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IR SPECTRUM ANALYSIS OF ZN(II) AND CD(II) COMPLEXES BASED ON OXYGEN AND NITROGEN LIGANDS

Abstract. On the basis of modification of urea-ticarbamide resin with aminoacetic acid, aminosuccinic acid, 2-aminopentane diacids, complex-forming ions containing nitrogen and oxygen were obtained. Zn(II) and Cd(II) salts were added to the obtained ionites and sorbed. The composition, structure and physicochemical properties of the obtained complexes were studied using IR spectroscopy, thermogravimetric and differential thermal analysis (TG-DTA) methods.

Key words: urea-tiurea resin, Zn(II) and Cd(II) salts, (TG-DTA)

Introduction. Currently, ionites (ion exchange ionites) are widely used in hydrometallurgy for the sorption concentration of various ions, as well as for the elimination of waste containing harmful components, which may be heavy metals. In wastewater treatment. polymer ionites with the property of complex formation. separation of rare and non-ferrous metals (molybdenum, copper, cobalt, nickel, etc.) important in technology by sorption methods is an urgent task of the industry [1]. In recent years, significant progress has been made in the production of ion-exchangeable ionites, but the low sorption efficiency and selectivity of most of their types do not meet the requirements of high quality, which leads to the need to synthesize new ion-exchangeable polymer ionites [2]. Therefore, great attention is being paid to the development of new ion exchange polymer ionites and improvement of their synthesis processes. Many artificially obtained natural compounds and chemicals have ion exchange properties. The first place among them is occupied by ionites obtained on the basis of synthetic polymers [3]. In the work, ionites based on cross-modification of (N-Si-Gly) and (N-Si-Glu) by cross-linking environmentally friendly nanosorbent nanosilica (N-Si) with glycine (Gly) and reduced glutamine thione (GSH) synthesized [4]. Silicon dioxide ionites were used for selective sorption of Pb(II) ion from aqueous solution. Bio-based adsorbents based on modification of chitosan and its derivatives with thiourea-formaldehyde (TF) resin were widely used, the structure of these adsorbents was studied by IR-Fourier spectroscopy[5]. The synthesis of new ionites was studied by replacing the hydrogen in the phenol ring in complex-forming groups from the interaction of phenolformaldehyde and resorcinformaldehyde resins. Polychronic esters containing nitrogen and sulfur were synthesized by immobilization of heterochronic esters in copolymers of styrene and divinylbenzene [6]. They are used for the sorption and selective separation of intermediate metal ions with similar properties, as well as for phase transfer catalysts. Synthesis of ion-exchange ionites at a temperature of 800C from the polycondensation of o- and p-hydroxybenzoic acid with resorcinol and catechol as a binder in the presence of formaldehyde. done The sorption of cadmium (II) and lead (II) ions in this ionite was determined by physicochemical methods [7]. Ion exchange ionites were synthesized based on polycondensation of formaldehyde with triethylenetetraamine and p-nitrophenol in the presence of 2 M NaOH. The selective sorption of Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions in solutions of various media was studied. During the analysis, it showed high selectivity in sorption of Cd^{2+}, Hg^{2+} and Pb^{2+} ions [8]. Methods of synthesizing monomers and polymers containing epichlorohydrin and nitrogen with high sorption capacity used in various industries have been studied [9].

Experimental part. Zn(II) and Cd(II) salt solution sorption was carried out on the basis of Amino acids formalin thiourea melamine $(NH_2)_2CS$. 0.01 mol of thiourea and 0.01 mol of formaldehyde were added to the porcelain mortar and melted at 80-100^{0}C, NH4OH solution was

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added dropwise until the mixture medium became pH=8. After the mixture reached a viscous mass, aqueous solutions of 0.01 mol of glycine and amino acid were mixed and added, the temperature was raised to 110^0C and heated for 2 hours until a plastic mass was formed. The resulting resin was dried in a drying oven at 50^0C for 30 minutes. The dried solid was washed 4-5 times with 0.1 N HCl, 5% alkali solution, and distilled water. A 0.1n 10 ml solution of the purified substance was prepared and 30 ml of zinc salt was added to it and sorbed for 1 day. The concentration and physicochemical properties of the resulting sorbed complex were studied.

Analysis of results. IR-spectroscopic analysis analyzes IRAffinity-1S SHIMADZU (Japan) (range 4000-600 cm^{-1}, scale 4 cm^{-1}) and IR Fourier IRTracer-100 SHIMADZU (Japan) (range 4000-400 cm^{-1}, o' 4 cm^{-1}) was measured using the powder method. The interpretation of the spectra was carried out with the help of basic software that performs automatic measurement of spectra, has tools for graphical display of spectra and their parts, and organizes work with the user's spectrum library. "Clean" and "chemically clean" brand reagents were used in the experiment. Reagent solutions were prepared by dissolving a specific sample in a certain volume of solvents.

