



Polymer Sorbents from "Nitron Fiber Waste"

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Abstract

New sorbents were synthesized from nitron fiber waste modified with various anion-exchange groups. The structure was studied by potentiometric titration and IR spectroscopy. The possibility of using them for immobilization is shown, and the physicochemical characteristics of polymer sorbents are studied.

Key Words: Microquantities, Zeolites, Hematites, Aluminosilicates, Cellulose, Synthetic Fibers.

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Introduction

Currently, sorption methods are the simplest in hardware design and allow you to concentrate microquantities TM from a large sample volume, thus increasing the representativeness of the analysis. Concentration methods include both simple evaporation and more complex extraction and sorption technologies that provide high separation and concentration factors. Various materials of natural and artificial origin are used for sorption technologies, such as zeolites, hematites, aluminosilicates, cellulose, synthetic fibers, etc. (Ahmad, Shoushtari, Mojdeh Zargaran, Majid 2006; Litmanovich, Plate 2005; Korshak 1970). The search for inexpensive sorbents from non-deficient renewable raw materials is relevant. Therefore, highly efficient utilization of nitron fiber waste is already an urgent task in itself, and obtaining immobilized carriers for the determination of ecotoxicants on its basis should truly be an innovative breakthrough in the decision solving environmental problems. It should be noted that in this case several tasks are solved simultaneously: recycling of production waste itself; wastewater treatment from toxic and ferrous

metals and harmful impurities in order to return them to the recycle (Leikin, Smirnov, Davankov, Korshak 1968). There is also a third way to use these reagents, namely, the manufacture of IMOR based on them for the determination of heavy metal ions for their concentration for analytical purposes, which has not been considered by analytical chemists until now (Madusmanova, Smanova, Zhuraev, 2020; Nurmukhammadov, Smanova, Tadjimukhamedov, Inatova, 2014; Smanova, Gafurova. Savchikov, Disodium 2011; Ermatova, Bobomurodova, Smanova, Gofurova, Shahidova 2021).

The Main Findings and Results

Research on the creation of immobilized reagents on various polymer sorbents for the determination of heavy toxic metal ions is currently one of the actively developing areas of analytical chemistry. As a rule, these studies are conducted at the intersection of several disciplines: organic and inorganic chemistry, polymer chemistry, biology, and medicine.

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It is known from the litera (Rustamov, Gafurova, Karimov, Bekchonov, Mukhamediev, 2014; Gafurova, Khakimzhanov, Mukhamediev, Musaev, 2002; Gafurova, Shakhidova, Mukhamediev, Mukhamedov 2014; Gafurova, Shakhidova, Mukhamediev 2013) that the treatment of polyacrylonitrile with polyfunctional amines makes it possible to obtain anionites of a strongly basic nature. For example, chemical modification of nitron with hexamethylenediamine (HMD) in non-aqueous solutions at temperatures above 373K was previously performed. A fibrous sorbent of the ASX-64 brand was obtained, which has a high sorption capacity with respect to hexavalent chromium ions (Gafurova, Shakhidova, Mukhamediev, Mukhamedov 2014; Korshak 1970). The sorbent had a cross-linked structure and contained a strongly basic group, which made it possible to use it for wastewater treatment of 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 quantitative values. The developed method made it possible to quickly and efficiently purify chromium-containing wastewater from electroplating and other industries [(Gafurova, Shakhidova, Mukhamediev, Mukhamedov 2014; Leikin, Smirnov, Davankov, Korshak 1968). However, the method of obtaining the ASX-64 sorbent is characterized by a high consumption of HMD and organic solvents. The process was carried out at temperatures of 403-413K, since the solvents used (kerosene, уайт-white spirit, decane) were not mixed with HMD at lower temperatures. This created a number of technological difficulties in separating and washing the product, and the process itself became explosive. In order to simplify the synthesis of nitron-based sorbents, we have studied the modification of fiber in solvents forming homogeneous solutions with hexamethylenediamine at any ratio and temperature.

