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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

New Nitrogen-and-Phosphorus-Containing Fibrous Ion Exchangers for Water Treatment

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Abstract—New nitrogen-and-phosphorus-containing fibrous ion exchangers were produced by two-stage synthesis from Nitron fiber. The ion exchangers are efficient sorbents of heavy and nonferrous metals from aqueous solutions under dynamic conditions.

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Nitrogen-and-phosphorus-containing granulated ion exchangers possess a whole set of unique sorption and service properties. These ion exchangers are selective sorbents of a number of nonferrous metals, rare-earth elements, uranium, and actinides, which makes them promising sorbents for numerous industries [1–3]. A disadvantage of granulated sorbents is their small specific surface area and the resulting low chemisorption rate. For fibrous ion exchangers, the sorption–desorption rate is one or two orders of magnitude higher. One more advantage of fibrous sorbents, compared with granulated ion exchangers, is the possibility of their use in various forms [multifilament yarn, thread, fabric, unwoven fabric, powder (knop)]. The developed surface and widely diverse forms of ion-exchange fibrous materials enable a rational design of filter apparatus. Chelate fibrous sorbents differ from other types of sorbents in that they contain chemically active groups that can interact with metal ions present in solutions to form chelate complexes. It is known that chelate nitrogen-and-phosphorus-containing polyampholytes exhibit a high sorption activity toward heavy metal ions [4–6].

The aim of this study was to synthesize new chelate fibrous nitrogen-and-phosphorus-containing ion-exchange materials and estimate their sorption capacity for cations of heavy and nonferrous metals.

EXPERIMENTAL

Chelate sorbents were synthesized from Nitron D polyacrylonitrile (PAN) fiber manufactured by Polimir Production Association (Novopolotsk). Functional groups were introduced by reactions of amination (stage I) and phosphorylation (stage II). The amination reaction was performed with 40% aqueous solutions of ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetraamine (TETA) at 95°C. The reaction duration was 10–12 h. Depending on an amine used for amination of the PAN fiber, the sorption materials synthesized were given the following commercial names: FIBAN R-1 in amination with EDA, FIBAN R-2 in amination with DETA, and FIBAN R-3 in amination with TETA.

The aminated fiber was phosphorylated by the Kabachnik–Fields reaction [7], with formaldehyde used as the carbonyl component, and sodium hypophosphite, as the phosphorylating agent. The reaction course is strongly affected by the pH of the reaction medium. It is known [8] that phosphorylation with disubstitution at the primary amino group occurs in strongly acidic media, which is accounted for by the shift of the tautomeric equilibrium in hypophosphorous acid toward the tricoordinated form of phosphorus [9]. Even at pH 1.0, only monosubstitution occurs in the amino group, and, therefore, to obtain disubstitution at the primary amino group, the phosphorylation reaction was performed at pH 0. In strongly acidic media, the role of the phosphorylating agent is played by methylphosphonic acid, which is formed in the reaction of formaldehyde with sodium hypophosphite at a rate increasing with the concentration of hydrogen ions. The optimal temperature of the phosphorylation reaction is 95°C, and its optimal duration, 3.0–3.5 h. By varying the

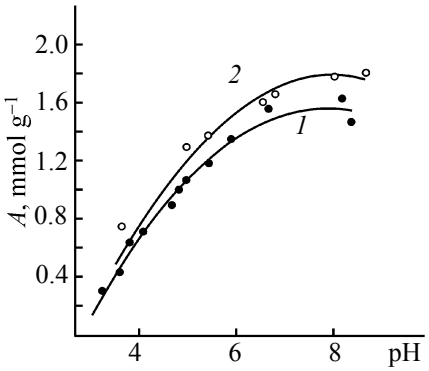
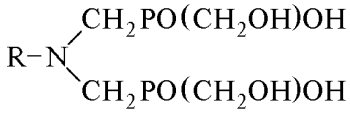


Fig. 1. Cadmium sorption *A* vs. the pH of the equilibrium solution. (*1*) FIBAN R-1 and (*2*) FIBAN R-2.

amounts of formaldehyde and sodium hypophosphite, the optimal amounts of the reagents for synthesis of nitrogen-and-phosphorus-containing materials (NPMs) were determined. Depending on the conditions of both stages of NPM synthesis, the fibrous ion exchangers obtained have static exchange capacity (SEC) for acid groups of 3.4 to 5.7 mmol g^{-1} and contain 4.7 to 10.78% phosphorus.

