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Application of Ion-Exchange Materials with High Specific Surface Area for Solving Environmental Problems

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Abstract—Sorbents possessing high exchange capacity, chemical resistance, and mechanical strength were prepared by modification of acrylic fiber Nitron and suspension polyvinyl chloride with various amines. Some applications of the resulting anion exchangers in treatment of wastewater to remove heavy metal ions and microorganisms and of gaseous waste to remove acid gases were presented.

Keywords: acrylic fiber, polyvinyl chloride, amines, sorbent, ecology, iodine complex, heavy metal ions, filter materials, acid gases

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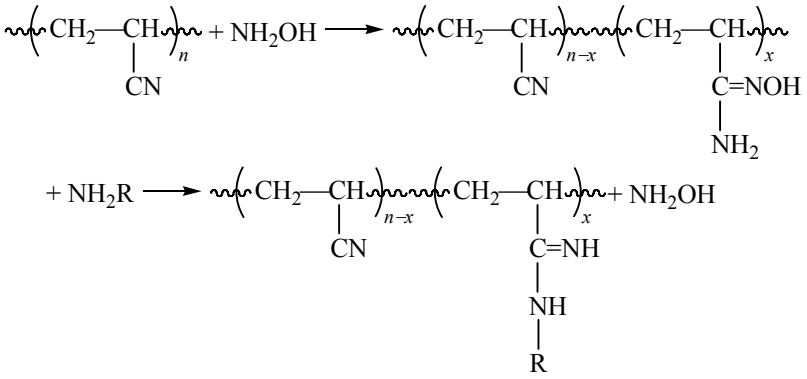
A variety of ion exchangers, or ion-exchange substances and materials, are currently used in various spheres, and ion-exchange processes are being rapidly and extensively incorporated into different branches of human activity. Some of ion exchangers, e.g., those based on fibrous materials or gel-type ion-exchange resins whose particle size is by nearly an order of magnitude smaller than that of the conventional granular sorbents, are effective in wastewater and gaseous waste treatment. A major technological advantage offered by such ion exchangers is their large specific surface area which enables high sorption rate, particularly important for the case of dilute systems [1–7].

Due to a very low resistance of fibrous ion exchangers the use of ion-exchange textiles provides a simple solution to the problem of treating large volumes of gaseous waste. This opportunity acquires great practical significance in the context of large-scale production of synthetic polymers, in particular, of acrylic fiber Nitron (PAN) and polyvinyl chloride (PVC). Because of high and diversified reactivity of its cyano groups, PAN can fairly easily be modified by treatment with various agents [8, 9]. In a similar way, the presence of reactive chlorine in PVC allows introduction of various ionic groups into its composition [10, 11].

For example, experiments on PAN modification with hexamethylenediamine showed that a change from aqueous to organic solutions of this amine enables preparation of materials with the best sorption properties and the highest chemical resistance. This is due to a greater accessibility of the cyano groups in organic solvents compared to aqueous media due to unfolding of PAN macrochains [12].

We carried out modification of Nitron fiber and suspension PVC (grain size <0.063 mm) with ammonia, urea, phenylhydrazine, mono-, di-, and triethanolamine, diethylamine, ethylenediamine, hexamethylenediamine, and some other compounds and obtained a number of fibrous and granular sorbents containing $–NH_2$, –NH–, and $–C(NH_2)=NH$ functional groups and possessing high sorption capacity and high chemical resistance. In this regard, the simplest and most cost-effective solution consists in the use of the sorbent obtained by Nitron modification with urea (PAN-KDM). Studies of the IR spectra and of the physicochemical properties of the polymers, combined with analysis of the available published data, showed that Nitron modification with nitrogen-containing bases leads to formation of a cross-linked structure, which is known [12–36] to cause the mechanical strength and chemical resistance of the polymers to increase. The formation reaction and the chemical structure of the

Scheme 1.



R = –NH_2, –$N(CH_3)_3$, –$(CH_2)NH_2$, –$(CH_2)_6NH_2$.

anion exchangers synthesized can be represented in Scheme 1.