The kinetics and mechanism of obtaining initial anion-exchange polymer materials based on polyacrylonitrile and the chemical interaction of nitron with hexamethylenediamine were studied depending on various factors.

Water and butanol were used as GMD solvents. When performing the reaction of HMD with PAN fibers in an aqueous solution of HMD, the efficiency of modification, as in previous studies, was evaluated by determining the degree of

transformation of samples by po and K - spectroscopic examination and determining the COE of the anionites formed by HCl. The effect of time and temperature on the course of the modification reaction is shown in Fig. 1.

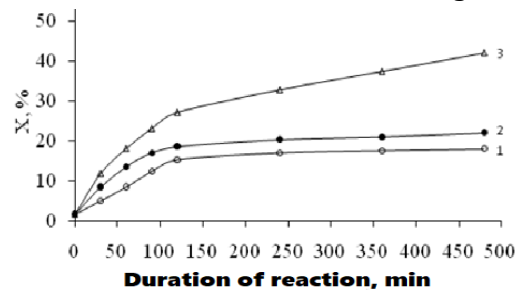
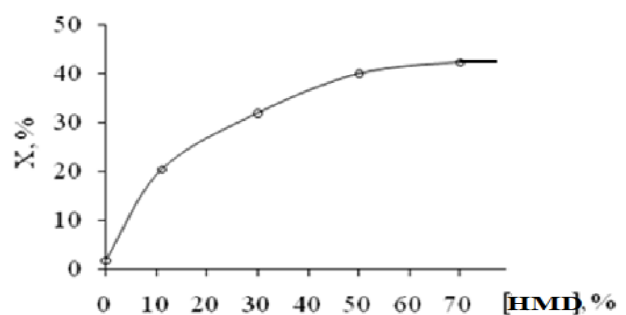


Figure 1. Dependence of the degree of transformation of modified GMD PAN fiber on the reaction time and reaction temperature 353, 363, 373 K, (1, 2, 3 curves, respectively). with $HMDA=50\%$, the bath modulus is 50.

As can be seen from Figure 1, an increase in the reaction time in aqueous solutions at a HMD concentration of 50 wt. % leads to an increase in the degree of conversion of the sorbent, and its maximum value is reached at a temperature of 373 K and at a reaction time of 7-8 hours. The resulting modified fibers do not dissolve in DMF and dimethylacetamide, i.e. in solvents that dissolve the original fiber. The modified fiber swells in DMF, 65 dimethylacetamide, and in aqueous solutions of acids and bases, which indicates the formation of ionogenic groups and crosslinking in fiber macromolecules as a result of modification of HMD. The effect of the concentration of HMD in an aqueous solution on the reaction of chemical modification of nitron was studied at 373 K, in the concentration range from 10 to 70%. The results obtained are shown in Figure 2.



T=373K, $\tau=6$ hours, bath modulus 50

Fig. 2. The effect of the HMD concentration on the degree of transformation of modified PAN fibers

As can be seen from the results presented in Fig. 2, with an increase in the concentration of HMD to 50%, the value of the degree of transformation of ion-exchange fibers increases markedly. A further increase in the concentration of HMD slightly affects the degree of transformation of modified

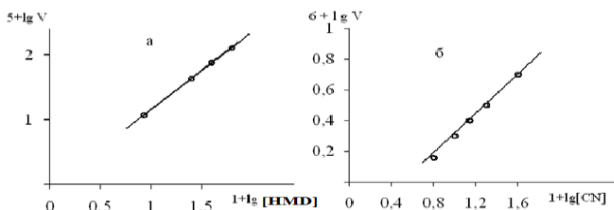


fibers.

2. The reaction orders for the GMD and CN groups of PAN were calculated. For this purpose, a logarithmic dependence of the reaction rate on the concentration of HMD and nitrile groups was constructed (Fig. 3). To find the reaction rate, the degree of transformation of the reaction was calculated based on the SOE of sorbents. The modification process takes place under heterogeneous conditions, where the concentration of substances in the curd phase is not taken into account, however, the nitron fiber has a very high specific surface area and therefore the availability of nitrile groups of the fiber is almost the same as that of the liquid phase.

