

POLYMERIC SORBENTS BASED ON POLYACRYLONITRILE AND POLYETHYLENEPOLYAMINE FOR SORPTION OF CHROMIUM (VI) IONS

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One of the most important areas in the field of chemistry of macromolecular compounds is the synthesis and study of ion-exchange materials with desired properties, which year by year are increasingly used in hydrometallurgy, the national economy, and in solving a number of problems of ecology and environmental protection [1-3].

Methods of chemical transformations of ready-made polymers or copolymers obtained using bifunctional monomers and polymers are widely used to obtain ion-exchange materials. In this regard, the production of ion exchangers based on polyacrylonitrile by chemical transformation of their functional groups is an important and promising direction in the development of ion exchangers. The latter are widely used in various sorption technologies that require their special mechanical and chemical resistance, when it is necessary to concentrate process solutions to extract especially valuable components from them and purify sources of water supply, industrial waste water from toxic ions and environmentally hazardous compounds [4-7].

Modification of polyacrylonitrile fibers (PAN) with nitrogen-containing inorganic bases makes it possible to obtain weakly basic sorbents. Such sorbents are easily oxidized by anions containing strongly oxidizing elements, for example, chromium (VI) ions [8-12]. It is known from the literature that the treatment of polyacrylonitrile with polyfunctional amines makes it possible to obtain strongly basic anion exchangers. For example, the chemical modification of nitrone was previously carried out using hexamethylenediamine and ethylenediamine. Fibrous sorbents of the SMA-1 and SMA-5 grades were obtained, which have a high sorption capacity with respect to hexavalent chromium ions. The sorbents had a cross-linked structure and contained strongly basic groups, which made it possible to use it for the purification of wastewater from electroplating shops from hexavalent chromium ions. At the same time, the degree of wastewater treatment according to the proposed method in a continuous stream reached a quantitative value. The developed method makes it possible

to quickly and effectively purify chromium-containing wastewater from electroplating and other industries [13].

In this regard, it was of interest to us to use polyethylenepolyamine (PEPA) for PAN modification, which contains polyethylenepolyamine groups, which, when interacting with PAN, form both weakly basic and strongly basic functional groups. The kinetics of the reaction of modification of PAN with polyethylene polyamine has been studied and an equation for the rate of this process has been compiled.

For modification with PEPA, hydroxylamine (HA) activated PAN fiber was used [14]. At the same time, the ion-exchange capacity of the modified HA fiber with respect to HCl was 1 mg-eq/g. The reactions were carried out at 353-373 K for 1-5 hours, while the maximum value of the static exchange capacity (SEC) of the modified PEPA fiber with respect to HCl was 5.4 mg-eq/g.

Figures 1 and 2 show the dependences of the SEC values of the modified PAN fiber on the reaction time, temperature, and PEPA concentration.

As can be seen from the figure, with an increase in the reaction time and temperature, the SEC value of the modified fiber increases, which means that the polyethylene polyamine chain is connected to the fiber. Figure 2 shows the dependence of the SEC value of the sorbent on the concentration of PEPA. As can be seen from the figure, at a PEPA concentration of 50%, the SEC reaches its maximum value, then, with increasing concentration, a decrease in the SEC value is observed. This is explained by an increase in the viscosity of the reaction medium as a result of an increase in the concentration of PEPA and the difficulty of polyamine diffusion in the polymer chain. As a result, the degree of polymer conversion decreases and the SEC value decreases.

