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PHYSICO-CHEMICAL PROPERTIES OF PHOSPHATE CATION-EXCHANGE RESIN

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There are investigated sorption and desorption characteristics of phosphate cation-exchange resin among metals: copper, nickel, cobalt, an uranyl-ion depending on pH-environment, the ionic form of cation-exchange resin, concentration of investigated cations. Interaction of cation-exchange resin in Na- and H-forms with solutions of salts sulphate of copper, nickel, cobalt, chloride sodium, calcium and nitrate of uranyl is studied. It is shown, that ions of copper, nickel, cobalt and an uranyl-ion by phosphate cation-exchange resin sorb at the expense of an ionic exchange and partially at the expense of formation of coordination communications with ionogenic group of cation-exchange resin. A study of the sorption of uranyl ions depending on the concentration of uranyl nitrate in the range of 0.01-0.1 N showed that with an increase in the concentration of uranyl in the studied interval, the value of sorption of uranyl increases slightly. The studied phosphate cation exchanger has a sufficiently high sorption and desorption ability to the ions of the tested metals.

Key words: *sorption, styrene, furfural, phosphorylation, cation exchange resin, ion exchange, thermochemical resistance, static exchange capacity, dynamic exchange capacity, mechanical strength.*

One of the most important scientific areas is the focused development of new polymeric materials, including ion-exchange polymers with desired properties. The use of ion-exchange polymers in various industries requires the creation of ion exchangers with high thermal, chemical resistance, resistance to ionizing radiation and a number of specific properties. The creation of an extensive assortment of domestic ion-exchange materials allows more complete extraction of metal ions from complex ores and various metallurgical products. Despite a significant number of studies on the ion-exchange method for the extraction and separation of metals, the solution to this problem continues to remain an important urgent task for the hydrometallurgical industry.

Currently used traditional brands of ion exchangers, especially polycondensation sip, have a number of disadvantages that limit the possibilities and scope of their application. The most significant drawbacks of known brands of ion exchangers include relatively low thermal and chemical stability, low selectivity and mechanical strength. Many polycondensation ion exchangers have poor kinetic properties. In this regard, the search for new ion exchangers possessing increased heat and chemical resistance, selectivity for rare and non-ferrous metal ions (molybdenum, copper, cobalt, nickel and others), which are important in technology, is one of the urgent tasks of modern science and industry. Phosphoric acid cation exchangers are characterized by various types of metal bonds with ionic ionite groups: ionic bonds, mixed ion-coordination bonds, and purely coordination ones [1,2]

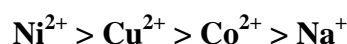
It was of interest to study such properties of phosphate cation exchanger as its sorption ability for copper, nickel, calcium, sodium, cobalt and uranyl ions, which are important in modern technology, to identify the influence of various factors on the sorption process of these cations, as well as the mechanism of their sorption using IR spectroscopic analysis [3]. To this end, the interaction of cation exchange resin in the Na and H forms with solutions of salts of

copper sulfate, nickel, cobalt, sodium chloride, calcium and uranyl nitrate was studied. The research results are shown in table 1.

Table 1.**Sorption of metal cations by phosphate cation exchanger**

0.1 N solutions	H-form			Na- form	
	pH of solutions	Sorbed, mEq/g	Distribution coefficient, ml/g	pH of solutions	Sorbed, mEq/g
NaOH	13	6.6-7.6	184	-	-
NaCl	8.13	0.8-1.0	11.5	-	-
CaCl ₂	6.5	1.1-1.2	120	6.5	3.57-3.6
CuSO ₄	4.8-5.0	1.2-1.3	66	4.8-5.0	1.75-1.8
CuSO ₄	11	2.64-2.7	733	11	3.08-3.1
CuSO ₄	-	-	-	2.35	1.0-1.1
NiSO ₄	7.6	1.1-1.2	20	2.25	1.0
NiSO ₄	10	2.0-2.1	84	3.8	3.6
NiSO ₄	-	-	-	7.6	2.0
NiSO ₄	-	-	-	10	3.75-3.8
CoSO ₄	8	2.0-2.05	35	2.36	0.8-0.9
CoSO ₄	-	-	-	3.18	2.4
CoSO ₄	-	-	-	8	2.65

The data in table 1 indicate the influence of the nature of the cation on sorption. It was found that the studied cations are sorbed by cation exchanger unequally and by their ability to sorption can be located in the following order:



A study of the effect of the ionic form of cation exchanger on the absorption of the tested cations showed that in the Na form, the ion exchanger has greater sorbability compared to the hydrogen form (Table 1), which is consistent with published data [4]. The effect of pH on the sorption of metal ions by cation exchanger was also investigated. So, at pH = 2-5, low values of the distribution coefficient of 10-120 are observed, which increase with increasing pH (Table 1.2, Fig. 1).