Samples for IR measurements were prepared by the standard procedure of compaction of finely cut fibers of a sample under study with a thoroughly dried powder of potassium bromide. The concentration of the sample in the mixture was 1.5%. The IR spectra were recorded on a Nicolet Protégé IR Fourier spectrometer.

The IR spectra of the NPM obtained contain an absorption band at 1167 ± 2 cm^{-1}, associated with stretching vibrations of the P=O group. The absorption bands at 1034 ± 2 and 920 cm^{-1} are related to symmetric and asymmetric stretching vibrations of the P–OH group. The absorption bands at 3422 ± 1 and 1712–1639 cm^{-1} are associated with bending vibrations of –OH groups in –PO(OH) and –OH group of secondary alcohols [10]. Comparison of the IR spectral data and results of an elemental analysis shows that, in the chosen conditions, the Kabachnik–Fields reaction occurs with disubstitution at the primary amino group to give NPMs with functional groups of the following structure



which can interact with metal ions present in solution to give chelate complexes.

First, the dependence of the sorption of cadmium cations on the solution pH in the static mode was studied. The sorption of Cd^{2+} was performed from a dilute 0.001 M solution on the background of 1 M NaCl at room temperature. A 0.1-g portion of FIBAN R-1 or R-2 ion exchanger was placed in a flask, the pH was brought to a required value by addition of 0.1 M NaOH, and the mixture was vigorously agitated. After equilibrium was attained, the content of cadmium ions in the solution was determined with a Varian AA-200 atomic-absorption spectrophotometer. The solution pH was measured with an OP-265-1 pH-meter. The results obtained (Fig. 1) demonstrate that FIBAN R-1 and R-2 sorbents well sorb Cd^{2+} ions at pH 5.5–7.5.

The sorption of cadmium ions under dynamic conditions was performed from a $CdCl_2$ solution with a concentration of 2×10^{-2} mM on the background of 2 mM of $CaCl_2$. This concentration of Ca^{2+} ions correspond to moderately hard water. Before the beginning of sorption, the ion exchanger (~1 g) was treated with an acetate buffer solution with pH 6.0. The model solution was passed through columns 12.5 mm in diameter, packed with the ion exchangers with a bed height of 30 mm and bulk density of 0.16–0.23 g cm^{-3}, at flow velocities w of 2, 5, and 10 cm min^{-1}. The results obtained in sorption of cadmium on FIBAN R-1 and R-2 sorbents are listed in Table 1, whence follows that NPMs well sorb cadmium ions from dilute solutions in

Table 1. Dynamic exchange capacity (DE) for cadmium ions to breakthrough (5% of the initial concentration)

Sorbent	Swelling, g g^{-1}	*P*, %	SEC, mmol g^{-1}		*W*, cm min^{-1}	Amount of solution, l	DE to breakthrough, mmol g^{-1}
			acid groups	basic groups			
FIBAN R-1	0.90	9.15	5.35	0.58	5	15	0.41
			5.35	0.58	10	14	0.38
FIBAN R-2	0.45	9.18	3.99	1.2	2	19	0.55
			3.99	1.2	5	15	0.40
			3.99	1.2	10	14	0.37

Table 2. Exchange capacity and swelling of nitrogen-and-phosphorus-containing sorbents

Sorbent	*P*, %	SEC, mmol g^{-1}		Swelling, g g^{-1}	
		acid groups	basic groups	H-form	Na, H-form
FIBAN R-1	10.75	5.06	0.1	0.9	1.3
FIBAN R-2	10.78	4.35	0.45	0.45	0.54
FIBAN R-2	8.21	4.01	0.98	0.45	0.5

the presence of calcium ions at different solution flow rates. The largest amount of cadmium is sorbed with the model solution flow velocity of 2 cm min^{-1}. Raising the flow velocity to 5 cm min^{-1} results in that the dynamic capacity to breakthrough decreases; further increase in the flow velocity to 10 cm min^{-1} affects the sorption of cadmium ions only slightly. It was found that FIBAN R-1 and R-2 ion exchangers containing equal amounts of phosphorus nearly equally sorb cadmium ions from dilute solutions.

Further, the sorption by NPMs of heavy and nonferrous metal ions from dilute solutions containing a mixture of metal salts was studied. The sorption characteristics of NPMs were studied by the dynamic method from a model solution containing metal salts [$CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$, $CdCl_2$, $Pb(NO_3)_2$] with a concentration of 2×10^{-2} mM on the background of 2 mM of $CaCl_2$. The ion exchangers were prepared as in the case of sorption of cadmium ions; the model solution was passed through the same columns packed with the ion exchangers at the same bed height, bulk density of 0.12–0.23 g cm^{-3}, and flow velocities of 2, 5, and 10 cm min^{-1}. The characteristics of the sorbents used are listed in Table 2.