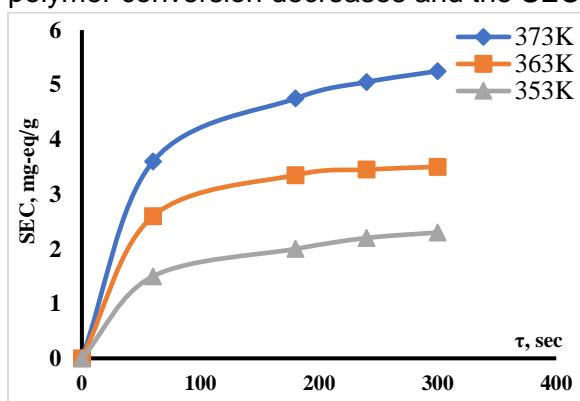


Figure 1. Dependence of SEC of a sorbent PPA-1 on the duration of the reaction. [PEPA]=50%;

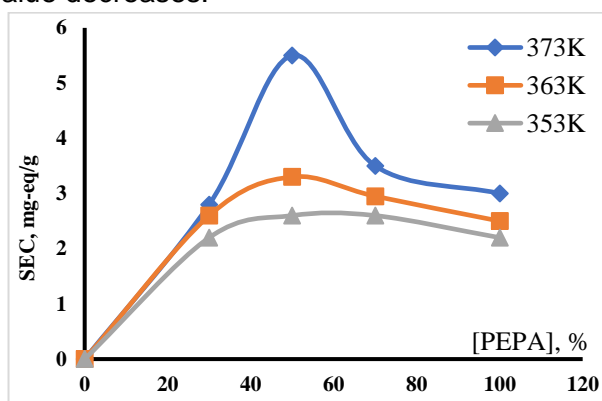


Figure 2. Dependence of the SEC of the sorbent PPA-1 on the concentration of polyamine. $\tau=3$ hours.

The activation energy for the reaction of PAN modification with polyethylenepolyamine was found to be 48.3 kJ/mol (Fig. 3). The low value of the activation energy is due to a preliminary increase in the reactivity of the nitrile groups of the polymer due to hydroxylamine at the beginning of the reaction.

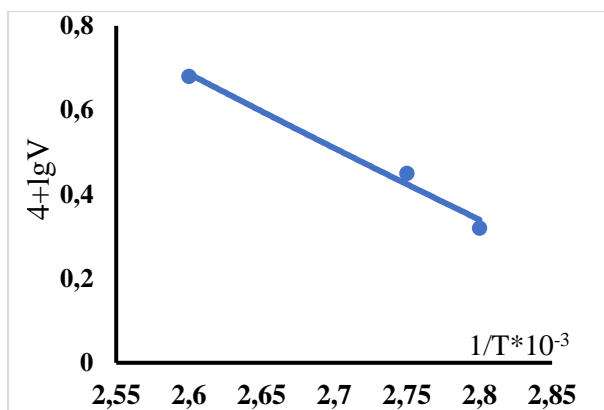


Figure 3. Dependence $\lg V$ from $1/T$. $[\text{PEPA}] = 50\%$, $\tau = 3$ hours.

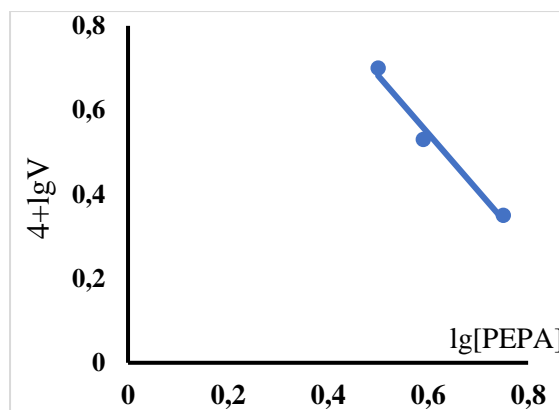


Figure 4. Logarithmic dependence of the reaction rate of PAN with PEPA on the concentration of PEPA ($T = 373\text{K}$, $[\text{PEPA}] = 50\%$, bath modulus 1:40).

The reaction rate of nitrile groups, i.e. their degree of conversion was determined by the value of the SEC of the resulting anion exchanger. To do this, with the complete conversion of nitrile groups, the theoretical value of SEC is presumably equal to 100% of the degree of conversion. As a result, using the found value of SEC, the degree of conversion of the nitrile groups of the polymer was calculated. The reaction of PAN fiber modification with PEPA is a heterogeneous process; the reaction rate in such processes depends on the concentration of the substance in the gas and liquid phases. Based on this, based on the values of the chemical modification of PAN with PEPA, the order of the reaction was calculated according to the concentration of PEPA (Figure 4).