Table 2.

Sorbed ion	pH	Static exchange capacity, mEq / g
Nickel	4.2	1.2
	2.5	0.6
	10.0	2.0
Copper	4.2	1.3
	2.5	0.8
	10.0	2.3

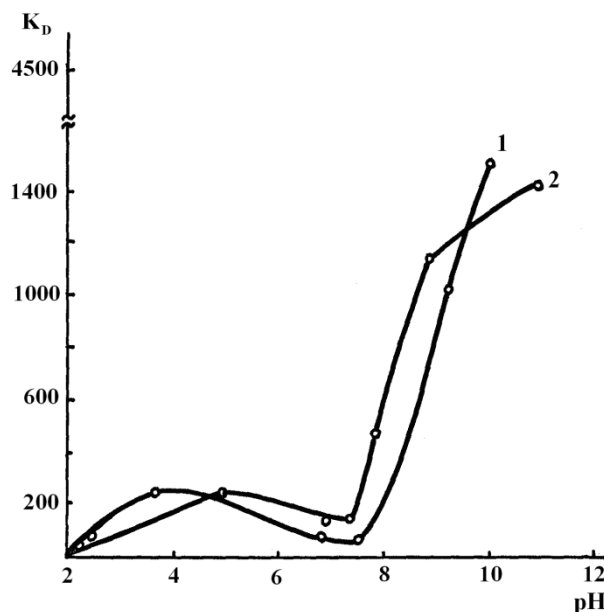


Fig. 1. Sorption of Ni²⁺ (1), Cu²⁺ (2) ions on phosphoric acid cation exchange resin depending on the equilibrium values of the pH medium

In order to elucidate the mechanism of sorption of the cations of these metals, we recorded the IR spectra of cation exchanger in the H and Na forms saturated with copper ions. A number of papers have been devoted to the IR spectroscopic method for studying phosphoric acid cation exchangers [5–10].

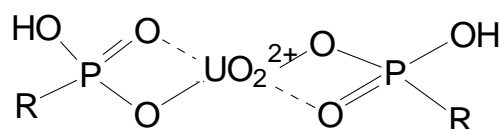
In the IR-spectroscopic study of cation exchanger in the H- and Na-forms, the main attention was paid to the absorption bands of the frequencies of deformation and stretching vibrations corresponding to P-(OH), P=O, OH. According to published data, the vibration frequencies for phosphoric acid groups lie in the range 2560 cm⁻¹ [9].

In the spectrum of cation exchanger in the H form, bands at 1150 cm⁻¹ are observed, which correspond to stretching vibrations of the phosphorus – oxygen bond.

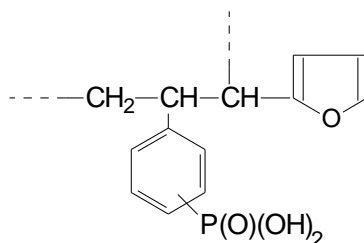
The absorption band at 1150 cm⁻¹ does not disappear in the spectrum of cation exchanger in the Na-form. The test cation exchange resin contains phosphate groups differing in their acidic properties pK₁ = 2.8; pK₂ = 7.5. The less dissociated the phosphate groups, the more strong the hydrogen bond is formed by phosphoryl oxygen with OH groups [11–13].

Therefore, it can be expected that as the cation exchanger is saturated with sodium, the maximum of the band corresponding to vibrations of the phosphorus-oxygen bond will shift somewhat to the long-wavelength region as a result of the destruction of the weaker hydrogen bond. In the spectrum of cation exchanger in the H-form, there are not sharp wide bands in the range of 2600–2860 cm⁻¹, 2100–2600 cm⁻¹, which we assigned according to [14–17] to the stretching vibrations of P-OH bound by hydrogen bonds. In the spectrum of sodium saturated cation exchanger, these bands disappear. When considering the spectra of cation exchanger saturated with metal ions, in contrast to the cation exchanger spectrum in the H form, bands appear at 1060 cm⁻¹ for uranyl and 1055 cm⁻¹ for copper and nickel.