From the data in Fig.3, the values of the reaction orders for the concentrations of nitrile groups and HMD are found. Which are respectively equal to 0.75 and 1.2. Thus, the reaction rate equation for the interaction of nitron with GMD has the following form: $V = K[\text{ГМД}]^{1,2} \cdot [\text{CN}]^{0,75}$.

The value of the K-reaction rate constant calculated from this equation is $12,55 \cdot 10^{-5} \text{сек} \cdot \text{л/МОЛЬ} \cdot$

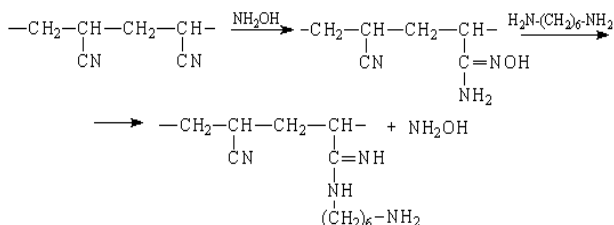


T=373K, $\tau=6$ hours, bath modulus 50

Fig. 3. Logarithmic dependence of the rate of the PAN modification reaction on the concentration of HMD (a) and Cof the N- groups (b).

Considering that HA facilitates the interaction of PAN fibers with amines (Sing, Madeley,1953) the effect of hydroxylamine sulfate supplementation on the interaction of PAN with HMD at various concentrations was studied. The results of these studies are shown in Figure 4.

The effect of HA on the interaction of PAN fiber with GMD can be described by the following scheme:



The presence of HA in the reaction mixture after the modification reaction was completed was confirmed by a qualitative reaction to the presence of HA using $\text{Fe}^{\text{Fe}3+}$.

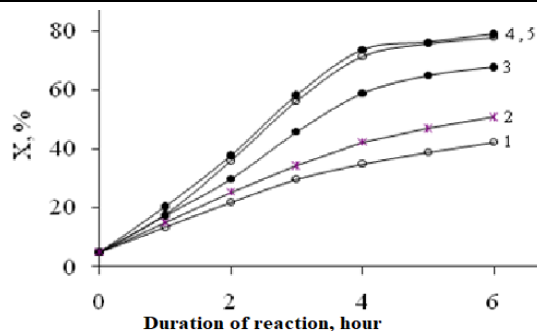


Fig. 4. Based on the degree of conversion of PAN fibers of the KMT duration of the reaction at different GA content in the reaction mixture. T=373K WITH_{GMDA}=50%_{DMF}=5%, the modulus bath 50. 1, 2, 3,4, 5- the HA content in the reaction mixture 0, 1, 2, 3, 5% respectively.

To determine the most acceptable conditions for producing ion-exchange fibers, it is important to study the effect of the bath modulus on the modification process. The dependence of the degree of transformation of nitrile groups of ion-exchange fibers on the bath modulus is shown in Fig.5.

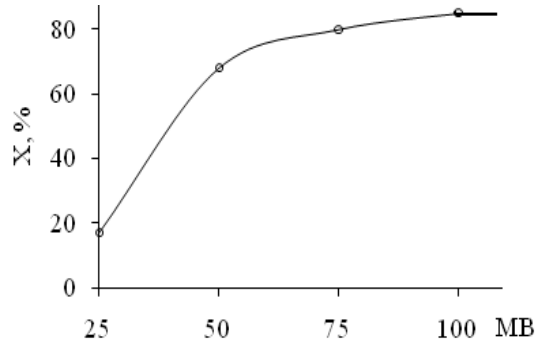


Figure 5. Dependence of the degree of transformation of nitrile groups fibers from the bath module. T=373K, $\tau=6$ hours, with $\text{GMDA}=50\%$, with $\text{HA}=3\%$

From the results shown in Figure 5, it can be seen that with increasing bath modulus, the degree of fiber transformation increases. However, the results obtained show that the most acceptable condition for carrying out the reaction can be considered a modification with a bath modulus of 1: 50.

