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MODIFICATION OF ULTRAFILTRATION POLYMERIC MEMBRANES WITH DISPERSED OXIDE NANOPARTICLES

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Organic-inorganic membranes containing the nanoparticles of hydrated zirconium dioxide and BaFe₁₂O₁₉ magnetic nanoparticles were prepared. The nanoparticles were inserted into polymer matrices. Ultrafiltration membranes were used as a polymer substrate. These materials consist of macroporous layer (non-woven polyester) and ultrathin active layer (polysulfone or polyacrylonitrile). Morphology of the membranes was investigated using scanning electron microscopy. It was established that inorganic nanoparticles form aggregates, a size of which is up to 20 nm in active layer and up to 2 μm in macroporous fibrous support. Larger aggregates are formed in the absence of a magnetic constituent (up to 5 μm). Fractal analysis showed the diffusion-limited aggregation model of particle formation. The inorganic particles form a «secondary active layer» inside the polymer pores: this layer determines water flux and rejection ability of the membrane. A thinner «secondary active layer» is formed in the polymer matrix containing smaller pores. The prepared membranes were tested for filtration of sugar beet juice. The modification was shown to improve the ability of the membranes to reject proteins. Due to smaller particle size, the membrane containing BaFe₁₂O₁₉ shows the liquid flux of 4.3·10⁻⁷–5.7·10⁻⁷ m³m⁻²s⁻¹ at 2 bar and the rejection towards vegetable protein of 55–87%. Regarding the membranes that do not include magnetic nanoparticles, these values are 3.8·10⁻⁷–5.5·10⁻⁷ m³m⁻²s⁻¹ and 38–77%, respectively.

Keywords: nanoparticles, membrane separation, magnetic nanocomposite, hydrated zirconium dioxide, barium ferrate.

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Introduction

Ultrafiltration technology is widely used for removal of colloidal particles from ground and brackish water, wastewater and seawater [1]. This stage of water treatment is before reverse osmosis to prevent membrane fouling. Ultrafiltration is also applied in beverage industry, for instance, for milk skimming, effluents treatment, etc. The main problem of filtration is a decrease of membrane permeability due to fouling by organics. This is especially important when liquids of biological origin are processed. In general, species of organic substances, microorganisms, iron oxide and silicon

dioxide significantly decrease the duration of filtration. The membranes need chemical regeneration that involves aggressive reagents. Frequent regeneration reduces a lifetime of the membranes. One of the ways to overcome these disadvantages is to enhance hydrophilicity of polymer membranes. Commonly, nanoparticles of inorganic ion-exchangers are used for modification of polymers. A number of inorganic compounds are applied for modifying [1]: zirconium hydrophosphate [2] (the attempt to use these materials as a filler for electromembrane processes is known [3]), moreover, they are used for modification of ion exchange resins

[4]), silica [5], hydrated zirconium [2] or iron oxide [6]. This approach allows enhancing liquid permeability and anti-fouling ability without sufficient changes of membrane structure.

Magnetic particles belong to other type of modifier that improves functional properties of polymer membranes. The membrane containing magnetic Fe_3O_4 nanoparticles and graphene oxide particles show high flow of pure water and high degree of rejection (up to 83.0%) [6]. Membranes containing iron nanoparticles can be used to remove copper and lead ions from wastewater [6,7]. Adsorption capacity increases due to improved hydrophilicity, on the one hand, and nucleophilic functional groups on the surface of nanoparticles, on the other. A nanocomposite membrane exhibits minimal interaction with whey protein due to its higher hydrophilicity, which leads to a polar-non-polar interaction between membrane surface and protein. This depresses membrane fouling.

The membranes modified with magnetic nanoparticles show an increase in water flow due to the changes in the average pore radius, porosity and hydrophilicity of the membranes. The membrane surface roughness and hydrophilicity are considered main factors, which minimize membrane fouling.

The aim of this work was to prepare organic-inorganic membranes containing inorganic modifier, particularly magnetic one, and establish the effect of the filler on the separation ability of composite membranes and their stability against fouling.