The reaction rate equation for the interaction of PAN with PEPA has the following form:

$$V = K [\text{PEPA}]^{0.9}$$

It should be noted that the heterogeneous nature of the process affects the order of the reaction, the order for polyethylene polyamine will be equal to unity and it does not depend on the concentration of fiber cyanogroups.

The insolubility of the resulting polymer in PAN solvents indicates the presence of three-dimensional systems. To characterize the ionogenic groups of the synthesized sorbent, potentiometric titration was performed. The titration was carried out under static conditions by the method of separate weights, while the concentration of $[\text{H}^+]$ ions was changed by adding a solution of 0.1 N HCl in 0.1 N NaCl to a weight of the sorbent. Figure 5 shows the differential curves of the potentiometric titration of the fiber modified with PEPA PAN. As can be seen from the presented data, a jump is observed on the titration curve at $[\text{H}^+] = 2.2$ mg-eq/g. Also, at $[\text{H}^+] = 1.1$ mg-eq/g, a small jump is observed. These results indicate the presence of major groups in the composition of the sorbent.

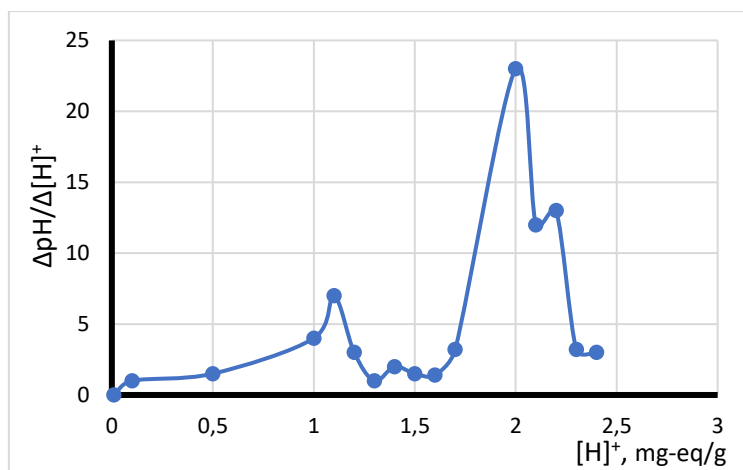


Figure 5. Differential curve of potentiometric titration anion exchanger PPA-1. SOE of the sorbent=5.0 mg-eq/g.

In order to assess the basicity of the functional groups of the sorbent, the potentiometric titration curves were analyzed by the Henderson-Hasselbalch equation. For this we used the equation:

$$pK_{\alpha} = pH - m \lg \frac{\alpha}{1-\alpha}$$

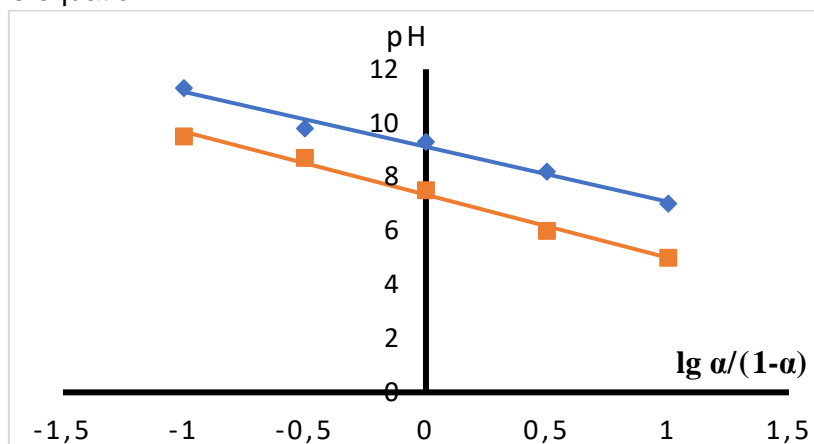
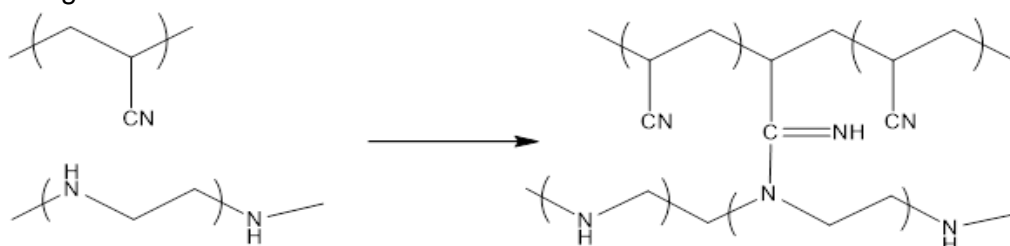