To reveal the structure of the polymer obtained by the modification of nitron GMD in aqueous solutions, IR spectra were studied and potentiometric titration of the obtained products was performed.

In the IR spectra of the obtained fiber sorbent (Fig. 6), in contrast to the IR spectra of the initial PAN, the intensity of the absorption band decreases at 2250 cm^{-1} , which is related to valence vibrations $=\text{C}=\text{N}$ -groups, a new absorption band appears at $3000\text{-}3600 \text{ cm}^{-1}$ corresponding to the stretching vibrations of the bonds in the $=\text{NH}$ and -NH_2 groups, the



absorption band at 1565 cm^{-1} corresponding to the deformation vibrations of the =NH groups and 1658 cm^{-1} corresponding to the stretching

vibrations of the =NH groups. C=N-bonds (Nakanishi, 1865; Oleinika, 1976).

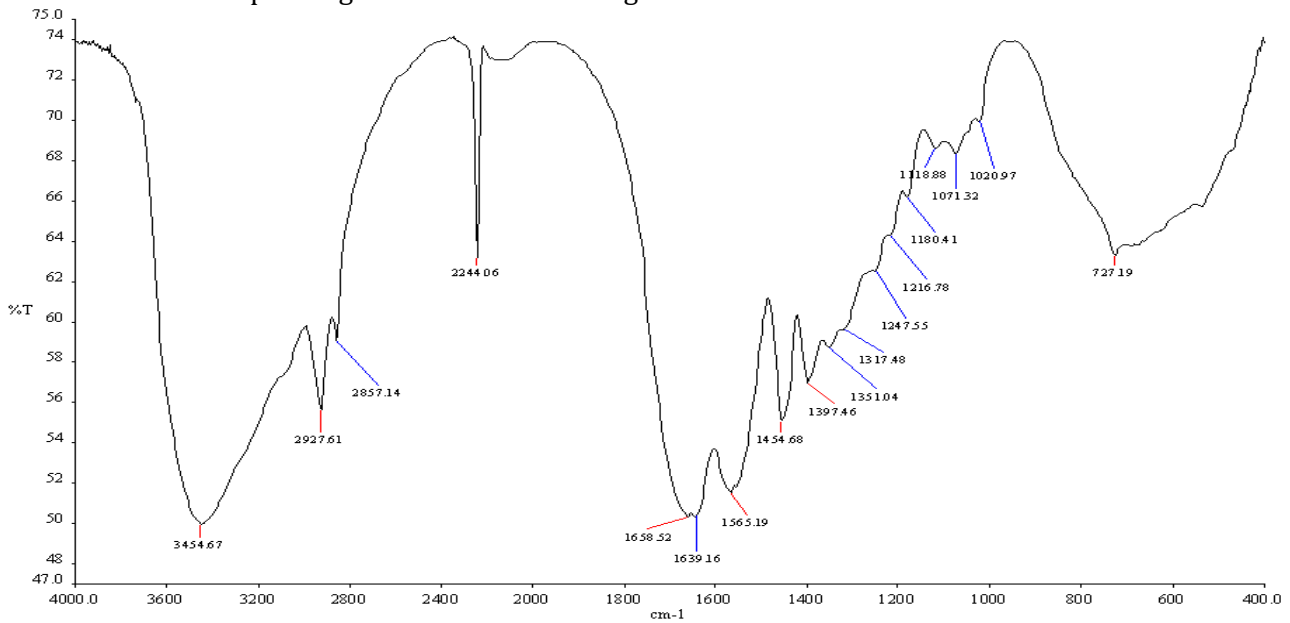


Figure 6. IR spectra of hexamethylenediamine-modified PAN fiber

To confirm the presence of strong base groups in the modified samples, the exchange capacity was determined by NaCl. For this purpose, the fiber sample was kept in 0.1 n NaCl aqueous solution and titrated with 0.1 n HCl solution a day HCl later (Fig. The addition of a 0.1 h NaCl solution to the ionite NaCl resulted in an increase in the pH of the medium from 6.8 to 9.5, which indicates the presence of strongly basic groups in the resulting ionite, which was not observed for hydrazidated fibers. The value of SOY for strongly basic groups calculated from the data in Figure 7 is 1.0 mg-eq/g. The potentiometric titration curves of modified HMD fibers are complex, which indicates the presence of functional groups of different basicity (Fig. 8).