Experimental

Modification of membranes

Ultrafiltration membranes (produced by the Institute of Physico-Organic Chemistry of the National Academy of Science of the Republic of Belarus) were used as polymer substrates. These materials consist of macroporous substrate (non-woven polyester) and ultrathin active layer (polysulfone (PS) or polyacrylonitrile (PAN)). Further, the membranes are marked according to the polymer forming the active layer. PS and PAN reject globular proteins, the molecular mass of which is 100 and 50 kDa, respectively.

Magnetic nanoparticles based on M-type barium ferrite with hexagonal structure $\text{BaFe}_{12}\text{O}_{19}$ were used. This material is environmentally friendly and chemically stable, it possesses magnetic characteristic (maximum magnetic induction $B_s=0.30$ T and coercive force $H_c=430$ kA/m). $\text{BaFe}_{12}\text{O}_{19}$ is widely used for permanent magnets and magnetic recording media [8]. These magnetic nanoparticles (MNP) were synthesized according to the procedure described elsewhere [9]. In order to

provide their fixation in membrane pores, hydrated zirconium dioxide (HZD) was used. First of all, a sol of insoluble zirconium hydroxocomplexes was obtained from a 0.25 M ZrOCl_2 solution similarly to procedure described in ref. [10]. MNPs were dispersed in zirconium sol and treated with ultrasound at 30 kHz. The membranes were degassed in deionized water under vacuum conditions at 343 K and impregnated with suspension of MNP in sol. Then, HZD and MNP were coprecipitated directly in the polymer with a 0.1 M NH_4OH solution. The membrane was dried at 50°C and cleaned with ultrasound to remove the precipitate from its outer surface. This approach, which involves impregnation of a membrane with the suspension of insoluble compounds followed by precipitation, was applied earlier to modify ceramics [11]. For comparison, the membranes containing only HZD were prepared. In this case, the polymer matrix was impregnated with zirconium-containing sol.

Morphology of the membranes was investigated using scanning electron microscopy (SEM). Fractal dimension of aggregates in macroporous support was determined by methods of cube counting, triangulation and power spectrum analysis [12].

Before the application of transmission electron microscopy (TEM), the active layer was separated from the macroporous substrate and milled in the medium of liquid nitrogen.

Testing of membranes

The experimental installation for filtration consisted of typical elements for baromembrane separation (magnetic pump, manometer and rotameter). A divided two-compartment flow-type cell was used. An effective area of the membrane was $2.82 \cdot 10^{-3}$ m². Before the measurements, the membrane was pressed by means of pumping deionization water at 4 bar. The effluent volume was measured after predetermined time. Filtration was stopped when the constant flow rate through the membrane was achieved.

Tap water containing 1.0 and 0.2 mol dm⁻³ Ca^{2+} and Mg^{2+} , respectively, was used for testing. The content of ions in permeate was determined by means of atomic absorption technique (SP9 Pye Unicam). Filtration was carried out at 2 bar. Sugar beet juice (fabricated by «Salyvonkivskyy sugar factory») was also applied for investigations. Before testing, juice was diluted by 10 times. The content of vegetable proteins (VP) was determined in permeate using Coomassie brilliant blue G-250 dye [13]. Selectivity of membranes (ϕ), i.e. rejection of species was estimated by the following equation [1]:

$$\varphi = \left(1 - \frac{C_p}{C_f} \right) \cdot 100\%, \quad (1)$$

where C_p and C_f are the concentration of feeding solution and permeate, respectively.

Results and discussion

Morphology of membranes

As an example, typical SEM images of the pristine PAN membrane are given in Fig. 1, a and b. It is seen that the microporous support consists of sprung fibers, the size of which is 10–20 μm . The active layer is attached to the support forming the membrane that is able to reject colloidal particles. During HZD precipitation, the particles, the size of which is up to 5 μm , are formed in the support when MNP are absent (Fig. 1,c). In the case of MNP in the sol, the size of aggregate is up to 2 μm (Fig. 1,d). Analysis of fractal dimension gives the value of 2.4–2.7 indicating diffusion as a limiting step in the course of aggregate formation. The mechanism involves sticking of particles to a small cluster (diffusion-limited aggregation (DLA model)) [14]. In our case, MNP particles are evidently additional precipitation centers.