The image below shows the IR-spectroscopic image of MFA ionite (Fig. 1) and the analysis based on the image.

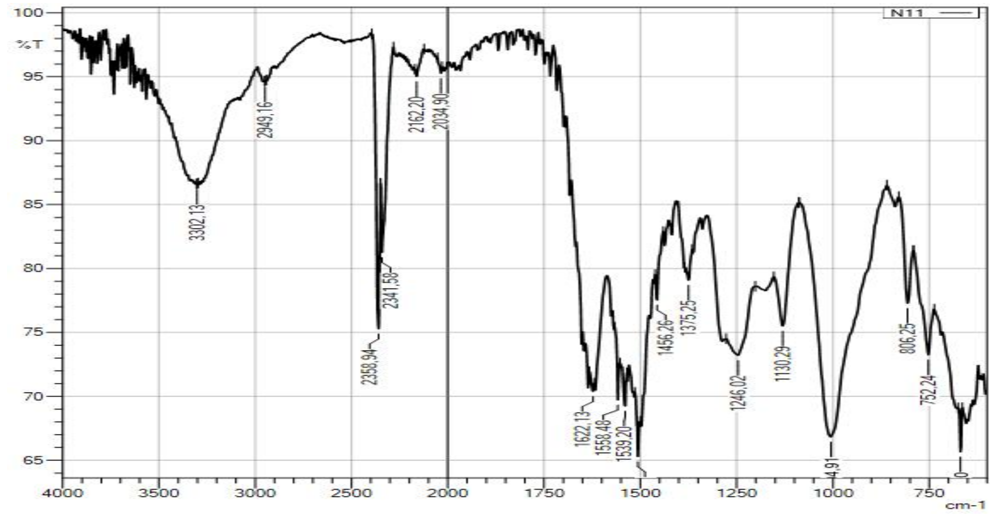

Fig 1. IR spectra of MTA ionite

In the IR-spectrum of the synthesized MTA, the frequencies of valence vibrations of the -OH group correspond to the regions of 3302-2949 cm^{-1}. In the region of 1622 cm^{-1} corresponds to the vibration of the C=O group, in the region of 1558 cm^{-1} we observe the vibration of the C-N group. Absorption lines of the R_2-NH group appear in the region of 1539 cm^{-1}. Bands of the methylene group $–CH_2$ appear in the bands in the region of 1456 cm^{-1}, and the vibration in the region of 1030 cm^{-1} corresponds to the valence vibrations of HCOOR. There are bonds of –CH groups in the region from 806-cm^{-1} to 752-cm^{-1}.

IR-spectroscopic analysis of the coordination compound formed by the sorption of Zn(II) and Cd(II) with MTA

As a result of the conducted research, the sorption of zinc (II) ion using MTA was studied, and the structure of the coordination compound formed during the sorption process was determined using

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the IR-spectral method. In this case, the zinc (II) ion is connected to the hydrogen atoms of the carboxyl group by ion exchange (Fig. 2).