One of the most acute environmental problems is treatment of electroplating wastewater to remove non-ferrous and heavy metal ions, particularly hexavalent chromium ions, a very strong oxidant which, if ingested, adversely affects human health. Experiments showed that the urea-modified ion-exchange materials are able of sorbing effectively dichromate ions from acid solutions over a broad pH range. The dynamic exchange capacity with respect to dichromate ion, exhibited by the resulting samples, reaches 250–300 mg g^{-1} at pH = 1.

Conditions for regeneration of the sorbents after they are saturated were found, and the suitability of the anion-exchange fibers for reuse was demonstrated. Based on the experimental results, application of some of the sorbents developed was recommended for treating chromium-plating wastewaters to remove hexavalent chromium ions and to concentrate the process solutions [12–16].

Comparison of the sorption properties of the ion-exchange materials prepared by us showed that the ethylenediamine-modified PAN fibers exhibit high sorption capacity toward divalent copper ions. This raises the possibility to adjust the selectivity of the anion-exchangers by choosing appropriate modifying agent.

Table 1 compares the sorption capacities exhibited by the sorbents in uranium removal from model solutions [37]. It was found that the sorption capacities of the Nitron-based anion exchangers developed (ASS-

Table 1. Sorption parameters with respect to uranium in relation to the sorbent nature (V_{soln} = 100 mL; $[U]_i$ = 3.27 mg L^{-1}; pH = 7.78; sorbent mass = 0.5 g)

Run no.	Sorbent name	Residual concentration, mg L^{-1}	Equilibrium uranium concentration in the sorbent, mg g^{-1}
1	Purolite 104	0.038	0.6464
2	Purolite S920	0.002	0.6536
3	Purolite A400	0.255	0.6030
4	Levatit K7367	0.180	0.6180
5	Levatit K6367	0.328	0.5884
6	VP–1AP	0.154	0.6232
7	AV–17–8	0.043	0.6450
8	ASS–2–3–2	0.023	0.6494
9	ASS–2–4–4	0.014	0.6512

2-3-2, ASS-2-4-4) are comparable with those of the ion exchangers widely applied in industry for uranium removal. Joint studies also showed that the anion exchangers developed are suitable for treatment of wastewater to remove heavy metal radioactive isotopes, including that of chromium.

Another common environmental problem is that of removal of acid vapors from waste gases emitted by industrial facilities. The sorbents developed, with their high exchange capacity (up to 6.0 meq g^{-1} for HCl) and carrying capacity, as well as porosity and chemical resistance (stability against concentrated HCl and HF), were recommended for treatment of waste gases to remove HCl, HF, HNO_3, H_2SO_4, H_2S, CH_3COOH, and other vapors (Table 2) at a number of large industrial plants [38]. Also, these sorbents can be usefully employed as filter materials in personal protection means.

We demonstrated that, by reacting iodine with the urea-modified materials, it is possible to prepare polyiodide complexes thereof. Studies of the iodine sorption kinetics and thermodynamics for these materials showed that the composition of the resulting polyiodide complexes can be controlled by varying the reaction temperature, the iodine concentration in solution, and the static exchange capacity (Fig. 1).

It is seen from Fig. 1 that the iodine sorption process occurs spontaneously, and a sharp increase in iodine sorption by the polymer with increasing temperature can be attributed to formation of polyiodide complexes.