The flux of particles (J) during precipitation is determined by the Fick's law:

$$J = D \text{ grad}C, \quad (2)$$

where D and C are the diffusion coefficient and the concentration of particles being formed, respectively.

The formation of smaller particles causes an increase in their concentration gradient, which moves from the outer sides of a membrane to its middle together with a precipitator. When deposition occurs, higher concentration gradient is realized for smaller particles. On the other hand, magnetic nanoparticles provide local magnetic fields inside the membrane. As found for solutions of NaCl, KCl, CaCl₂ and Na₃PO₄, their conductivity increases under the influence of magnetic field [15]. The reason is suggested to be the structuring of water in hydrate shells of ions; this result in an increase in their diffusion coefficient. It is possible to assume that bonded water around the particles is also structured promoting faster diffusion. Enhancement of particle movement affected by magnetic field leads to the formation of smaller aggregates comparing with the case of MNP absence.

TEM image of the active layer (Fig. 2,a) shows

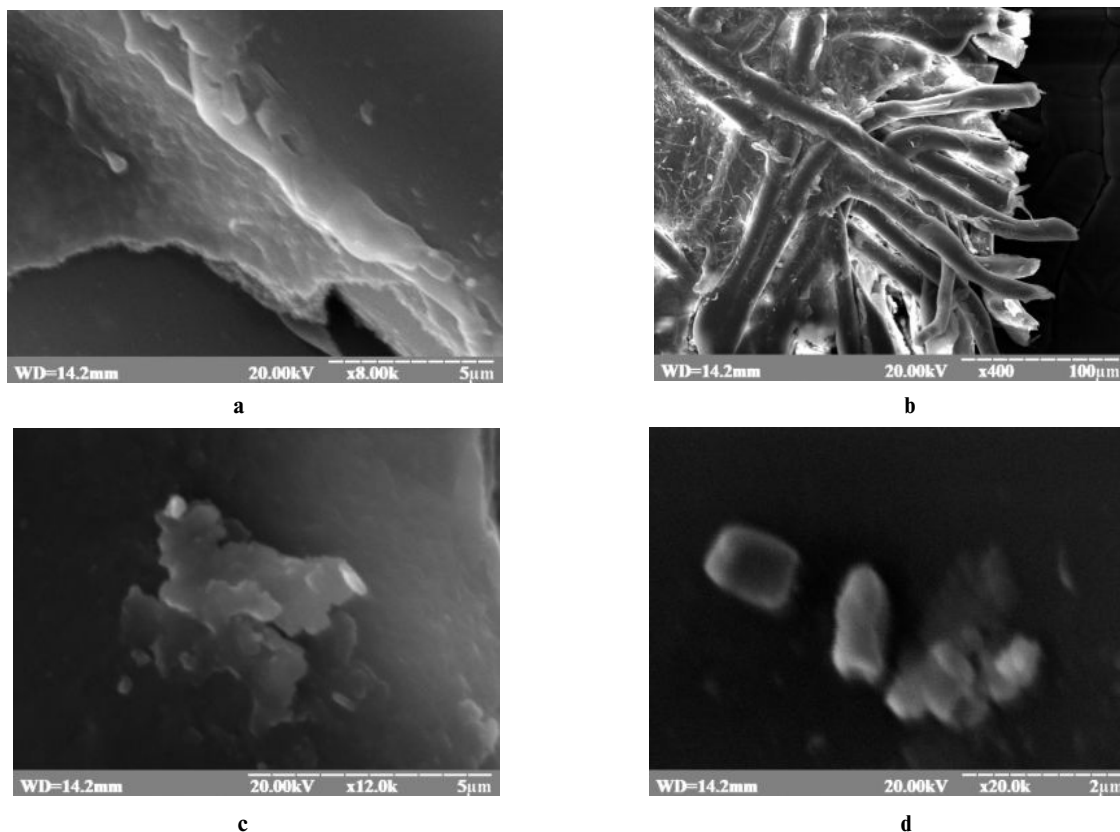


Fig. 1. SEM images of pristine (a, b) and modified (c, d) PAN membranes: active layer (a) and macroporous support (b–d). One-component HZD (c) and HZD containing MNP (c, d) were used as a modifier