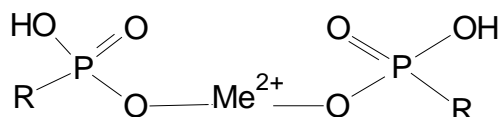
A sharp decrease in the intensity of phosphorus-oxygen bond vibrations is observed in the spectrum of the uranyl ion-saturated ion exchanger. The same picture is observed in the spectra of cation exchange resin saturated with copper and nickel ions. However, a significant decrease in the intensity of this band for the cation exchange resin saturated with uranyl ion as compared with the ionite saturated with copper and nickel ions indicates the participation of phosphoryl oxygen (-P = O) in the formation of the coordination bond with the uranyl ion, i.e. the formation of a complex compound of a uranyl ion with a P = O group of cation exchanger, which has the following structure:



where, R –



A decrease in the intensity of vibrations of the P – OH groups for the cation exchange resin containing copper, nickel, and sodium ions is declared to be a decrease in the number of P – OH groups, which correspond to deformation vibrations in the region of 2100–2600 cm^{-1} . This suggests that copper, nickel, and sodium ions are absorbed by cation exchange resin, mainly due to the formation of a coordination bond, i.e. ion coordination compounds of the following structure:



where, Me^{2+} - Ni^{2+} , Cu^{2+} , Na^+ .

Sorption of uranyl ions from a solution of uranyl nitrate under static conditions was also studied on cation exchange resin in hydrogen and sodium forms. The sorption of uranyl ions on cation exchanger in the H-form was 175-200 mg/g, and in the sodium form - 200-250 mg/g. The effect of the pH of the medium on the sorption of uranyl ions by cation exchanger in the H and Na forms was studied (Table 3). From table 3 it is seen that the tested cation exchanger in the Na-form sorbes the uranyl ion quite well in the studied pH range.

The maximum adsorption on cation exchange resin in the Na form reaches 250 mg/g. A study of the sorption of uranyl ions depending on the concentration of uranyl nitrate in the range of 0.01-0.1 N showed that with an increase in the concentration of uranyl in the studied interval, the value of sorption of uranyl increases slightly.

Table 3.

Dependence of the sorption of uranyl ions by the obtained cation exchanger on the pH of the medium ($C=0.1$ N solution (UO_2) NO_3)

Cation exchanger in H-form								
pH of solution	1	2	3	4.2	7	9	10	11
Sorbed uranyl ions, mg/g	25	62	95	86	54	160	162	162
Cation exchanger in Na-form								
pH of solution	2	3	4.2	6	7	8	9	10
Sorbed uranyl ions, mg/g	80	110	108	120	102	160	220	245

The results of desorption of sorbed ions by cation exchange resin in the Na form are shown in table 4. An analysis of the data obtained (Tables 1 and 4) indicates that the studied phosphate cation exchanger has a sufficiently high sorption and desorption ability to the ions of the tested metals. The desorption of copper and nickel ions was carried out with a 1 N sulfuric acid solution.

Table 4.**Desorption of metal ions from cation exchanger**

Desorption cation	Sorbed, mEq/g	Desorption solution		Desorbed, mEq/g
		H ₂ O	2 N solution H ₂ SO ₄	
Calcium	3.57	0.2	2.9	3.1
Copper	3.08	0.06	2.7	2.76
Nickel	3.6	0.56	2.83	3.39
Cobalt	1.4	0.2	0.9	1.1

In this case, cation exchange resin, which adsorbed a copper ion during washing with a solution of sulfuric acid, releases 80% of the total amount of sorbed copper and 95% nickel. During desorption of a uranyl ion with cation exchange resin with a 0.01 N nitric acid solution, about 28% of sorbed uranyl was isolated. The treatment of cation exchanger sorbing uranyl with a 1 N soda solution results in the release of 95% of the uranyl ion from the sorbed amount.

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