

CATION-EXCHANGE MEMBRANES WITH POLYANILINE SURFACE LAYER FOR WATER TREATMENT

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ABSTRACT

Ion-exchange membranes are widely used in modern technologies, particularly in the field of water treatment and make it possible to considerably reduce expenses for wastewater treatment and ensure high degree of purification. Currently, perfluorinated sulfated proton-conducting membranes are often used, such as NAFION and its Russian analogue, MF-4SK based on co-polymerization product of a perfluorinated vinyl ether with tetrafluoroethylene. However, with development of the industry, materials with improved properties and lower cost are required. The aim is to obtain ion-exchange membranes for water treatment from metal ions and to study physico-chemical properties of obtained membranes. In this study, cation exchange composite membranes with modified polyaniline surface layer on nylon and PTFE substrate have been obtained. Changes in the structure of membranes were recorded using a microscope. Throughput capacity of the membranes was determined by passing a certain volume of distilled water through the membrane. The experiment intended to determine electivity of membranes was performed by passing a certain volume of metal salt solutions of a known concentration, after which the filtrate was collected. Concentrations of the studied metal ions in the original solution and in the filtrate were determined by the method of atomic adsorptive spectrometry with electro thermal atomization "Quantum Z.ETA". Prepared highly selective ion exchange membranes. Properties of modified membranes, such as selective permeability and ion-exchange capacity have been determined. The membranes feature high selectivity for heavy metal ions. Moisture-retaining power and swelling ability of the membranes have been studied. Selectivity of the membrane to heavy metal ions is between 70 and 99%. Ion-exchange capacity of the obtained nylon polyaniline membrane is not inferior to some commercially available cation-exchange membranes. Use of the modified membranes in the stage of tertiary wastewater treatment will ensure achieving established standards.

Keywords: Exchange Capacity, Selectivity, Membrane, Metal Ions, Polyaniline

1. INTRODUCTION

Membrane-based separation methods, ion-exchange membranes in particular, are most promising and make it possible to considerably reduce expenditures for wastewater treatment and obtain water of any required quality (Sudilovskiy, 2007).

Nafion perforated sulfocationite ion exchange membranes (Polycom, 2013) manufactured by Dupont company are known, as well as their domestic analogue, the MF-4SK membrane (Falina and Berezina, 2010), featuring high proton conductivity. Disadvantages of such membranes are insufficiently high proton conductivity, which prevents their use for

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intensification of treatment processes, separating various solutions and spontaneous concentration of solutions without applying electric potential and reduces their efficiency in water treatment.

In this respect, the most promising way is to create composite membranes that feature high permeability and cation conductivity of substances. In practice, surface layer of the membrane is often modified in order to increase membranes performance (Ma *et al.*, 2001) and to ensure or increase selectivity to protons (Li and Barbari, 1994) and other ions (Sata *et al.*, 1999; Tan *et al.*, 2002).

Change of transport properties in such systems is observed mainly due to sorption processes in cation exchange group. In this respect, we propose to view hydrated zirconium oxides as dopants, as well as polyaniline that have a nitrogen atom in its composition, which is capable of absorbing protons (Ghosh *et al.*, 1999).

The process of charge transferring in composite membranes modified with polyaniline depends on the degree of membrane surface coating with polyaniline, which enhances interphase transfer of charge. Charge transfer in the volume of the membrane depends on the level of Polyaniline Intercalation (PANI), which varies depending on the used method of polymerization (Asif *et al.*, 2011). This study shows relationship between charge transfer mechanism in PANI composite membranes and the degree of PANI content in the membrane.

PANI attracts researchers' attention because of its optical and electrochemical properties, as well as high chemical stability. Some cation-exchange materials with PANI surface layer are characterized by high selectivity of transfer (Ivanov *et al.*, 2004). In order to obtain a conducting form of PANI, it is doped with various acids.

In work (Nagarale *et al.*, 2004) composite membranes were obtained by chemical polymerizing polyaniline with a thin layer on the surface of an anion-exchange membrane in presence of high concentrations of ammonium persulphate. According to results of experiments, we have come to the

conclusion that these ion-exchange membranes may be used for separating electrolytes.