Figure 6. Dependence of pH on $\lg \alpha/(1-\alpha)$

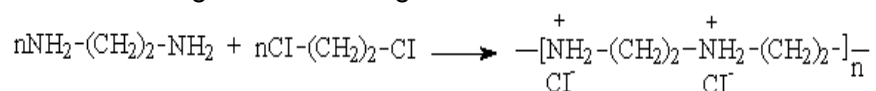
On the curves of the potentiometric titration of the modified PAN, there are two jumps corresponding to pKa values of 9.3 and 7.4 (Figure 6). As a result of the determination, the SEC value in terms of the number of strongly basic groups was 2. mg-eq/g. In the IR spectra of PEPA-modified samples in the region of 2240 cm^{-1} , a decrease in the intensity of the absorption bands of stretching vibrations of nitrile groups is observed, in the region of $3200 - 3500$ and 1580 cm^{-1} absorption bands of stretching and bending vibrations of the $>\text{NH}$ group are observed; in the region of 1640 cm^{-1} , an absorption band of the stretching vibration of the $>\text{C}=\text{N}$ - group is observed. The structure of the resulting polymer can be represented by the following scheme:



As a result of studying the kinetics of modification of PAN with PEPA, the optimal reaction conditions were determined and anion-exchange fibers (**PPA-1**) were synthesized with a SEC of 5.3 mg-eq/g in HCl. To achieve these results, the reaction conditions were selected as follows: PEPA concentration 50%, temperature 373K, reaction time 3 hours, bath modulus 40.

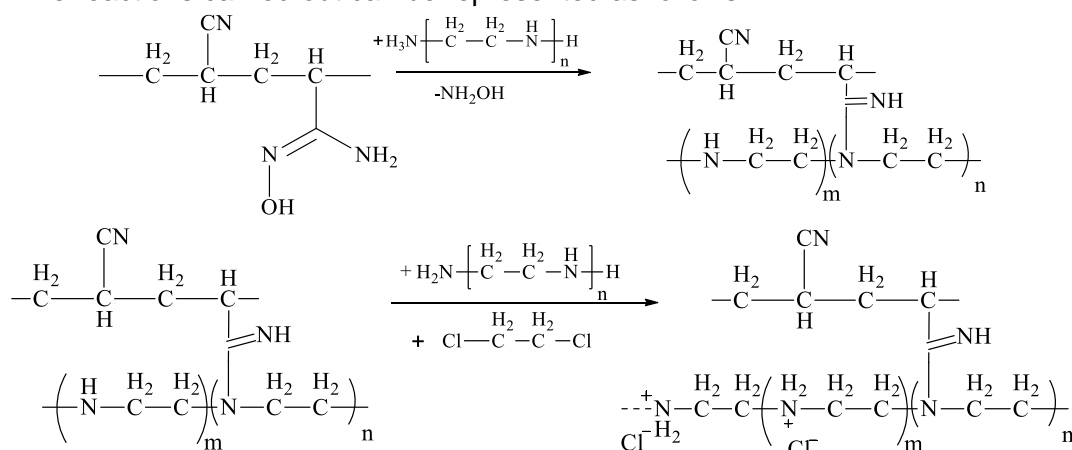
To increase the SEC value for strong basic groups when modifying PAN fiber with PEPA, it was additionally modified with DCE. As is known, the value of the SEC of sorbents depends on the number of functional groups that give them ion-exchange properties. The number of functional groups can be increased by lengthening the side chains of the modified polymer.