The results obtained in sorption of cations of nonferrous and heavy metals on FIBAN R-1–R-3 sorbents are shown in Figs. 2a–2c in the form of output sorption curves. The solution flow velocity was 10 cm min^{-1}. Figure 2d shows output curves of metal ion sorption on FIBAN R-1 ion exchanger, obtained at a twice lower flow velocity of 5 cm min^{-1}.

As a rule, data on recovery of metals from solutions containing various concentrations of accompanying elements are reported in the literature. The metal sorption with the ion exchangers obtained was performed from

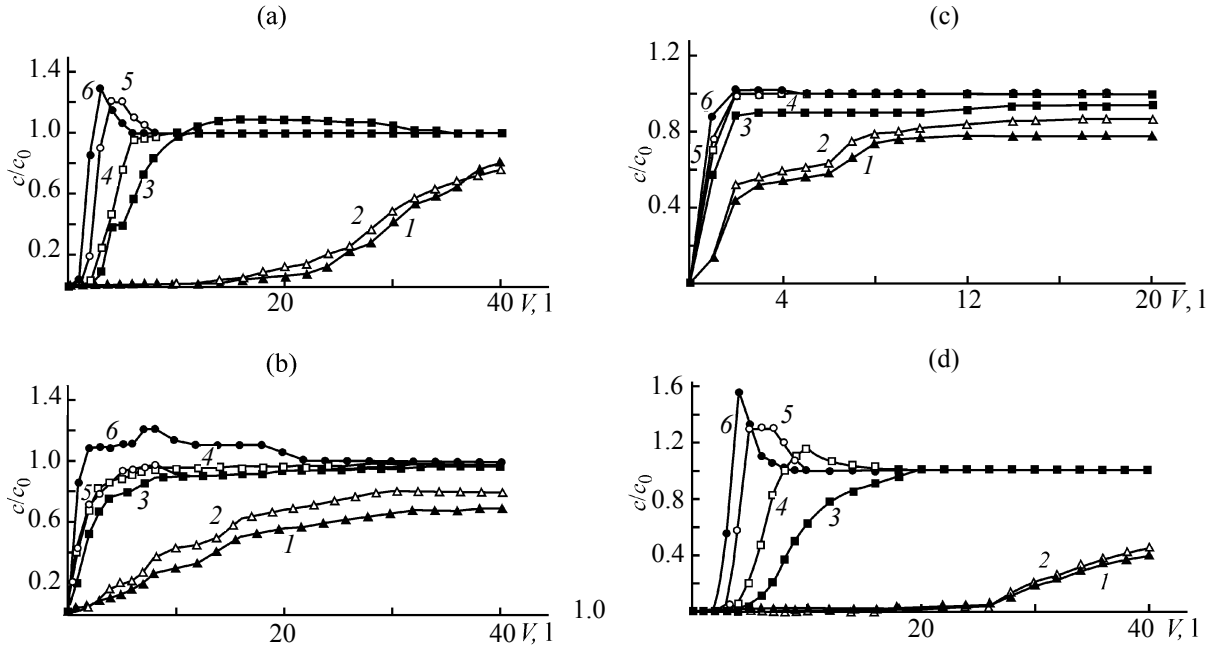


Fig. 2. Output curves of sorption of heavy and nonferrous metals on FIBAN fibrous ion exchangers. (c/c_0) Concentration ratio and (*V*) solution volume. FIBAN: (a, d) R-1, (b) R-2, and (c) R-3. Flow velocity (cm min^{-1}): (a–c) 10 and (d) 5. (*1*) Pb^{2+}, (*2*) Cu^{2+}, (*3*) Cd^{2+}, (*4*) Zn^{2+}, (*5*) Ni^{2+}, and (*6*) Co^{2+}.