The structure of a composite membrane modified with polyaniline was studied in work (Tan *et al.*, 2003). A cation-exchange Neosepta CMX membrane pretreated with 0.5 M NaCl solution was used as the substrate. The membrane was kept in aniline hydrochloride solution followed by polymerization with ammonium persulphate. Using X-ray Photoelectron Spectroscopy (XPS), spectra of the absorption were obtained, basing on which we have made a conclusion that CMX-PANI composite membrane has three layers. In the outer layer, PANI chains are doped with chlorine ions, in the middle layer, they are doped with sulphonate groups; the inner layer is the substrate made of a CMX membrane.

PANI (**Fig. 1**) attracts researchers' attention because of its optical and electrochemical properties, as well as high chemical stability and increased transfer selectivity (Ivanov *et al.*, 2004).

Ion-selective membranes have high solution separation ability, both with low and high concentrations of dissolved salts; separation of solutions using ion-selective membrane occurs in low operating pressures of 0.1-2 bar, depending on the substrate, onto which the working layer is applied.

2. MATERIALS AND METHODS

In this study, we obtained ion-selective membranes with Polyaniline (PANI) as a working layer. Studies were performed on a laboratory membrane separation installation (Fazullin *et al.*, 2012).

PTFE and nylon membranes with pore size 0.45 μm . were used as the matrix for polymerization of aniline. Modification of membranes with forming PANI layer on the surface and in the pores, which is a cation-active, makes it possible to obtain ion-exchange membranes that are not inferior to the reverse osmotic ones in selectivity by the number of cations.

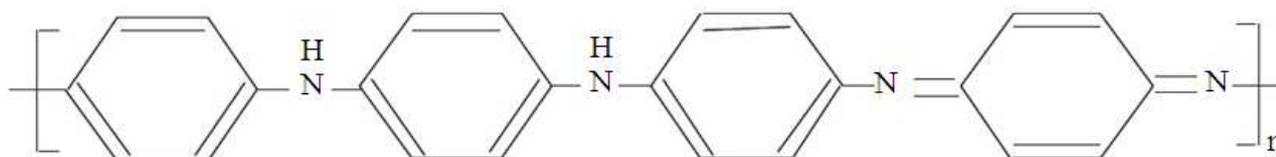


Fig. 1. Structural formula of polyaniline

Membranes with PANI surface distribution were synthesized by polymerization of aniline directly in the matrix of the membranes. In the former case, the membrane had been pre-treated for 5 h in a solution of ammonium per sulfate (method 1), in the latter, it had been kept in the solution of aniline hydrochloride for 5 h (method 2). After that, the membrane was placed in a solution of the second reagent. PANI particles formed directly in the matrix of the membrane, which fact was evidenced by changing the polymer color to dark green. Duration of membrane processing with each reagent was 5 minutes with constant stirring with a laboratory shaker. Concentration of the solutions was 1 mol/L each.

Changes in the structure of membranes were recorded using a microscope. Production of the membranes was determined by passing a certain volume of distilled water through the membrane. One of membrane characteristics is selectivity. Through the membranes, a certain amount of metal salts solutions of known concentration was passed under vacuum. Concentrations of the studied metal ions in the original solution and in the filtrate were determined by the method of Atomic Adsorptive Spectrometry (AAS) with electrothermal atomization "Quantum Z.ETA" Selectivity was calculated from the results obtained by the formula:

$$\phi = (C_f - C_p) / C_f$$

where, C_f is concentration of metal ions in initial solution and C_p is concentration of the Permeate in the filtrate.

In order to study membranes swelling, samples with diameter 45 mm were placed in distilled water and membrane weight was measured using analytical weigher with accuracy 0.0001 grams before and after the experiment.

