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SORPTION AND ION-EXCHANGE PROCESSES

Synthesis and Sorption Properties of Filled Fibrous Sorbents with Immobilized Hetarylformazan Groups

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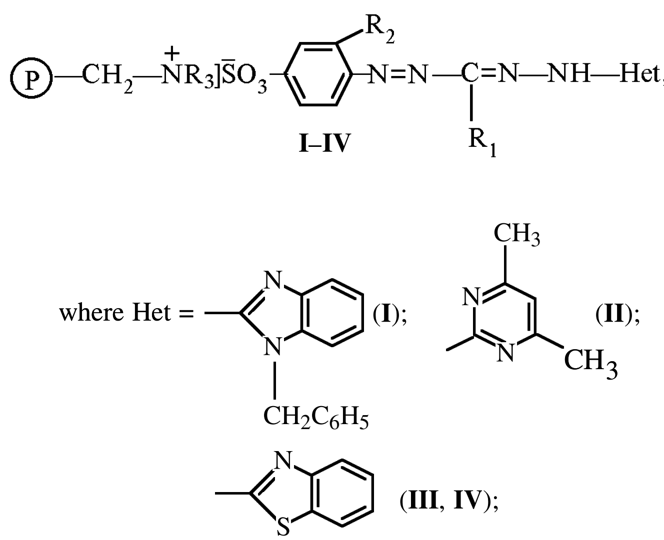
Abstract—New sorbents were prepared by immobilization of structurally different sulfur-containing hetarylformazans on nonwoven polyacrylonitrile fiber filled with AV-17 anion exchanger. Sorption of some heavy metals on these materials was studied as influenced by various factors. Sorbents for selective recovery of copper(II) in the presence of nickel(II), zinc(II), and cadmium(II) cations were found.

Fibrous ion-exchange sorbents widely used for recovering metal ions from solutions attract growing attention [1, 2]. Introduction of complexing groups into fibrous materials increases their selectivity with respect to some metals. These modified sorbents are used for selective recovery of valuable elements of multicomponents solutions and for removal of toxic metals from natural waters [3, 4]. Filled fibrous materials are the most promising [5] since they exhibit good sorption and kinetic properties and can be used for recovery of metals under dynamic conditions. A finely divided complexing sorbent is used as a filler.

Previously we showed [6–8] that immobilization of complexing formazan groups on AN-20, AN-18, and AV-17 anion exchangers substantially improved their sorption activity and selectivity with respect to some metals. In this work, sulfur-containing hetarylformazans were immobilized on nonwoven polyacrylonitrile fiber filled with AV-17 anion exchanger, and the properties of the resulting sorbents were studied.

EXPERIMENTAL

Nonwoven polyacrylonitrile fiber filled with AV-17 anion exchanger was prepared by the special procedure (Russian Research Institute of Manmade Fibers, Tver). The thickens of a swollen fiber thread was 30–100 μm; the filler content was 50%. The fiber was modified with various formazans with different heterocyclic fragments containing different substituents at the aromatic ring (Table 1). The possible structure of the resulting sorbents is shown below:



$R_1 = CH_3$ (**I, II**), C_2H_5 (**III, IV**); R_2 = H (**I–III**), OH (**IV**).

The content of formazans (*A*) in **I** and **II** was 0.15 and 0.09 mmol g^{-1}, respectively, and that in **III** and **IV** was 0.10 mmol g^{-1}.