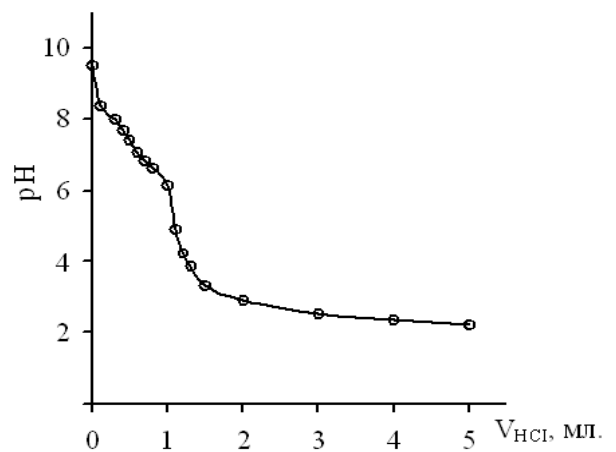


Figure 7. Potentiometric titration of a 0.1 n NaCl solution that has been in contact with the sorbent for 24 hours.

Indeed, processing titration data in the coordinates of the equation Henderson's - Hasselbach (Fig.9) shows the presence of two functional groups with pK_α of 9.3 and 7.2. These values of pK_α can be attributed to amine and amidine groups (Goodman, Gregg, 1960).



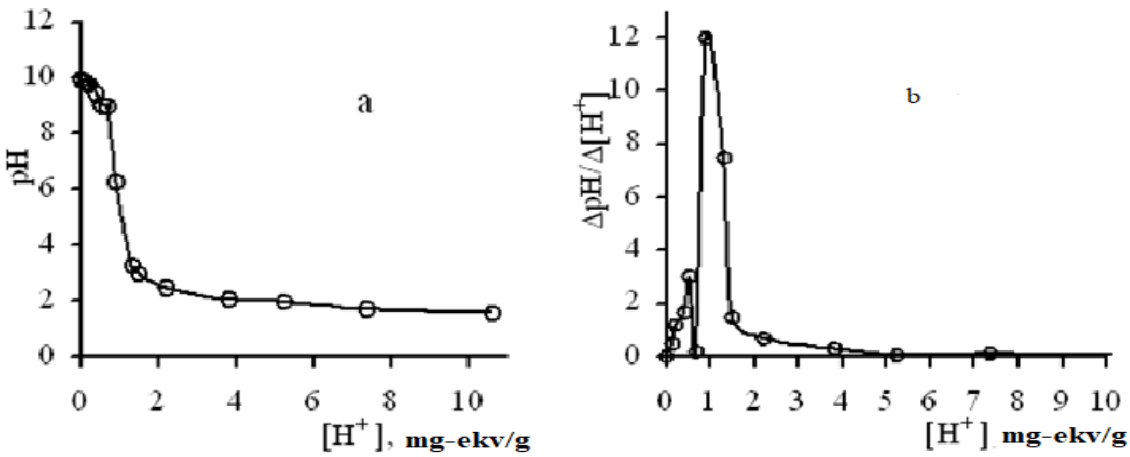


Figure 8. Integral (a) and differential (b) curves of potentiometric titration of modified GMD PAN fiber in an aqueous medium.