Exchange capacity was determined under dynamic conditions by passing certain amounts of model solutions with known concentrations of cations through the membrane. Using the AAS method, concentration of cations in the filtrate was determined and weight of cations absorbed by the membrane was calculated. Filtering was continued till selectivity decreased to 10%. Exchange capacity was calculated per 1 gram of the membrane.

After each experiment, the membrane was regenerated by placing it in 3% solution of hydrochloric acid followed by rinsing it in deionized water.

3. RESULTS

Structures of the original and the modified membranes are shown in **Fig. 2**.

Main properties of ion-exchange membranes are indicators such as exchange capacity, swelling, permeability and selectivity.

Permeability and specific permeability of the membrane calculated basing on the results of the experiment is shown in **Table 1**. After applying PANI layer to the surface of the membrane using the first method, its permeability reduced by 2.2-3.5% as compared to initial membrane, when the second method was used and permeability dropped by 5.6-15.7%. Permeability of the initial membrane decreases due to arrangement of PANI chains both in the surface and in the pores of the membranes. Hence, initial pore size of 0.47 μm after applying PANI layer may correspond to membrane pore size of nylon-PANI membrane of 0.45 μm and to membrane pore size of PTFE-PANI membrane of 0.4 μm . By adjusting monomer concentration during polymerization, one can obtain modified membranes with various pore sizes.

In order to examine selectivity of initial and modified membranes, solutions of heavy metal salts (Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Cr^{3+}) were passed through the membranes. After each experiment, the membrane was regenerated by placing it in hydrochloric acid solution in order to set the membrane to the hydrogen form. The results are shown in **Table 2**.

From the results it can be concluded that the initial microfiltration membrane with 0.47 μm pore size does not feature selectivity for metal ions. Membranes obtained using the second method feature selectivity higher than that of the membranes obtained using the first method, with respect to metal ions. Therefore, when membranes are obtained using the second method, membrane saturation with aniline is more intensive. For some metals (Cr, Co, Cd, Zn), selectivity is not high, in spite of their low concentration in the initial solution. Apparently, this is caused by different degrees of metal salts solubility, depending on water pH value.

Figure 3 shows results of the experiment for selectivity of a nylon-PANI membrane in dynamic conditions by passing iron ($^{3+}$) and manganese ($^{2+}$) salts solutions with low and high concentrations of the starting solution through the membrane. In case of low initial concentrations, selectivity gradually drops to 55%, after which selectivity stabilizes at the 50% level. Selectivity for iron ions is higher than that for

manganese. Evidently, part of iron ions is tied in the form of colloids, since the pH value of the solution is 3.5-4.5 pH units, thus the retention ability of a nylon-PANI membrane is limited not only by ion exchange, but also by retention of colloids in membrane pores. Dynamics of membrane selectivity at higher concentrations of manganese ions in **Fig. 3b** shows a sharp drop to 3% already after passing of more than 150 ml of the solution.

Some studied properties of modified membranes, compared to ion-exchange membranes from domestic and foreign manufacturers are listed in **Table 3**.

Swelling and absorptive capacity of the membranes are essential characteristics of ion-exchange membranes that determine availability of ion-exchange groups and the speed of reaching ion-exchange equilibrium. According to research results and literature, the lowest values of swelling in a solution of metal salts have PTFE-PANI membranes, followed by MF-4SK and Nafion-117 anion-exchange membranes.

The highest swelling value corresponds to nylon-PANI cation exchange membranes and RALEX AM (H). As a result of the modification, swelling of nylon membranes increased by 4%, PTFE membranes after the modification became hydrophilic.

