Modified cationic membranes for water purification, and their selective permeability

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Abstract. Wastewater containing heavy metal ions pose a significant toxicological risk to aquatic ecosystems and humans. The common problem of modern engineering technology is the development of environmentally friendly systems with a closed-circuit and a minimum waste. The ion exchange membrane can significantly reduce the cost of wastewater treatment and provide a high degree of purification.

1. Introduction
One of the main categories of wastewater at the enterprises of machine-building industry are the galvanic wastewater with high content of ions of metals. Membrane separation methods, in particular the reverse osmosis (RO) are ones of the most promising, allowing to significantly reduce the costs of wastewater treatment and water of any required quality [1; 2]. But in baromembrane processes in particular in reverse osmosis high operating pressure of 4 - 5 bar for waters with mineralization up to 2 g/l is required. Research of influence of salt concentrations on the capacity of membranes was conducted on the membrane reverse osmosis EMO-N 45-300. The research was conducted on the laboratory unit membrane separation [3].

1.1. Back osmotic separation solutions
With increasing concentration of sodium chloride in a partial solution permeability and selectivity of the membranes have deteriorated. Curves characterizing the dependence of selectivity membrane concentration of sodium chloride are given on Fig.1.
According to research results, it can be concluded that the reverse osmosis at low concentration of the electrolyte is ineffective. The region of values of concentration of the electrolyte in the initial solution of 0.1 g/l to 2 g/l is an optimal selective permeability for reverse osmosis for separation of the solutions.

1.2 Ion-selective membrane
Ion-selective membranes possess a high degree of separation solutions [4], with both low and high concentration of dissolved salts, as well division of solutions by the use of ion-selective membranes occurs at low operating pressures of 0.1 to 2 bar, depending on the substrate, into which a working layer is applied.

2. Methods
In this paper an ion-selective membrane was obtained, working layer of which is polyaniline (PANI). PANI (Fig. 2) attracts the attention of researchers due to their optical and electrochemical properties, high chemical stability and increased selectivity of migration [5; 6; 7].
In the present work as a matrix for the polymerization of aniline PTFE membranes and nylon with pore dimensions 0.45 microns were used. The modification of the membranes to form on the surface and in the pores of the layer PANI, which is cationic [8], and allows to receive the ion-exchange membranes, not inferior to the selectivity of the reverse osmosis on a number of cations. The synthesis of membrane surface PANY distribution was carried out by polymerization of aniline directly into the matrix of the membranes. Particles of PANY were formed directly in the matrix membrane, as evidenced polymer color changing to dark green. The change in the structure of membranes recorded with the help of a microscope, the image of the structure of the original and modified membranes is presented in figure 3.

3. Results and discussion
The pictures show that the introduction of ammonium persulfate in the membrane aniline saturated (method 2), immediately leads to the flow of oxidation, polymerization, as the concentration of aniline high in it.

The capacity of membranes was determined to pass through the membranes of certain volume of distilled water. The results are represented in table 1.
It is known that the cation-exchange membrane is capable in a greater degree to adsorb cations than anions [9]. To study the selectivity of the original and modified membranes, iron chloride(III), zinc sulfate(II) and chromium ions (GSO), copper sulfate, Nickel ions (GSO), the ions of manganese (GSO), cobalt ions (GSO) solutions were let through membranes. The results are presented in table 2.

The selectivity of the membranes was calculated by the formula:

\[ \varphi = \frac{(C_f - C_p)}{C_f} \]

where \(C_f\) is the concentration of the solute in the initial solution and \(C_p\) is the concentration of dissolved substances in the filtrate[10].
Table 2. Selectivity nylon membranes with working PANI layer

| No. | Indicator | The concentration of ions, mg/l | Selectivity, % |
|-----|-----------|---------------------------------|---------------|
| 1   | Fe        | 5,57, 0,015                     | 99,3          |
| 2   | Fe*       | 5,57, 0,040                     | 99,7          |
| 3   | Cu        | 10,3, 0,092                     | 99,1          |
| 4   | Mn        | 16,5, 5,11                      | 69,0          |
| 5   | Cr        | 1,19, 0,54                      | 48,9          |
| 6   | Cr*       | 1,19, 0,62                      | 55,0          |
| 7   | Ni        | 316, 30,3                       | 90,4          |
| 8   | Zn        | 8,22, 3,38                      | 59,0          |
| 9   | Zn*       | 8,22, 3,95                      | 51,6          |

*nylon membrane with a working layer MRS obtained by method 1

4. Conclusions.

According to the results we can conclude that the original microfiltration membranes with pore size 0.47 microns have no selectivity on ions of metals. Modified polyaniline membranes have high selectivity and permeability to remove metal ions compared to reverse osmosis membranes.

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