As is known from the literature, diamines, including EDA, interact with dihaloalkyls forming oligomers according to the following scheme:



Proceeding from this, we have investigated the possibility of obtaining ion-exchange sorbents based on nitron, containing links from polyethylene polyamine groups in the side chains. For this, the PAN fiber was modified with PEPA in the presence of dichloroethane (DCE), and this led to an increase in the SEC for the strongly basic groups of the sorbent (**PPD-2**) to 3.0 mg-eq/g.

The reactions carried out can be represented as follows:



As can be seen from the reaction, the addition of DCE to the modification of PAN fiber with PEPA leads to polycondensation reactions between the components and elongation of the oligomeric chain. The results obtained make it possible to obtain sorbents with high SCE by the reactions of polycondensation of polymer side groups.

As noted above, ion-exchange materials are used for the concentration of heavy metals from process solutions, wastewater treatment from toxic metal ions, dyes, surfactants, and others [1-5].

The study of the kinetics and thermodynamics of the sorption process of the above-mentioned substances makes it possible to reveal the selectivity and sorption capacity of ion-exchange materials with respect to this compound. One of these compounds are chromium (VI) ions. These ions have a high oxidizing ability, and therefore the selection of a sorbent with this ion is very difficult, therefore, sorbents with strongly basic groups are mainly used to solve this problem.

Therefore, the obtained sorbents PPA-1 and PPD-2 were used as an adsorbent for ions $\text{Cr}_2\text{O}_7^{2-}$ from aqueous solutions under static conditions. In both cases, with increasing temperature, an increase in specific adsorption is observed (Figure 7).

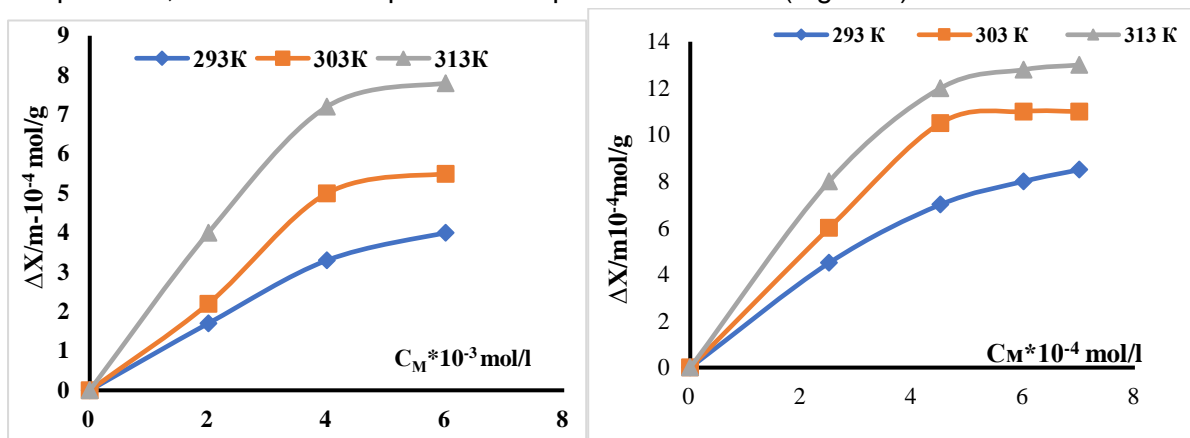


Figure 7. Kinetics of sorption of dichromate ions by sorbents PPA-1 (a) and PPD-2 (b)

As can be seen from the figure, an increase in the temperature and concentration of $\text{Cr}_2\text{O}_7^{2-}$ ions in the initial solution leads to an increase in the sorption of ions by sorbents. This indicates that the sorption process occurs due to chemical binding, that is, chemisorption is observed.

