCS <sup>-</sup> concentration	746.3	0.011	0.423	0.9498	57.21	39.56
Low NCS <sup>-</sup> concentration	245.7	0.0506	0.25	0.9756	127.0	--
Dubinin – Radushkevici model	S <sub>D-R</sub>	K <sub>D-R</sub>	E, kJ mol <sup>-1</sup>	R <sup>2</sup>	χ <sup>2</sup> (complete isotherm)	χ <sup>2</sup> (C <sub>NCS</sub> > 1000 mg L <sup>-1</sup> )
Large NCS <sup>-</sup> concentration	184.93	0.09129	2.34	0.9898	--	39.9
Low NCS <sup>-</sup> concentration	39.646	0.000269	43.1	0.9285	276.93	--



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The existans of the coordinative nodes M-NCS-Ag and M-NCS-Cu are well shown in IR spectroscopy data (Table 3). So, when AV-17(Cr-NCS) , AV-17(Fe-NCS), AV-17(Cr-NCO) or AV-17(Fe-NCO) composites interact with  $Ag^+$ ,  $Cu^{2+}$ , the new **AV-17(Cr-NCS-Ag)**, **AV-17(Cr-NCO-Ag)**, **AV-17(Fe-NCS-Cu)** and **AV-17(Fe-NCO-Cu)** composites are obtained. A lot of new composites can be obtained if instead  $Ag^+$  and  $Cu^{2+}$  cations will be other metal cations, able to form coordinate bonds. In the composites  $\{R_4N[M_3(OH)_6(NCS)_6Ag_6]\}_n(NO_3)_{4n}$  and  $\{R_4N[M_3(OH)_6(NCS)_6Cu_6]\}_n(SO_4)_{5n}$  the  $Cu^{2+}$ ,  $Ag^+$  cations are coordinatively unsaturated. Therefore, these cations may further coordinate the ions and molecules containing electron donor atoms, forming in the polymer phase various ionic-molecular construction with special properties. For example, the composite AV-17(Cr-NCS-Ag) is able to absorb again a new portion of  $NCS^-$  ions through their coordination with  $Ag^+$ . This idea has been confirmed by the following investigation. Has been obtained  $NCS^-$  sorption isotherm on AV-17(Cr-NCS-Ag) at 48 h contact of composite with KNCS solutions (Fig. 7, curve 1).

The duration of composite contact with solution has been taken taking into consideration that rate of coordination process of  $NCS^-$  ligand with  $Ag^+$  is rather high, incomparable with ligand exchange rate in  $Cr^{3+}$  compounds. The Fig. 7 and Table 4 data show that the isotherm, obtained in a wide range of the  $NCS^-$  concentration, is best described by the Sips and Langmuir sorption models but worst described by the D-R model. Parameters of the isotherm obtained in a low range of  $NCS^-$  ions concentration (Fig. 8, Table 4), are best described by Freundlich and Sips sorption models. Although the Dubinin-Radushkevich sorption model less adequately describes the sorption of  $NCS^-$  ions by the AV-17(Cr-NCS-Ag), the values of E (Table 4), with a certain approximation, confirms that the sorption of anions is conditioned by the chemical forces, as well as physical ones. The results of this research demonstrate that by the construction of ionic-molecular combinations in the phase of ionic crosslinked polymers, we can obtain a wide variation of composites with special properties.

### IV. CONCLUSION

We have reported the simple and original methods to produce a large number of new composites with special properties. The originality of the methods consist in fact, that, although the strongly basic polymers do not contain negatively charged or electron donor atoms in their matrix, in certain conditions they are able to interact with some metal cations, forming different composites. The primary composites were formed by the synthesis of the jarosite mineral type compounds ( $R_4N[M_3(OH)_6(SO_4)_2]$ ), where M is  $Cr^{3+}$  and  $Fe^{3+}$ , ( $R_4N^+$  functional group of the polymer) in the phase of commercial cross-linked polymers AV-17 (produced in Ukraine) and Varion-AD (produced in Hungary). Were obtained a lot of composites: AV-17(Cr), AV-17(Fe), Varion-AD(Cr), Varion-AD(Fe), AV-17(Cr-NCS), AV-17(Cr-NCO), AV-17(Fe-NCS), AV-17(Fe-NCO), AV-17(Cr-NCS-Ag), AV-17(Cr-NCO-Ag), AV-17(Fe-NCS-Cu) and AV-17(Fe-NCO-Cu). The composites AV-17(Cr) and Av-17(Cr-NCS-Ag) and also the polymer AV-17(Cl) (for comparison), have been tested in selective sorption of  $NCS^-$  ions from solutions containing 0.01 mol/L  $KNO_3$ . The experimentally obtained isotherms were calculated using Freundlich, Langmuir, Sips and Dubinin-Radushkevich sorption models (Figs. 2-8, Tables 1, 2, 4). It is found that sorption isotherms consist from two parts-one in a low concentration and another part, in a large range of  $NCS^-$  ions concentration. The FT-IR spectroscopy data show that in some composites, the  $NCS^-$  and  $NCO^-$  ions are coordinated bidentate with metal ions in the composites phase and in others – monodentate.

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