Table 3. Dynamic exchange capacity of the ion exchangers to breakthrough of metal ions

Sorbent	*P*, %	*W*, cm min^{-1}	SECacid, mmol g^{-1}	DC to breakthrough, mmol g^{-1}					
				Cu^{2+}	Pb^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}
FIBAN R-1	10.7	10		0.43	0.39	0.03	0.05	0.08	0.07
		5	5.06	0.65	0.63	0.05	0.08	0.10	0.09
		2		0.65	0.64	-	-	0.14	0.13
FIBAN R-2	9.15	10	435	0.05	0.03	Breakthrough			
		5		0.50	0.28	0.03	0.06	0.06	0.04
FIBAN R-3	9.0	5	4.0	Breakthrough of all ions					
VION KN-1	–	10	6.67	0.17	0.19	0.02	0.04	0.08	0.03

a complex-composition solution containing a mixture of metal ions in the same concentrations on the background of calcium ions with a concentration 100 times higher than that of any other metal ion. It can be seen from Figs. 2a–2c that, when the solution is passed through columns packed with ion exchangers at a flow velocity of 10 cm min-1, the output sorption curves are different for different metals. The output curves for sorption of

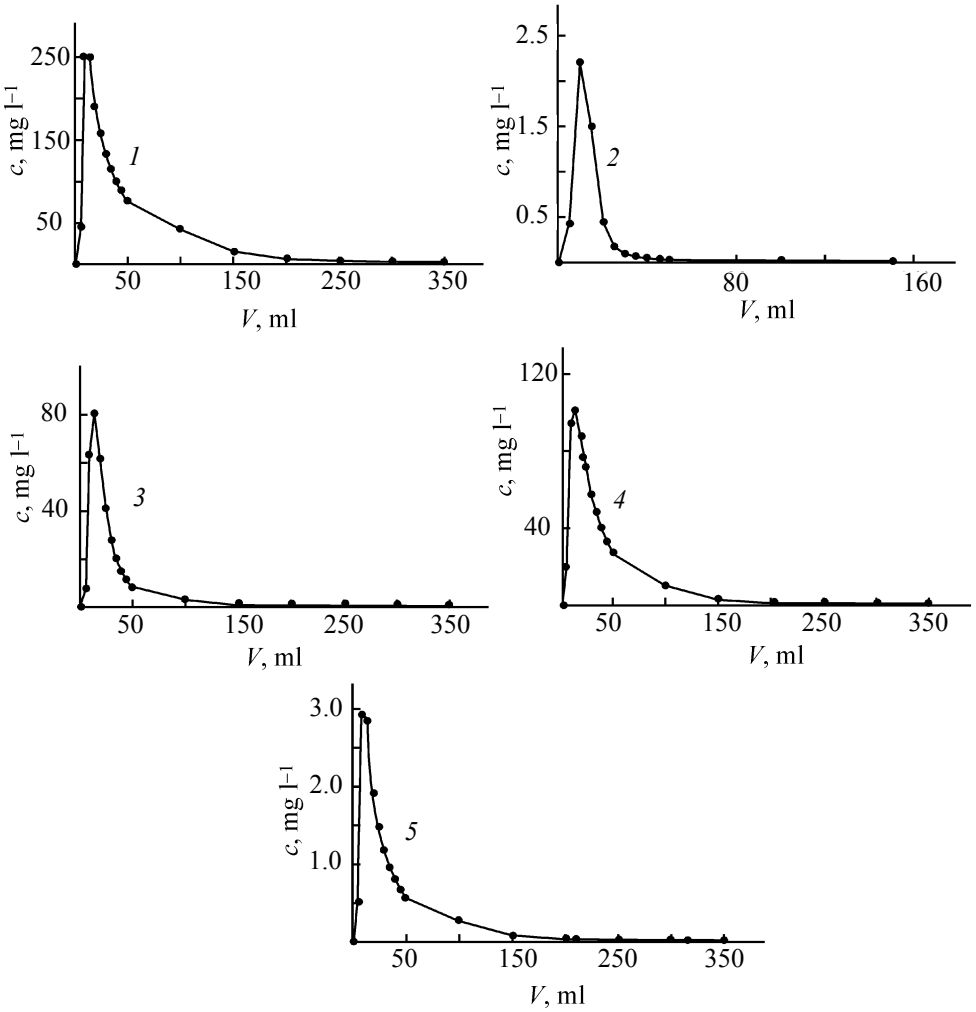


Fig. 3. Curves of elution of (*1*) Cd^{2+}, (*2*) Cu^{2+}, (*3*) Ni^{2+}, and (*4*) Zn^{2+} on FIBAN R-2 ion exchanger at 20°C with 0.5 N HCl solution and (*5*) Pb^{2+} with a 0.5 N HNO_3 solution. (*c*) Metal ion concentration and (*V*) acid volume.