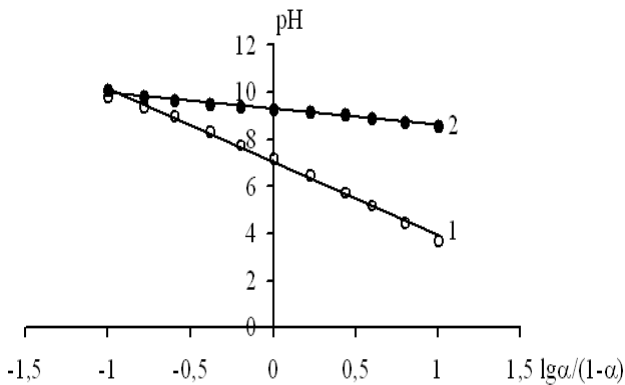


Figure 9. pH dependence on $\lg\alpha/(1-\alpha)$. 1, 2-pK values of 7.2 and 9.3, respectively

As noted above, the modification of the nitron GMD PAN fiber in organic solvents that dissolve the latter only at high temperatures was previously performed. We chose butanol as the organic solvent of HMD, which forms homogeneous solutions with it at wide ratios and temperatures.

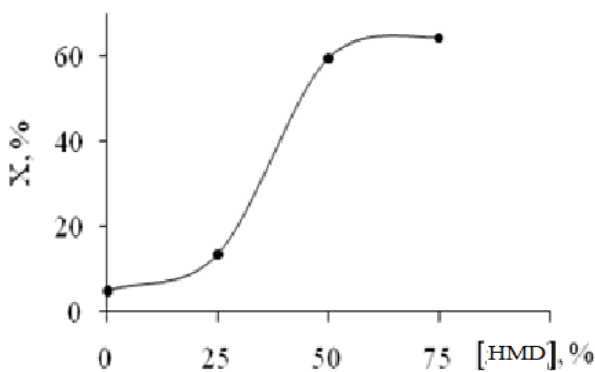


Figure 10. The effect of the HMD concentration on the degree of transformation of the modified PAN fiber. $T=403K$, $t=6$ hours, $[HA]=1.5\%$

The reagent concentration has a significant effect in heterophase processes. Figure 10 shows the dependence of X% of the obtained ionites on the concentration of HMD in butanol.

It can be seen that an increase in the concentration of HMD from 25 to 50% leads to an increase in the degree of polymer transformation by almost 3 times. A further increase in the concentration of the low-molecular-weight product has virtually no effect on the conversion process. Therefore, further studies of the modification of PAN fibers were carried out at a concentration of $[HMD]=50\%$. It should be noted that a similar pattern is also observed in the interaction of PAN with GMD in aqueous media.

Consequently, the addition of HA to the reaction mixture leads to a noticeable increase in the degree of conversion and, accordingly, the value of SOE. Thus, in the absence of a catalyst (HA), the degree of conversion of the sorbent at a temperature of 373 K is $\sim 7\%$, and the addition of HA as a catalyst led to an increase in the degree of conversion of the sorbent to 54%.

Thus, it should be noted that the regularities of the nitron modification reaction in butanol medium practically do not differ from those obtained during the reaction in an aqueous solution of HMD (Greg, Sing 1970).

To characterize the functional groups and chemical structure of the obtained polymers, IR spectra were taken and potentiometric titration of the obtained samples was performed.