The formazan groups were immobilized by the following ion-exchange procedure. To a weighed portion of the fiber filled with AV-17 anion exchanger in the OH^- form (0.4 g), an aqueous–ethanolic solution (1 : 1) (100 ml) of formazan (0.05 g) was added. The mixture was stirred with a vibrator for 4–6 h. The sorbent was filtered off, washed with distilled water, and dried in air. The residual formazan concentration

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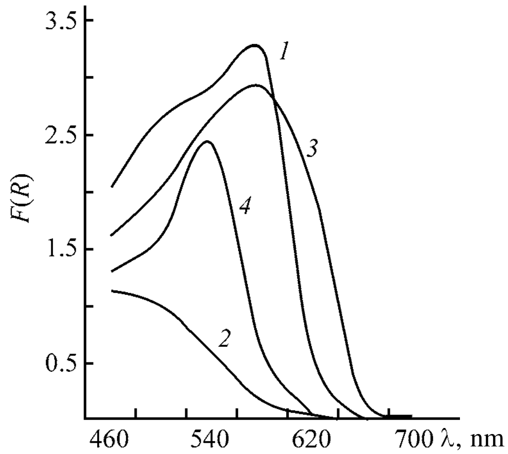

Fig. 1. Diffuse reflectance spectra of modified fibrous sorbents (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV** filled with AV-17. (λ) Wavelength.

in the filtrate was determined photocolorimetrically. Immobilization of formazan was indicated by a change in the fiber color from colorless to yellow or red-violet depending on the formazan structure. Diffuse reflectance spectra of modified sorbents **I**–**IV** are shown in Fig. 1. As seen from Fig. 1, sorbents **I, III**, and **IV** strongly absorb in the range 530–640 nm. In the spectrum of sorbent **II** containing pyrimidinylformazan, a hypsochromic shift of λ_{max} to 500 nm is observed. The content of formazan groups *A* in modified fibers **I**–**IV** was 0.09-0.15 mmol g^{-1}.

We studied sorption of Cu(II), Ni(II), Zn(II), and Cd(II) cations on the initial and modified fibers. The sorption under static conditions was performed for 3 days by intermittent stirring of a mixture of aqueous solutions of copper(II) sulfate, nickel(II) nitrate, zinc(II) chloride, and cadmium(II) chloride with the sorbent at the solution volume–sorbent weight ratio of 500 : 1. The metal concentration in the electrolytes was 100 and 1000 mg l^{-1}; pH was 3.5 and 6.9. The contact time in the sorption kinetic experiments varied from 10 to 90 min.

Sorption capacity of modified fibrous sorbents. Contact time 3 days, $V : m$ = 500

Fiber	c_M, mg l^{-1}	pH	SC, mg-equiv g^{-1}			
			Cu(II)	Ni(II)	Zn(II)	Cd(II)
Initial	100	6.9	0	0.09	0.25	0
I	100	6.9	0.32	0.10	0.13	0
II	100	6.9	0.91	0.10	0.08	0
III	100	6.9	0	0	0.59	0.60
IV	100	6.9	0	0.08	0.69	0.60
I	1000	6.9	0.62	0	0.39	0.90
II	1000	6.9	0.50	0	0.39	0.90
I	1000	3.5	1.09	0.31	0.47	0.78
II	1000	3.5	0	1.38	0.60	1.00

The sorption under dynamic conditions was performed by passing an electrolyte solution at a 0.5 ml min^{-1} flow rate through a 50-mm sorbent bed packed in a glass column 10 mm in diameter.

The metal concentration in model solutions of pure salts, solutions after the sorption, and eluates was determined photocolorimetrically, and in mixed electrolyte solutions, by atomic absorption analysis.

To determine the sorption capacity of the fibers (SC), we measured sorption of heavy metal cations from 100 mg l^{-1} aqueous solutions of their salts at pH 6.9 (see table).

The sorption capacities for Cu(II) of fibers filled with AV-17 anion exchanger and modified with benzimidazolyl and pyrimidinylformazan groups (sorbents **I** and **II**, SC 0.32 and 0.91 mg-equiv g^{-1}, respectively) are higher than those of the initial fiber.

Fibers modified with benzothiazolylformazans (sorbents **III** and **IV**) have high sorption capacity for Zn(II) and Cd(II) and do not sorb Cu(II) and Ni(II).