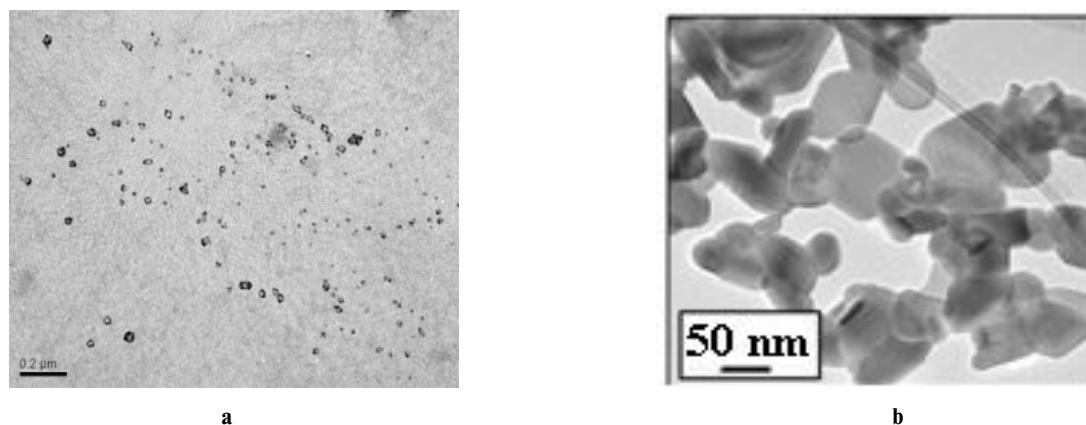


Fig. 2. TEM images of active layer of PAN membrane containing HZD and MNP (a). The image of MNP that are outside the membrane is also given (b). Dark contrast spots evidently correspond to MNP and grey traces are related to HZD

very small aggregates of nanoparticles (up to 20 nm).

For comparison, the image for MNP is also given. The shape of nanoparticles is seen to be close to globular. A size of the primary particles is about 10 nm.

The size of aggregates embedded in the active layer corresponds to pore size of the polymer according to its rejection ability towards proteins, the molecular mass of which is 50 kDa.

Water filtration. Secondary active layer

Figure 3 illustrates a volume of permeate (V) as a function of time of water filtration (τ). As seen, the dependences are linear. This allows estimating the water flux (J) as follows:

$$J = \frac{dV}{d\tau} \cdot \frac{1}{A}, \quad (3)$$

where A is the membrane surface area.

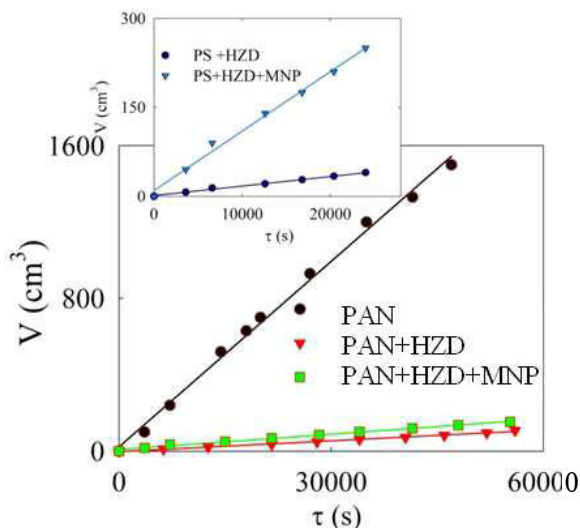


Fig. 3. Permeate volume as a function of time of water filtration through the PAN membrane. Insertion: it is the same for the PS membrane

The calculations were performed from the slopes of the lines and the results are given in Table. As can be seen, the PAN membrane containing HZD and MNP shows lower permeate flux than the pristine membrane due to the filling of polymer pores. At the same time, the rejection of hardness ions becomes higher due to a decrease in pore size in the active layer and charge effect. The values are similar for both the membranes containing MNP and those free of them. However, the PS membranes show higher values of fluxes and lower rejection of Ca^{2+} and Mg^{2+} . This means that the PAN polymer membrane, which is characterized by smaller holes in the active layer, is more attractive for the modification.