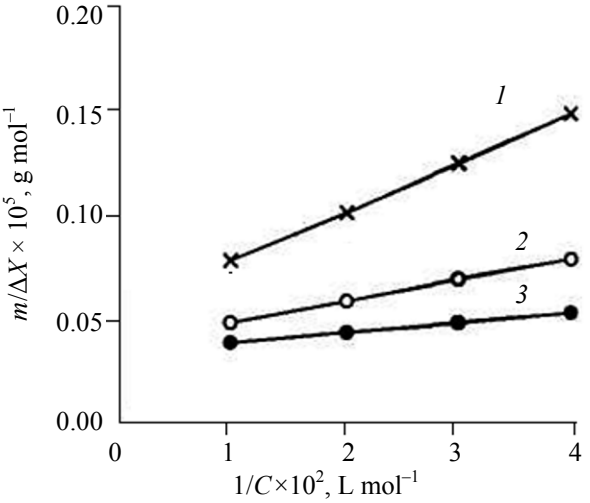


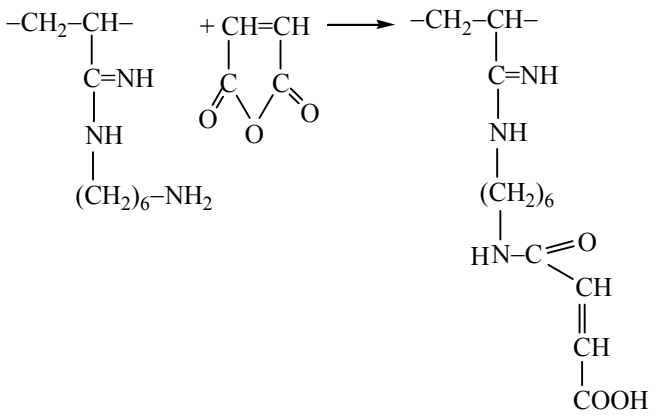
Fig. 1. The $1/\Gamma$ vs. $1/C$ dependences for iodine sorption by PAN–KDM ion-exchange fiber at temperature of (*1*) 308, (*2*) 298, and (*3*) 288 K.

The resulting iodine-containing samples exhibited high antibacterial activity toward a number of common cultures [34–40]. This made them good candidates to be used as disinfectants in drinking and service water treatment plants, as filter materials in wastewater treatment systems of special-purpose organizations [38], and as agents for removing mercury ions from wastewater [41].

Table 2. Influence of the number of HCl and HNO_3 sorption–desorption cycles on the sorption capacity of PAN–KDM fibrous ion exchanger (3 columns, total weight of the sorbent 30 g, desorbate 0.1 N NaOH)

Volume of the acid solution passed through the column, mL	Amount of the substance sorbed, mg	Sorption, %	Desorbate volume, mL	Desorption, %
1050	5223	97.2	1000	96.4
1041	5160	96.0	995	97.1
1027	5090	94.8	979	96.8
1016	5036	93.7	965	96.5
1005	4981	92.2	957	96.8
998	4946	92.1	953	97.0
985	4882	90.9	938	96.7
974	4828	89.8	928	96.8
969	4803	89.4	922	96.7
962	4768	88.7	919	96.1

Scheme 2.



As known, natural waters in areas accommodating non-ferrous metal ion production facilities are contaminated with toxic heavy metal ions, in particular copper ions. The use of these waters in agriculture leads to deterioration of the environmental situation in the area concerned, and they are virtually unsuitable for production of drinking water. Copper binding by sorbents is known to occur not only through ion-exchange but also through chelation mechanism. For this reason, since recently, complexing sorbents obtained by polymer-analogous transformations have widely been used for removing transition metals from solutions.

With the view of obtaining ion-exchange fibers containing chelating functional groups, the reaction between SMA-1 sorbent (the product of Nitron modification with hexamethylenediamine) and maleic acid anhydride was carried out according to the Scheme 2.

The resulting polycomplexon was used for removal of copper ions from ammine solutions. The interaction of the functional groups of fibrous materials with low-molecular-weight ions is commonly interpreted as a heterogeneous chemical reaction characterized by specific thermodynamic features. Sorption of the Cu^{++} ions by the sorbent prepared has an equilibrium character. Consequently, we determined the sorption equilibrium constant and the changes in the thermodynamic parameters to most adequately characterize the processes involved.

The sorption isotherms are typically described, and the sorption equilibrium constants determined, by the Langmuir equation in the following form:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{B}{\Gamma_\infty} \cdot \frac{1}{C},$$

where $B = 1/K$. By plotting $1/\Gamma$ vs. $1/C$, it is possible to estimate B/Γ from the slope of the straight line, and $1/\Gamma$, from the intercept on the ordinate axis. Based on these data, we determined the limiting specific sorption Γ_∞ at different concentrations and temperatures and the sorption equilibrium constant K_e.