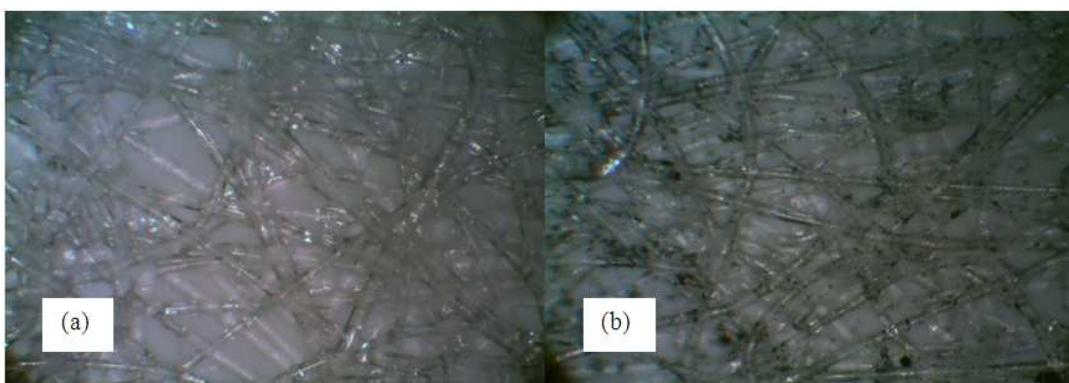


Fig. 2. Structure of a PTFE membrane: (a) Original PTFE membrane, (b) PTFE membrane modified with PANI layer using method 2 (zoom 200 times)

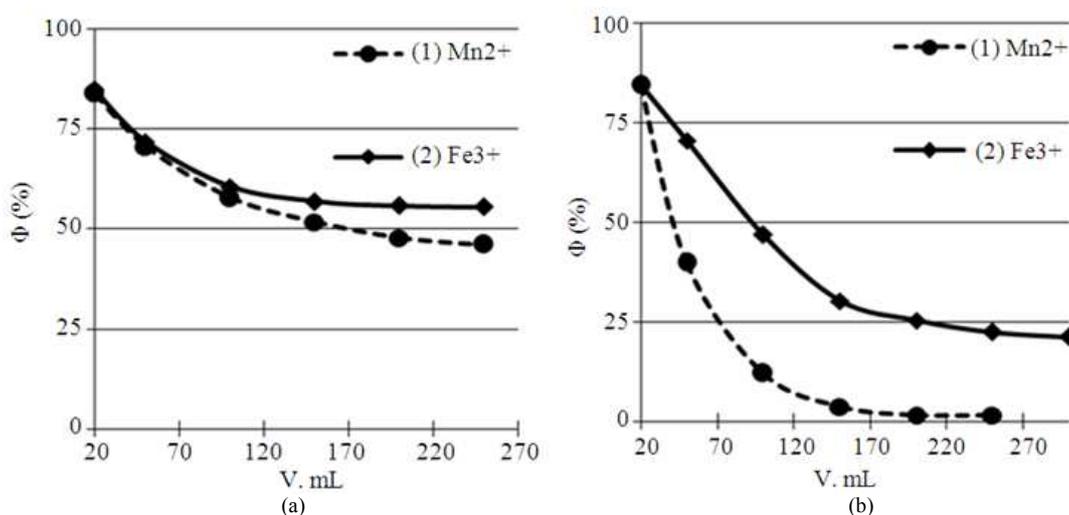


Fig. 3. Curves of a nylon-PANI membrane dynamic selectivity: (a) Initial concentrations of manganese ions 0.041 mg L^{-1} , iron- 0.025 mg L^{-1} ; (b) manganese- 95.5 mg L^{-1} , iron- $5, 94 \text{ mg L}^{-1}$ in the solution

Table 1. Average permeability of membranes for distilled water

Membrane	Permeability, l/h	Specific permeability, l/h
PTFE*	2.29	0.144
PTFE-PANI (method 1)	2.21	0.139
PTFE-PANI (method 2)	1.93	0.121
Nylon	5.04	0.317
Nylon-PANI (method 1)	4.93	0.310
Nylon-PANI (method 2)	4.76	0.299

Table 2. Selectivity of a nylon-PANI membrane

#	Indicator	Ion concentration, mg/L		Selectivity (%)
		Initial	After treatment with a membrane	
1	Fe ^{3+*}	5.57	0.015	99.3
	Fe ³⁺		0.040	99.7
2	Cu ²⁺	10.30	0.092	99.1
3	Mn ²⁺	191.00	31.700	80.2
4	Cr ^{3+*}	1.19	0.620	48.9
	Cr ³⁺		0.540	55.0
5	Ni ²⁺	316.000	30.300	90.4
6	Co ²⁺	0.025	0.006	76.0
7	Cd ²⁺	6.590	2.030	69.2
8	Zn ²⁺	8.220	3.380	59.0
9	Zn ^{2+*}		3.950	51.6