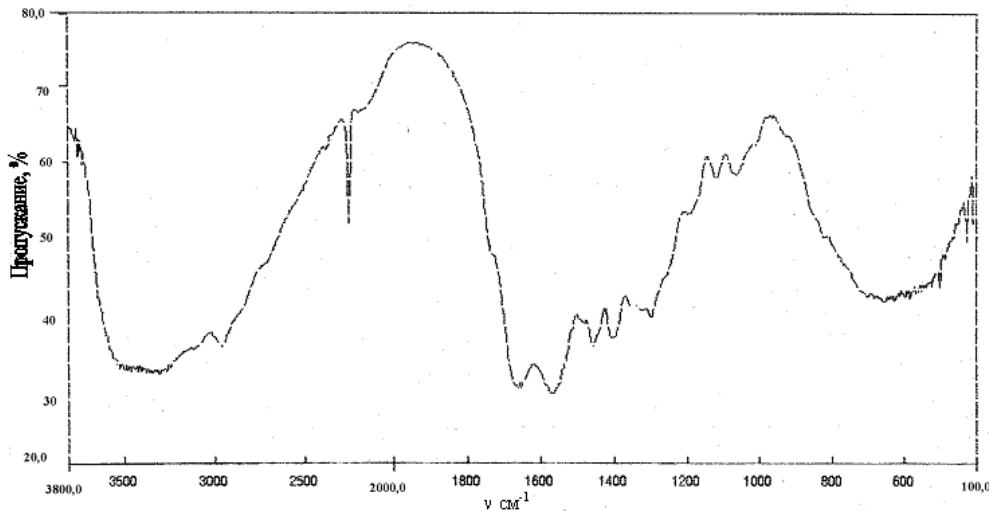


Figure 11. IR spectra of modified PAN fiber with hexamethylenediamine

In the IR spectra of the product of the modification (Fig. 11) a decrease in intensity of the absorption bands at 2244cm^{-1} , related to the stretching vibrations of nitrile groups of PAN fiber, new absorption bands in the region $3300\text{-}3500\text{cm}^{-1}$ corresponding to the stretching vibrations of bonds N-H secondary and primary amino groups, the absorption band at 1544cm^{-1} , which can be attributed to the deformation vibrations of N-H bonds of secondary amino groups, as well as 1673cm^{-1} , corresponding to the stretching vibrations $=\text{C}=\text{N}$ - ties (Nakanishi 1965; Oleinika, 1976)

In Fig. 12 (a, b) shows the results of potentiometric titration of a sorbent obtained by modifying nitron with hexamethylenediamine in butanol solution. Figure 1-2 shows that titration of ionite with acid in the presence of a Na-Cl shows a jump at $[\text{H}^+]$ equal to 1.8 mg-eq/g . There are also two jumps at $[\text{H}^+]$ equal to 0.26 and 1.1 mg-eq/g . This indicates the presence of functional groups of different bases in the ionite.

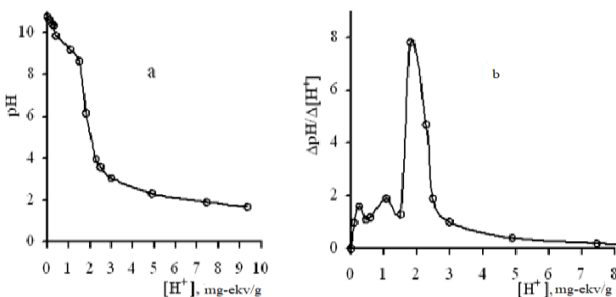


Figure 12. Integral (b) and differential (a) curves of potentiometric titration of modified HMD nitron in butanol medium

Immersion of the resulting ionite in 0.1 n NaCl aqueous solution led to a sharp increase in the pH of the medium (the pH of the solution increases

from 6.5 to 10.71). Potentiometric titration of the NaCl solution with 0.1 n HCl solution (Fig.1-3) was used to determine the exchange capacity of the sorbent for NaCl , which was 1.6 mg-eq/g .

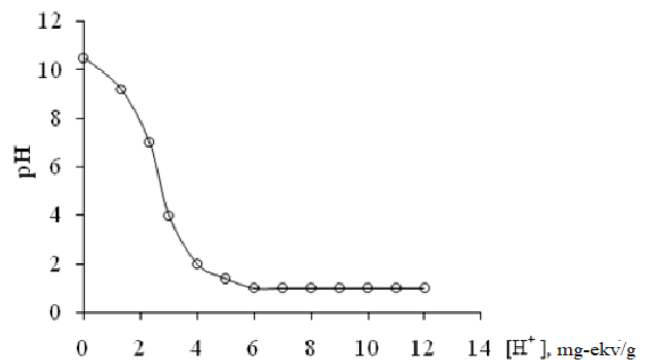


Figure 13. Potentiometric titration of a 0.1 n NaCl solution that has been in contact with the sorbent for 24 hours