Table 3 presents the results of calculation of the changes in the thermodynamic functions of the sorption process. It is seen that, in the course of Cu^{++} sorption by SMA-1-MA sorbent, the Gibbs free energy, the enthalpy, and the entropy of the system decrease. Essentially, spontaneous occurrence of the process is provided mainly by a decrease in the enthalpy of the system.

Thus, the revealed changes in the thermodynamic functions give some insight into the thermodynamic features of Cu^{++} complexing with the sorbent tested. A decrease in the enthalpy of the system is indicative of Cu^{++} binding mainly by the ion-exchange mechanism.

In order that the sorbent prepared can be usefully employed for treatment of wastewater and process solutions to remove copper ions, we developed the operating conditions for the process of dynamic sorption of the copper ions from artificial solutions. To this end, a $CuSO_4$ solution with the concentration of 1 g L^{-1} was passed through a column packed with the sorbent (packing density 0.2 g cm^{-3}) activated with 0.1 N NaOH. The dynamic exchange capacity (DEC) of the sorbent toward Cu(II) ions reached 63 and 113 mg g^{-1} at pH 4.2 and 12, respectively. Our results indicate that the copper sorption by the sorbent is pH-

Table 3. Changes in the thermodynamic functions of the Cu^{++} sorption by SMA–1–MA fibrous sorbents

T, K	$\Gamma_\infty \times 10^{-3}$, mol g^{-1}	K, L moL^{-1}	$-\Delta G$, J mol^{-1}	$-\Delta H$, J mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}
293	1.0	1333.3	17519.6	28000	35.8
303	1.4	943.4	17245.5		35.5
313	1.6	877.2	17626.4		33.1

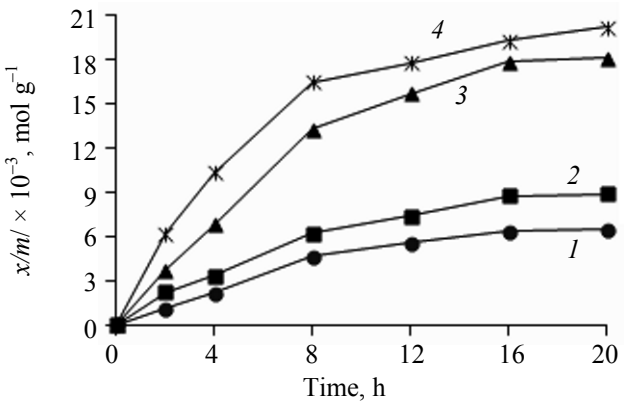


Fig. 2. Kinetics of the vanadyl ion (VO_2^+) sorption by MDA–1–R ion exchanger. (*1–4*) Initial adsorbate concentration: (*1*) 0.0075, (*2*) 0.01, (*3*) 0.02, and (*4*) 0.03 M; $T = 303$ K.

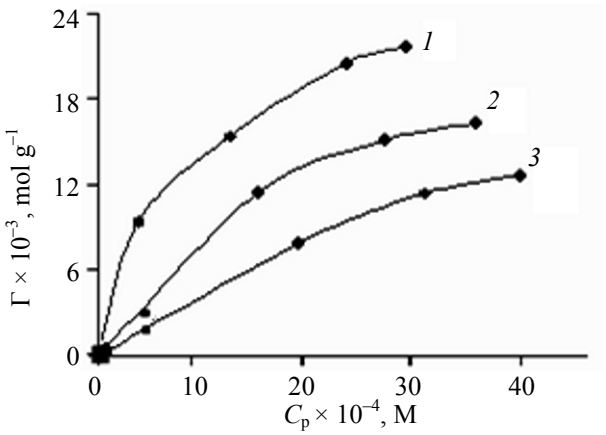


Fig. 3. Isotherms of VO_2^+ sorption by MDA–1–R ion exchanger at different sorption temperatures: (*1*) 313, (*2*) 303, and (*3*) 293 K.

dependent and is determined by the ionic state of the copper ions; it is observed even in acidic media, where carboxy groups are not ionized. Consequently, under the actual conditions, the copper sorption proceeds mainly via chelation.

For practical use of sorption materials, the sorbent regeneration cycle is of much significance.