Not only Cu(II) but also Zn(II) and Cd(II) are sorbed on **I** and **II** from 1000 mg l^{-1} solutions of salts of these metals at neutral pH. In acidic solutions (pH 3.5) the sorption of all the examined metals on **I** and **II** increases [except for sorption of Cu(II) on **II**] as compared to that at pH 6.9. In acidic solutions sorbent **II** sorbs Ni(II), Zn(II), and Cd(II), and its sorption capacity for Cu(II) and Cd(II) is lower than that of **I**.

The study of sorption of heavy metal ions on the modified fibrous sorbents filled with AV-17 anion exchanger showed that immobilization of hetarylformazans on the fiber enhances not only the sorption capacity but also selectivity with respect to some metals.

Thus, sorbent **II** can be used for concentration and recovery of Cu(II) from neutral solutions containing Ni(II), Zn(II), and Cd(II) at the total metal concentration of up to 100 mg l^{-1}, and sorbents **III** and **IV**, for joint recovery of Zn(II) and Cd(II) in the presence of Cu(II) and Ni(II) under the same conditions.

With polyacrylonitrile fiber **I** filled with AV-17 anion exchanger and modified with formazan with benzylbenzimidazole groups was example, we studied in more detail how the sorption of heavy metal ions

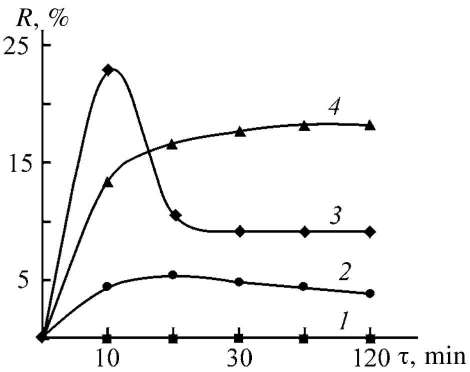

Fig. 2. Degree of sorption R of (*1*) Cd^{2+}, (*2*) Ni^{2+}, (*3*) Zn^{2+}, and (*4*) Cu^{2+} (the same for Fig. 3) on fiber **I** from model solutions of their pure salts under static conditions as a function of the phase contact time. Concentration c_M, mg l^{-1}: Ni^{2+} 25; Cd^{2+}, Cu^{2+}, and Zn^{2+} 75; pH 5.5–6.9; $V:m$ = 500; the same for Fig. 3.

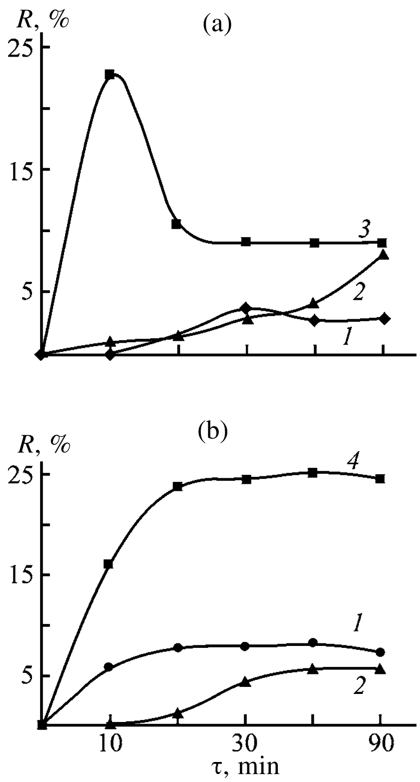

Fig. 3. Degree of sorption of the metal ions R on fiber **I** from model solutions containing a mixture of (a) Cd^{2+}, Ni^{2+}, and Zn^{2+} and (b) Cd^{2+}, Ni^{2+}, and Cu^{2+} ions under static conditions as a function of phase contact time.

depends on the phase contact time. The sorption kinetics on this sorbents was studied under the static conditions (R is the degree of sorption of metal ions) on the sorbent. The kinetic curves of sorption of Cd(II), Ni(II), Zn(II), and Cu(II) ions from model solutions of pure salts of these metals are shown in Fig. 2. Sorption of Zn(II) and Cu(II) cations on fiber **I** is characterized by good kinetic parameters favorable for recovery of these metals from multicomponent solutions.