Table 3. Physico-chemical properties of membranes in swollen state

Membrane	Membrane type	Thickness, cm	Exchange capacity, mmol/g	Swelling by weight, %
MF-4SK	homogeneous perfluorinated sulfocationite	0.033	0.56	20.0
MK-40	heterogeneous sulfocationite	0.060	1.55	30.0
RALEX AM(H) (RM, 2012)	heterogeneous quaternary ammonium reinforced with polyethylene	0.070	1.80	<60.0
Nafion-117	homogeneous perfluorinated sulfocationite	0.0170	0.56	20.0
Nylon-PANI	homogeneous polyaniline on a nylon substrate	0.0125	0.59	59.0
PTFE-PANI	homogeneous polyaniline on a PTFE substrate	0.0050	0.17	3.6
Phenex AF0-0504 Nylon	nylon	0.0125	0.00	55.0
Phenex AF0-0514 PTFE	PTFE	0.0050	0.00	<0.1

4. DISCUSSION

In work (Ivanov *et al.*, 2004) it was said that PANI in the form of emeraldine has a block structure characterized by alternating quinoneimine and amine units. In the semi-oxidized state, emeraldine has electronic conductivity caused by transfer of non-localized electrons along the chain of conjugated bonds. Formation of this form gives PANI form gives an unpainted transparent MF-4SK membrane green color, in our work, a white nylon membrane also became green.

It is known that a cation exchange membrane can absorb cations more than anions (Lysova *et al.*, 2011). Cation-exchange membranes are relatively well saturated

with aniline hydrochloride (if the form of phenyl ammonia cation), but is much worse saturated with oxidant, persulphate anions. As it was shown in the research of diffusion permeability of reagent solutions through the initial MF-4SK membrane, diffusion of even sufficiently large cation of phenyl ammonia occurs much faster, which is caused by its positive charge. So, selectivity for some metal ions is equal to 48-99%.

Selectivity for iron ions is high, according to the source (Svyatohina, 2002), solubility of iron salts in the pH range between 4 and 12 is minimal and for manganese salts, the minimum solubility is in the pH range between 9 and 12, which ensures formation of colloids in solutions within these pH ranges. Same as

in work (Volkov *et al.*, 2008) in the example of track-etched membranes, fundamental role belongs to such factors as changing pores shape to conical. In our work, pores may be narrowing due to absorption of volumetric polyaniline molecules.

According to data (Falina and Berezina, 2010), compared to the initial MF-4SK membrane, conductivity of membranes modified with PANI is higher by 25% on the average. And obtained PANI-nylon membranes in terms of conductivity are not inferior to some commercially available ion-exchange membranes.

5. CONCLUSION

Cation-exchange membranes have been obtained by polymerizing aniline in the structure of nylon and PTFE membranes. Physicochemical properties of the membranes have been determined. Membranes selectivity has been proven for cation ions in test solutions of metal salts. However, in case of high concentrations of metal ions, in dynamic conditions, selectivity drops abruptly. Ion-exchange capacity of the obtained nylon-PANI membrane is not inferior to some commercially available cation-exchange membranes.

Use of the modified membranes in the stage of post-treatment of electroplating wastewater and lubricating-and-cooling wastewater will make it possible to reach established performance standards for discharging contaminants into water basins.

In the future we plan to study properties of obtained cation-exchange membranes, in particular, such factors of the initial solution as temperature, pH, concentration. Study of a nylon-PANI membrane structure, types of molecular bonds formed as a result of aniline hydrochloride polymerization. Obtaining an anisotropic ion-exchange membrane is also planned.