Sorbent regeneration was performed with 0.1 N H_2SO_4 solution. It was found that the sorbent exhibits high chemical resistance and is reusable. As seen from Table 4, after ten sorption–desorption cycles, the DEC of the sorbent changed by 25% only.

Next, we examined the features of sorption of the VO_2^+ ions from artificial sulfuric acid solutions $(VO_2)_2SO_4$ by the polyvinyl chloride-based ion exchanger with amine- and phosphorus-containing functional groups (MDA-1-R).

Vanadium oxide V_2O_5 is known to effectively catalyze, e.g., oxidation of sulfur dioxide SO_2 to sulfur trioxide SO_3 in sulfuric acid production. Spent catalysts are stored in the vicinity of industrial facilities, thereby causing environmental pollution. Disposal of this waste and recovery of valuable components therefrom may provide a solution to this environmental problem. In this context, exploration of the possibility for removing vanadium(V) ions from sulfuric acid solutions with the sorbent developed can be helpful to certain extent.

Figure 2 presents the kinetic curves of the vanadyl ion sorption by the sorbent developed. These curves exhibit a classic pattern with attaining saturation; it is seen that the equilibrium in the system is reached within 20 h, and the sorption process is significantly affected by the process temperature and the initial concentration of the vanadium solution.

Table 4. Influence of the regeneration cycle on the DEC of the sorbent for the Cu^{++} ion

DEC, mg g^{-1}	Before regeneration	After regeneration with 0.1 N aqueous HCl									
		1	2	3	4	5	6	7	8	9	10
with respect to Cu	113	108	109	103	97	88	85	82	82	82	82

Table 5. Rate constants and changes in the thermodynamic functions of the VO_2^+ sorption by MDA–1–R ion exchanger

T, K	$\Gamma_\infty \times 10^{-3}$, mol g^{-1}	K, L moL^{-1}	$-\Delta G$, J mol^{-1}	$-\Delta H$, J mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}
293	1.36	233,4	13276		85.10
303	1.43	591,7	16072	38182	73.18
313	1.92	1540	19091		57.37

Based on these data, the maximal static exchange capacity of the ion exchanger with respect to vanadium(V) ions was estimated at 3.47 meq g^{-1}, which finding is fairly consistent with the characteristics of such sorbents. The percentage removal of the vanadium(V) ions tends to decrease with increasing concentration of the initial solution of the vanadium salt.

The isotherms of VO_2^+ sorption by MDA-1-R sorbent at different temperatures are presented in Fig. 3. It is seen that sorption tends to increase with increasing both the VO_2^+ concentration and temperature of the initial solution.

Table 5 presents the adsorption equilibrium constants and the changes in the thermodynamic parameters of the system in the course of the process, calculated with the use of the data from Fig. 3.

It is seen that the VO_2^+ sorption is a spontaneous process characterized by negative changes in the free energy, enthalpy, and entropy of the system. Increases in Γ_∞ and in the adsorption equilibrium constant with increasing temperature evidence the dominance of chemical over physical sorption. A decrease in the enthalpy of the system indicates proceeding of an ion-exchange reaction between the hydrogen ions of the sorbent and the vanadyl ions of the solution, and a decrease in the entropy of the system, binding of the vanadium ion by the sorbent also via complexing.

Thus, studies on the VO_2^+ sorption from sulfuric acid solutions by MDA-1-R sorbent demonstrated the suitability of this sorbent for vanadium removal from various objects that allow transferring vanadium to solution by sulfuric acid leaching, e.g., from spent catalysts for sulfuric acid production.

CONCLUSIONS

Acrylic fiber Nitron and suspension polyvinyl chloride, with their fibrous structure and high dispersity, can be modified with various nitrogen-containing bases to obtain sorbents with high specific surface area, chemical resistance, and mechanical strength.

High sorption capacity makes the resulting sorbents good candidates for treating industrial wastewater to remove toxic metal ions and for filtering acid vapors emitted by industrial facilities.

The sorbents obtained can be useful in preparation of iodine-containing materials for disinfection of natural waters and for removal of mercury ions from wastewaters.

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