Selective sorption on **I** of Zn(II) in the presence of Ni(II) and Cd(II) (Fig. 3a) and Cu(II) in the presence of Ni(II) and Cd(II) (Fig. 3b) confirms the good kinetic properties.

To find whether Zn(II) and Cu(II) cations can be selectively recovered under dynamic conditions, we compared the dynamics of sorption of these cations on fiber **I**.

As seen from the outlet curves for Zn(II) and Cu(II) (Fig. 4), Cu(II) can be completely recovered from Zn(II)-containing aqueous solutions under dynamic conditions. The time during which a filter based on sorbent **I** ensures protective effect with respect to Cu(II) cations is longer than that with respect to Zn(II) cations.

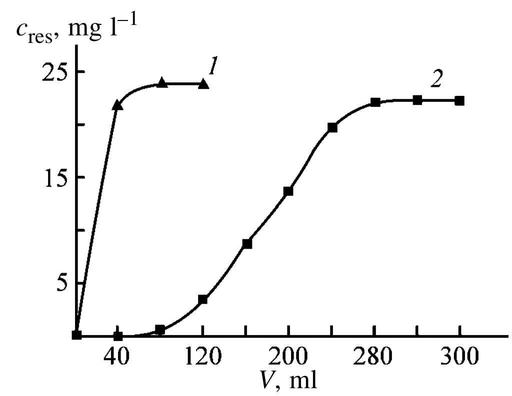

Fig. 4. Outlet curves characterizing sorption of (*1*) Zn^{2+} and (*2*) Cu^{2+} on sorbent **I**. (c_{res}) Residual metal concentration in the solution and (V) solution volume.

CONCLUSIONS

(1) The prepared fibrous polymers with hetarylformazan groups are promising sorbents for recovering Cu(II) cations from solutions containing nickel(II), zinc(II), and cadmium(II) cations.

(2) Sorbents modified with fragments of benzothiazolylformazans can be used for concentrating Zn(II) and Cd(II) cations from dilute solutions and for separating these cations from Cu(II) and Ni(II); sorbents modified with pyrimidinylformazan, for concentrating and separating Cu(II) from solutions containing Ni(II), Zn(II), and Cd(II); and sorbents modified with benzylbenzimidazolylformazans, for concentrating Cu(II) from dilute solutions and for separating Cu(II) from Ni(II) and Cd(II).

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REFERENCES

1. Soldatov, V.S. and Sergeev, G.I., *Zh. Vses. Khim. O–va.*, 1990, no. 1, pp. 101–135.
2. Andreeva, I.Yu., Min'ko, I.A., and Kazakevich, Yu.I., *Zh. Prikl. Khim.*, 1991, no. 6, pp. 1276–1280.
3. Myasoedova, G.V., Shcherbinina, N.I., and Savvin, S.B., *Zh. Anal. Khim.*, 1983, vol. 38, no. 8, pp. 1503–1514.
4. Simanova, S.A. and Kukushkin, Yu.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1986, vol. 39, no. 5, pp. 3–15.
5. Myasoedova, G.V., Nikashina, V.A., Molochnikova, N.P., and Lileeva, L.V., *Zh. Anal. Khim.*, 2000, vol. 55, no. 6, pp. 611–615.
6. Lipunova, G.N., Pervova, I.G., and Lipunov, I.N., *Vysokomol. Soedin., Ser. B*., 1997, vol. 39, pp. 1523–1526.
7. Lipunov, I.N., Pervova, I.G., Lipunova, G.N., *et al.*, *Koord. Khim.*, 1997, vol. 23, no. 12, pp. 934–937.
8. Pervova, I.G., Yushkova, O.G., Lipunova, G.N., and Lipunov, I.N., *Persp. Razv. Est. Nauk Vyssh. Shkole*, 2001, vol. 1, pp. 258–261.