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7. REFERENCES

Asif, A., M. Margaret and A. Darrell, 2011. Surface and charge transport characterization of polyaniline-cellulose acetate composite membranes. *J. Phys. Chem.*, 115: 1652-1661. DOI: 10.1021/jp109455m

- Volkov, V.V., B.V. Mchedlishvili, V.I. Roldugin, S.S. Ivanchev and A.B. Jaroslavtsev, 2008. Membrane and nanotechnology. *Russian Nanotechnol.*, 3: 656-687.
- Ghosh, M., A. Barman, A.K. Meikap, S.K. De and S. Chatterjee, 1999. Erratum to: Hopping transport in HCl doped conducting polyaniline. *Phys. Lett., A*, 263: 138-148. DOI: 10.1016/S0375-9601(99)00752-5
- Ivanov, V.F., O.L. Gribkova, K.V. Cheberyak, A.A. Nekrasov and V.A. Tverskoy *et al.*, 2004. Matrix synthesis of polyaniline in the presence of poly-2(acrylamido-2-methyl-1-propan)-sulfonic acid. *Electrochemistry*, 40: 299-304.
- Li, R.H. and T.A. Barbari, 1994. Protein transport through membranes based on toluene diisocyanate surface-modified poly (vinyl alcohol) gels. *J. Membrane Sci.*, 88: 115-124. DOI: 10.1016/0376-7388(93)E0182-J
- Lysova, A.A., I.A. Stenina, S.V. Dolgopopov, Y.G. Gorbunov and N.A. Kononenko *et al.*, 2011. Obtaining composite MF-4SK membranes with anisotropic distribution of polyaniline and asymmetry of ion transport therein. *High-Molecular Compositions, Series*, 53: 130-136.
- Ma, H.M., D.R. Nielsen, C.N. Bowman and R.H. Davis, 2001. Membrane surface modification and backpulsing for wastewater treatment. *Separat. Sci. Technol.*, 10: 1557-1573. DOI: 10.1081/SS-100103888
- RM, 2012. Heterogeneous ion-exchange membranes Ralex. RALEX membranes.
- Nagarale, R.K., G.S. Gohil, V.K. Shahi, G.S. Trivedi and R. Rangarajan, 2004. Preparation and electrochemical characterization of cation-and anion-exchange/polyaniline composite membranes. *J. Colloid Interface Sci.*, 277: 162-171. PMID: 15276053
- Polycom, 2013. Perfluorinated Nafion Ion Exchange Membranes.
- Sata, T., Y. Ishii, K. Kawamura and K. Matsusaki, 1999. Characterization of sulfonated cation-exchange membranes modified with polyaniline. *J. Electrochem. Society*. 146: 585-585.
- Svyatohina, V.P., 2002. Study of heavy metal ions reagent treatment method. Ufa State Aviation Technical University, Ufa.
- Sudilovskiy, P.S., 2007. Development of a combined flotation-membrane process for wastewater purification from heavy metals. Abstract from thesis of Candidate of Engineering Sciences, D. Mendeleev University of Chemical Technology of Russia, Moscow.

- Tan, S., A. Laforgue and D. Bélanger, 2002. Characterization of a cation-exchange/polyaniline composite membrane. *Electrochem. Solid-State Lett.*, 19: 744-751. DOI: 10.1021/la0263054
- Tan, S., A. Laforgue and D. Bélanger, 2003. Characterization of sulfonated cation-exchange membranes modified with polyaniline. *Fuel Chem. Division Preprints*, 48: 386.
- Fazullin, D.D., G.V. Mavrin and R.G. Melkonian, 2012. Factors influencing barometric membrane processes of separating aqueous solutions. *Industrial ecology: Interindustry scientific-practical magazine (FSUE All-Russian Research Institute of Inter-Industry Information)*, 4: 65-70.
- Falina, I.V. and N.P. Berezina, 2010. Diffusion of solutions in the course of the matrix synthesis of composite membranes MF-₄SC-polyaniline and their transport properties. *Polymer Sci. Series B*, 52: 244-251. DOI: 10.1134/S1560090410030176