It should be noted that the PPD-2 sorbent absorbs more chromium ions due to the fact that its SEC of strongly basic groups is higher than that of the PPA-1 sorbent. Based on the results of absorption of bichromate ions by PPA-1 and PPD-2 sorbents, the thermodynamic parameters of the process were calculated (Table 2).

Table 2. Changes in thermodynamic functions during absorption of $\text{Cr}_2\text{O}_7^{2-}$ ions by sorbents PPA-1 and PPD-1

T, K	q_∞ l/mol	K, l/mol	$-\Delta G$, J/mol	ΔH , J/mol	ΔS , J/mol K
by sorbent PPA-1					
293	2,0	195	12852,4	31500	151,02
303	2,7	296	14342,8		
313	4,0	416	15702,0		
by sorbent PPD-2					
293	2,9	800	16293,0	9250	87,1
303	3,3	900	17145,7		
313	5,0	1000	17985,6		

As can be seen from the table, the process of absorption of $\text{Cr}_2\text{O}_7^{2-}$ ions by sorbents PPA-1 and PPD-2 proceeds with a decrease in free energy, an increase in enthalpy and entropy. An increase in the enthalpy of the system indicates the presence of a bond between chromium ions and the sorbent. The abundance of strongly basic groups in the PPD-2 sorbent makes it possible to better absorb chromium ions.

A technical regime for dynamic sorption of chromium ions from artificial solutions has been developed in order to recommend a sorbent for the purification of wastewater and technological solutions from chromium ions. To do this, the PPD-2 sorbent was placed in a column with a density of 0.2 g/cm^3 , activated with a solution of 0.1 N HCl and a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ with a concentration of 0.1 g/l .

The sorbent was regenerated in 5% NaOH solution. It was found that the sorbent has a high chemical stability and can be used repeatedly. As can be seen from the data in the table, the dynamic exchange capacity (DEC) of the sorbent in the process of sorption-desorption changed only by 28%, and the change in DEC for the chromium ion was in the range of 70-50 mg/g. The synthesized sorbent PPD-2 in terms of its sorption properties is not inferior to Amberlite and other sorbents used in industry.

Table 4. Influence of the regeneration cycle on the DEC of the PPD-1 sorbent by chromium atoms and $\text{Cr}_2\text{O}_7^{2-}$

DEC, mg/g	Before regeneration	After regeneration with 5% water NaOH solution									
		1	2	3	4	5	6	7	8	9	10
by $\text{Cr}_2\text{O}_7^{2-}$	200	195	190	185	178	173	168	162	155	152	145
by Cr	70	68	65	61	61	59	55	53	51	51	50

Thus, the study of the DEC of the sorbent under dynamic conditions from artificial solutions showed that the sorption process proceeds without diffusion delays and the sorbent capacity reaches 70 mg/g for the Cr (VI) ion. The developed sorbents can be recommended for wastewater treatment of chromium plating departments of electroplating shops from Cr (VI) ions.

CONCLUSION

The influence of various factors on the processes of obtaining anion exchanger by modifying polyacrylonitrile with polyethylene polyamine has been studied. It has been shown that the processes under study obey the laws characteristic of heterogeneous reactions, such as activation energies, the study of the fact that the reaction rate depends only on the concentration of the modifying agent. The study of the physicochemical aspects of the production and properties of anion exchangers and polycomplexons made it possible to find the optimal conditions for the production of new ion-exchange fibrous materials.

The kinetics and thermodynamics of the process of sorption of chromium (VI) ions by the anion exchanger were studied. Certain kinetic and thermodynamic parameters show that the anionite has a high tendency to chromium (VI) ions, and its resistance to strong oxidizing agents is due to the presence of strong basic groups in the composition.

The processes of sorption and desorption of chromium (VI) ions by the synthesized anion exchanger under dynamic conditions have been studied. The results obtained indicate that the anion exchanger is chemically stable and can be used repeatedly. Thus, the obtained ion-exchange fibrous sorbents are promising for use in hydrometallurgy, in the purification of industrial wastewater from toxic chromium (VI) ions.

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