Zn^{2+}, Ni^{2+}, and Co^{2+} ions and, to a certain extent, for Cd^{2+} show a clearly pronounced rise, i.e., a breakthrough of metal ions is already observed after several liters of the model solution are passed, and for FIBAN R-3 ion exchanger, a breakthrough of metal ions was observed even in the very first portions of the outflowing solution (Fig. 2c). The output curves for Cu^{2+} and Pb^{2+} ions are more gently sloping. Analysis of Figs. 2a–2c shows that the equilibrium sorption is observed under the chosen conditions only for Cd^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}, and is not attained for Pb^{2+} and Cu^{2+} ions even on passing 40 l of the solution for FIBAN R-1 and R-2 ion exchangers.

It can be seen from the output curves for metal ion sorption on FIBAN R-1 ion exchangers, obtained at different flow velocities of the model solution, that the sorption efficiency substantially increases as the flow velocity is lowered (Figs. 2a, 2d) for all the metal ions. For example, on passing 40 l of the solution through a column packed with FIBAN R-1 sorbent, the concentration ratio c/c0 for Pb^{2+} and Cu^{2+} ions is 0.8 at a solution flow velocity of 10 cm min-1 and only 0.4 at 5 cm min^{-1}. A breakthrough of these best sorbed ions (c = 5% of the initial value) occurs on passing 16 l of the model solution at a flow velocity of 10 cm min^{-1}, and only on passing 20–22 l at a velocity of 5 cm min^{-1}.

To compare the efficiencies of the sorbents in sorption of metal ions, the dynamic capacities to breakthrough of metal ions in a concentration of 5% relative to the initial value were calculated from the output curves. The efficiencies of the sorbents were compared with that of the known VION KN-1 fibrous cation exchanger. The data obtained are listed in Table 3, whence follows that the DCs of FIBAN R-1 and R-2 ion exchangers increase as the solution flow velocity is lowered from 10 to 5 cm min-1. Further decrease in the flow velocity for FIBAN R-1 ion exchanger to 2 cm min^{-1} does not lead to any considerable increase in the DC. At a high flow velocity of the model solution, FIBAN R-1 twice exceeds the widely used VION KN-1 ion exchanger in the efficiency of absorption of lead, copper, and zinc ions.

The results of the study demonstrate that, among all of the ion exchangers examined, the best sorbent for all heavy and nonferrous metal ions from aqueous solution is FIBAN R-1 obtained in the first stage of synthesis by amination of the PAN fiber with EDA. As the chain of the amine used in amination of the PAN fiber becomes longer, the DC of the sorbents falls even for Pb^{2+} and Cu^{2+}. The activity of the sorbents toward metal ions decreases in the following order: FIBAN R-1 > FIBAN R-2 > FIBAN R-3. The ion selectivity series for NPM has the form: $Cu^{2+} \geq Pb^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$.

The desorption of heavy and nonferrous metal ions was studied under dynamic conditions at room temperature. As eluents served 0.5, 1.0, and 2.0 M solutions of hydrochloric or nitric acid. It was found that the sorbents are easily regenerated with 0.5 M hydrochloric acid, with all the metal ions removed, except lead ions, for whose recovery a 0.5 M solution of nitric acid is necessary (Fig. 3). Of particular importance for practical purposes is the possibility of multiple use of ion-exchange materials in sorption–desorption without changes in the exchange capacity. Therefore, sorption–desorption cycles of the ion exchangers obtained were studied. Sorption tests performed with regenerated sorbents demonstrated that the materials do not lose their sorption and mechanical properties and can be used in, at least, ten sorption–desorption cycles more.

Thus, the results of the study show that FIBAN R-1 and R-2 fibrous ion exchangers exhibit high sorption activity and have good kinetic properties and convenient form for recovery of heavy and nonferrous metals. Therefore, the ion exchangers are promising for use in filters for purification of drinking and technological water.

CONCLUSIONS

(1) New fibrous nitrogen-and-phosphorus-containing ion exchangers, FIBAN R-1, R-2, and R-3, were synthesized by polymer-analogous conversion of a polyacrylonitrile fiber, which includes its amination with ethylenediamine, diethylenetriamine, or triethylenetetraamine and subsequent phosphorylation under the conditions of the Kabachnik–Fields reaction.

(2) It was demonstrated that FIBAN R-1 and R-2 fibrous chelate ion exchangers based on ethylenediamine and diethylenetriamine, respectively, are efficient sorbents of heavy and nonferrous metal cations from aqueous solutions with a complex cation composition under dynamic conditions. It was found that sorption of cadmium cations from dilute solutions on the background of calcium cations is possible under both static and dynamic conditions.

(3) It was demonstrated that chelate ion exchangers are easily regenerated and do not lose their sorption and mechanical properties.

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