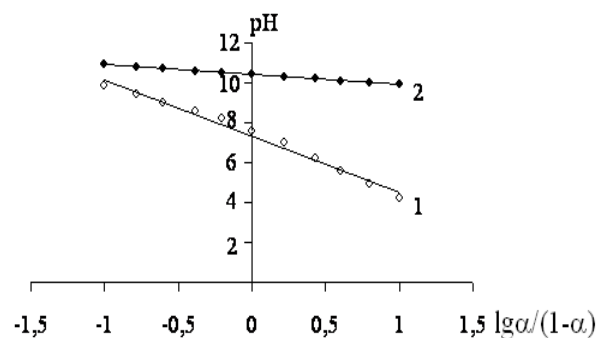


Figure 14. pH dependence on $\lg\alpha/(1-\alpha)$. 1, 2 - values of $\text{pK}_a=7.6$ and 10.4 , respectively

In Fig. 14 shows the potentiometric titration curves in coordinates of the Henderson-Hasselbalch equation. Titration curves were processed separately for each neutralization point (Kuznetsova,1978). As can be seen from Fig. 14 in



the polymer, there are two functional groups with pK_a of 10.4 and 7.6.

Thus, the potentiometric titration data confirm the presence of weak- and strong-base groups in hexamethylenediamine-modified fibers in butanol medium, with corresponding capacities of 1.8 and 1.6 mg-eq/g. Consequently, when modifying nitron fiber in an organic medium, the number of strongly basic groups turned out to be higher than during synthesis in aqueous solutions.

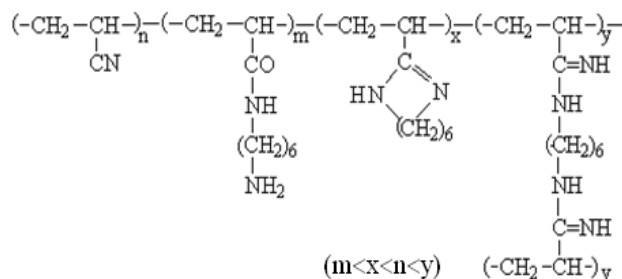
Table 1. Results of determining the functional composition of modified fibers

SOY, mg-eq/g						
of 0.1 n HC I	of 0.1 n NaC I	of 10 % NaC I	of primary amino	groups secondary amino	groups tertiary amino	groups of 0.1 n HSiO ₄
3,7	1,6	1,6	0,4	1,6	3,4	5,4
3,9	1,8	1,8	0,5	1,5	3,9	5,9
4,4	2,0	1,9	0,5	1,7	4,6	6,8

Determination of the functional composition of anion-exchange fibers provides the most complete picture of its chemical structure. Therefore, the amounts of primary -NH₂NH₂, secondary = NH, and tertiary = N - amino groups modified by the method of reverse titration in anhydrous acetic acid medium were determined. and tertiary = N-amino groups modified PAN-fibers. The essence of the method is as follows. The sum of amino groups is determined by the interaction of an anionite sample with an excess of 0.1 n perchloric acid solution in anhydrous acetic acid medium and subsequent determination of the amount of non-reactive perchloric acid by titration with 0.05 n potassium biphthalate solution in the same medium. Tertiary amino groups were determined similarly after preliminary acetylation with acetic anhydride of primary and secondary amino groups. The sum of primary and secondary amino groups was calculated by the difference between the first and second definitions. The content of primary amino groups was determined by binding them with salicylic aldehyde and then determining the sum of tertiary and secondary amino groups using the same method as determining the sum of amines.

Conclusion

Thus, analyzing the results obtained from IR spectra and potentiometric studies, the chemical structure of the product of modification of NMDA nitron can be represented by the following scheme:



Synthesized highly basic anion exchangers are used as carriers for immobilization of various organic reagents and for wastewater treatment from heavy metal ions.

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