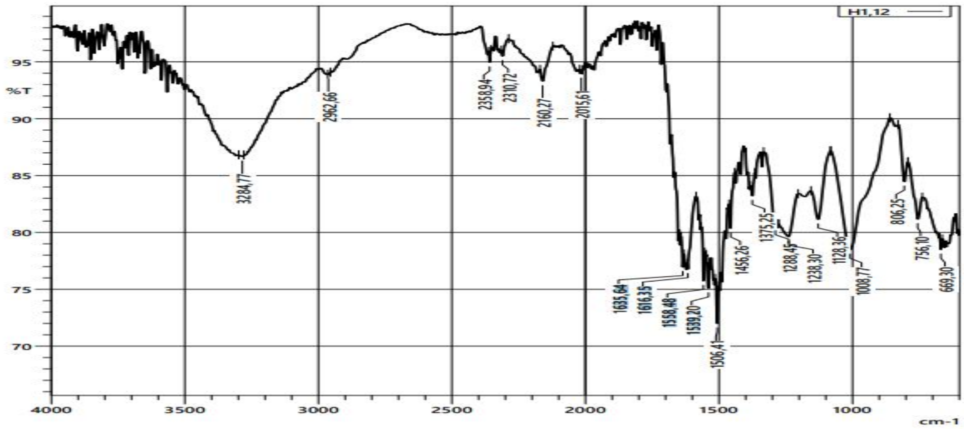

Fig. 2. of the combination of MTA ion exchanger with Zn^{2+} ions IR spectra

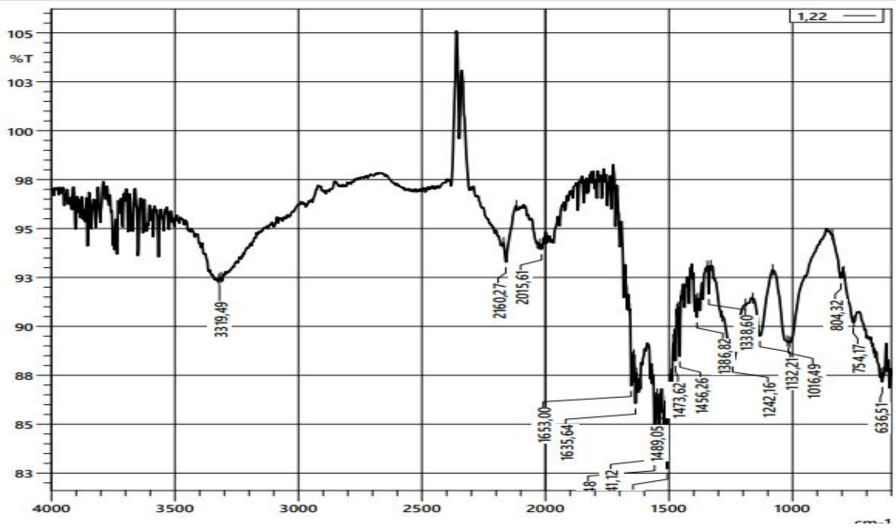

Fig. 3. IR-spectra of the combination of MTA ion exchanger with Cd^{2+} ions

Absorption lines appeared at the following frequencies of the IR spectra of the complex compound formed by MTA with Cd^{2+} ions. In the region 3284 cm^{-1} -2962 cm^{-1} lies unbonded OH-vibrations in the ionite content. The vibration at 1635 cm-1 indicates the presence of –C=O group in different groups. Valence vibrations at 1539 cm^{-1} correspond to the C-N group. 1506 cm^{-1} corresponds to the region of the R_2-NH group. There are vibrations of the CH_2 group in the region of 1456 cm^{-1}. In the region 1128-1008 cm^{-1}, it corresponds to the vibrations of the HCOOR group. The frequency 806 – 756 cm^{-1} corresponds to the deformed area of the C-H group (Fig. 4).

The IR-spectra of the complex combination of MFA with Cd^{2+} ions can be described as follows. The OH- group appears at the vibration frequency of 3319-2160 cm^{-1}. IR spectrum absorption frequency 1653 cm^{-1} vibration corresponds to the -C=O group, C-N group lines correspond to 1541 cm^{-1}. Vibrational frequencies of 1565 cm^{-1} correspond to R_2-NH group, i.e. secondary amines. The deformation waves of the bonded –CH_2- group correspond to the vibrational region of 1456 cm^{-1}. We

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can observe the vibrations of the R-O-H group at 1386 cm-1. The spectrum absorption frequency of 1132-1016 cm^{-1} corresponds to vibrations of the HCOOR group. There are bonds of –CH groups in the region from 804 cm-1 to 754 cm^{-1}.

The structure of the sorbed compound of nickel (II), cobalt (II), zinc (II), cadmium (II) and copper (II) ions by the synthesized ion exchanger can be expressed as follows:

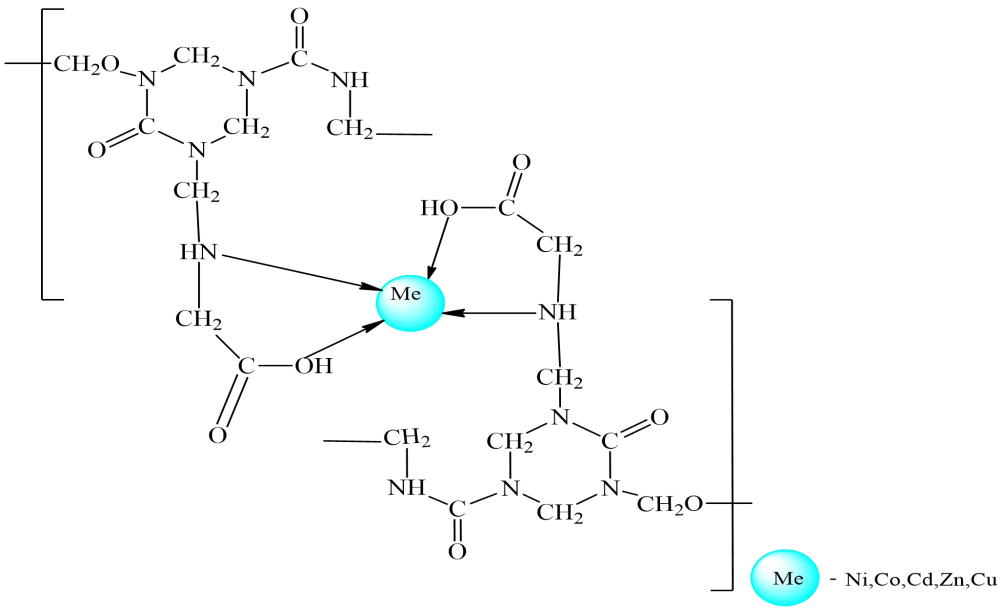

Fig. 4. Sorption of divalent metal ions on MTA ionite under static conditions

In the IR-spectra of the complex compounds formed by the MTA ion exchanger with Zn (II) and Cd (II) ions, the recorded shift of spectrum absorption frequencies by primary amines, ketone group and carbon-hydrogen groups is shown in Table 2 below.

Changes in spectral absorption frequencies of MTA +Me(II) compounds

Table 2

Compounds	ν (R-OH), sm^{-1}	Δν, sm^{-1}	ν C=O, sm^{-1}	Δν, sm^{-1}	ν R-NH, sm^{-1}	Δν, sm^{-1}	νHCOOR, sm^{-1}	Δν, sm^{-1}
MTA	3302	-	1622	-	1539	-	1130	-
MTA +Zn (II)	3284	18	1635	13	1506	33	1128	2
MTA +Cd (II)	3319	17	1653	31	1565	26	1132	4

As can be seen from Table 2, the vibrational frequency of n (R-OH) in ionite is relatively high and the vibrational frequency of ($R-NH_2$) has shifted to a relatively lower region. It can be concluded

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that the OH groups in the ionite are exchanged for the metal ion, the NH_2 group ensures coordination and a four-membered chelate ring is formed.

Conclusion: The physico-chemical properties of the MTA complex-forming ionites obtained for the experiment, as well as the analysis of complex compounds forming these ions with some d-metals, were carried out using the IR-spectoscopy method. It was proved that Cd(II), Zn(II) ions coordinate by forming a four-membered chelate ring due to amino and carboxyl groups. Based on the results of the analysis, the structural formulas of the ionites that formed the complex were given.

List of references:

1. Игитов Ф. Б. и др. New ion-exchange polymers of polycondensation type // Modern materials, engineering and technologies. – 2016. – No. 4 (7). – P. 80-88.
2. Балановский Н. В. и др. Use of modifiers of dispersion medium properties in the synthesis of acrylonitrile-based copolymers // Advances in Chemistry and Chemical Technology. - 2016. - Vol. 30. - No. 2 (171). - P. 99-100.
3. Спирин Э. К., Миськевич Л. В. The influence of low temperatures on ion-exchange resins // Privolzhsky Scientific Bulletin. - 2013. - No. 4 (20). - P. 5-9.
4. Божар В. и др. Acidic polymeric sorbents for removing metal contaminants from water: a review // Reactive and functional polymers. - 2020. - Vol. 152. - P. 104599
5. Бабуев М. А., Увайсова С. М. Study of the conditions of interaction of polystyrene-azo-o-phenol-azorhodanine with zinc and cadmium ions // Polythematic network electronic scientific journal of the Kuban State Agrarian University. - 2016. - No. 118. - P. 1086-1096.
6. Пулатов Х. Л., Турабжанов С. М. Sorption properties of ion-exchange resins of polycondensation type //Universum: technical sciences. – 2016. – No. 12 (33). – P. 41-46.
7. Махмуд М.Е. и др. Fast microwave sorption of heavy metals on the surface of nanosilica-functionalized glycine and reduced glutathione // Bioresource technologies. - 2018. - Vol. 264. - P. 228-237.
8. Фан Х.Т. и др. Selective removal of lead (II) from aqueous solution by ion-imprinted silica sorbent functionalized with chelating N-donor atoms // Journal of Chemical and Technical Data – 2014. – Vol.59. – No.6. – P.2106-2114.
9. Шалбафан А., Хасаннежад Х., Рахманиния М. Adsorption capacity of chitosan derivatives to formaldehyde as bioadsorbents for wood boards // International Journal of Adhesion and Adhesives - 2020. - Vol. 102. - P. 102669.