A FIBROUS SULFONATED CATION EXCHANGE RESIN
FOR PURIFYING WASTE-WATER FROM ELECTROPLATING
FROM CHROMIUM (III) IONS

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The preparation of sulfonated cation exchange resins based on various types of fibres presents particular interest, since the assortment of fibrous cation exchange resins, which operate over a wide pH range, is extremely limited, while granulated ion exchange resins of this type, for example KU-8 and KU-2-8, are produced on an industrial scale. Mainly, recommendations on the preparation of fibres with strongly acid properties are based either on sulfonation of the fibres with such aggressive reagents as oleum, or sulfuric or chlorosulfonic acid [1, 2], or on treatment with sulfites or bisulfites of the alkali metals, which do not ensure good exchange capacity [3]. Moreover, the use of direct sulfonation methods is not applicable to all carbochain fibres. In particular, as applicable to polyacrylonitrile (PAN) fibres, it appeared advisable to study the possibility of grafting vinyl monomers to them — sodium or potassium p-styrenesulfonate (NASS or KSS). Along with this, there was sense in making an attempt also to solve an important accompanying problem: to evaluate the possibility of strengthening PAN fibre which had been subjected to graft polymerization.

The result of studies in this area was the development of a method of preparing a fibrous sulfonated cation exchange resin [4] PAN-TgrPSSNA, which had the following properties: static exchange capacity \( \text{SEC}_{\text{NaCl}} 2.2 \pm 0.1 \text{ mmole/g} \), \( \text{SEC}_{\text{NaOH}} 3.3 \pm 0.2 \text{ mmole/g} \), degree of swelling 130 \( \pm 10\% \), breaking strength 16.2 \( \pm 0.2 \text{ cN/tex} \), and moisture absorption 11.5 \( \pm 1.5\% \).

It is to be noted that realization of such exchange values with respect to sulfonic acid groups is possible when the graft copolymerization is carried out on preliminarily thermally "cross-linked" (after activation) PAN fibre [4].

We used the method of potentiometric titration [5] to evaluate the ionic strength of the functional groups of the sorbent obtained. Titration of the investigated fibres, taken in the H-form (All-Union State Standard (GOST) 10896-72), was carried out with potassium hydroxide having a concentration of 0.5 mole/liter in a background of potassium chloride solution of the same concentration. The potentiometric titration curve of PAN-TgrPSSNA (Fig. 1) has two inflections, which indicate the presence of two types of acid groups in the ion exchange resin: strongly acid groups — sulfonic acid groups — and weakly acidic groups — carboxyl groups, in distinction from PAN-Tcarb-T (curve 2), which is a partially hydrolyzed PAN fibre (SEC_{NaOH} 2 mmole/g), which is used as a starting material in the graft copolymerization of the p-styrene sulfonates. The apparent ionization constants \( pK_{a} \) of the acidic groups of the sulfonated cation exchange resin and the point of half-neutralization were determined using the Henderson—Hasselbach equation. It should be noted that because of the specifics of the polymeric nature of the ion exchange resin \( pK_{a} \) of its functional groups changes during the titration process. With increase in the degree of neutralization, the density of the charge along the polymer chain increases, which hinders replacement of the protonic hydrogen of the remaining acid groups. To obtain a constant nominal value of \( pK_{a} \), a coefficient \( m \) is introduced into the Henderson—Hasselbach equation, which characterizes the strength of the electrostatic interaction of the functional groups in the polymer [6]:

Fig. 1. Potentiometric titration curves of cation exchange resins PAN-T_{gr}PSSNA (1) and PAN-T_{carb}-T (2).

Fig. 2. Dependence of pH on log [\alpha/(1 - \alpha)] for fibrous cation exchange resins based on PAN: 1) sulfonic acid groups of PAN-T_{gr}PSSNA fibre; 2) carboxyl groups of PAN-T_{gr}PSSNA fibre; 3) carboxyl groups of PAN-T_{carb}-T fibre.

\[ pK'_\alpha = pH - m \log \frac{\alpha}{1 - \alpha} \]

where \( \alpha \) is the degree of dissociation of the ionogenic groups.

Values of the parameter are calculated from the slope of the straight line on the graph of the dependence of pH on log [\alpha/(1 - \alpha)] (Fig. 2). The segments cut off by the lines on the ordinate axis correspond to the values of pK\_\alpha of the functional groups in the cation exchange resin. In Table 1, we give values of pK\_\alpha of the functional groups of the fibrous sorbent PAN-T_{gr}PSSNA.

As follows from the data presented, pK\_\alpha of the sulfonate groups in the cation exchange resin is 1.98, which corresponds to the pK\_\alpha values for strongly acidic resin cation exchange resins and to the second stage in dissociation of sulfuric acid. The pK\_\alpha value for the carboxyl groups of the cation exchange resin is 4.7 and is very close to the pK\_\alpha of the starting PAN-T_{carb}-T fibre on whose basis the graft copolymer was prepared. The decrease in content of carboxyl groups, on grafting the metal styrene sulfonate to the heat-treated carboxylated PAN fibre, from 2.0 to 1.1 mmole/g (Fig. 1) is relative and may be explained as the result of "dilution," since the rise in weight of the samples during the process of graft copolymerization is 100-120%. A certain decrease in acidity of the carboxyl groups in the PAN-T_{gr}PSSNA ion exchange resin as compared with the starting PAN-T_{carb}-T is obviously connected with the effect of the strongly ionized sulfonated groups in the fibre on them.