The inorganic particles form a «secondary active layer» inside the polymer pores: this layer determines the water flux and rejection ability of the membrane. Its thickness (l) was calculated from the Kozeny-Carman equation:

$$\frac{\Delta P}{l} = \frac{180\mu(1-\varepsilon^2)}{\Phi^2 d^2 \varepsilon^3} J, \quad (4)$$

where ΔP is the pressure drop, ε is the porosity (0.33 for compact bed of globules), Φ is the particle sphericity (it is assumed that $\Phi=1$), d is the particle diameter (≈ 10 nm), and μ is the dynamic viscosity ($9 \cdot 10^{-3}$ Pa s at 298 K).

The calculations give $l \approx 0.58$ μm for both the PS and PAN membranes containing HZD. This value is comparable with a thickness of the active layer of the membrane. Regarding the membranes containing also MNP, $l=95$ nm (PAN) and 0.87 μm (PS). Thus, a thinner «secondary active layer» is formed in the polymer matrix containing smaller pores. In the case of PS, the nanosized inorganic particles are dispersed through the polymer active layer.

Filtration of liquids at 2 bar

Membrane	Water		Sugar beet juice	
	J ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)	φ (%), Ca^{2+} , Mg^{2+}	J ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)	φ (%), VP
PAN	$1.1 \cdot 10^{-5}$	6–7	$1.1 \cdot 10^{-6}$	16–26
PAN+HZD	$5.9 \cdot 10^{-7}$	8–19	$3.8 \cdot 10^{-7}$	58–77
PAN+HZD+MNP	$9.5 \cdot 10^{-7}$	7–20	$4.3 \cdot 10^{-7}$	78–87
PS	$2.3 \cdot 10^{-5}$	2–3	$2.4 \cdot 10^{-6}$	6–13
PS+HZD	$5.7 \cdot 10^{-7}$	5–7	$5.5 \cdot 10^{-7}$	38–49
PS+HZD+MNP	$3.6 \cdot 10^{-6}$	5–6	$5.7 \cdot 10^{-7}$	55–60

Filtration of sugar beet juice

Sugar extraction is based on the diffusion of cell juice with water from destroyed beet cells. Not only sucrose but also other substances (proteins, amino acids, pectin and organic acids) pass into the diffusion juice. The obtained diffusion juice rapidly becomes dark. It should be filtered and clarified before evaporation. The main purpose of ultrafiltration was the clarification of sugar beet juice to obtain purified product. Vegetable proteins partially penetrated into the permeate (Table). Modification was shown to improve the ability of the membranes to reject this valuable component. Higher j values were found for the membranes containing MNT. As can be seen from Fig. 4, the V vs. τ dependences can be fitted by using linear functions (organic-inorganic membranes) or tend to plateau formation (pristine membrane). The depression of filtration is

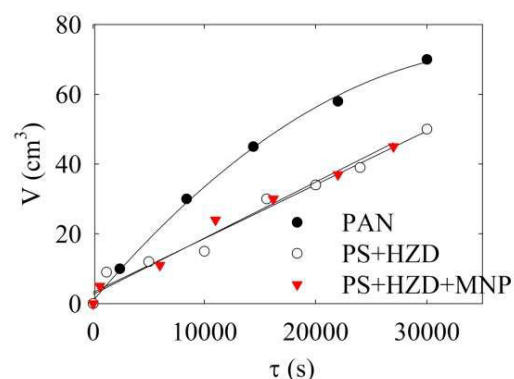


Fig. 4. Permeate volume vs. time of filtration of sugar beet juice

due to the fouling by organics: the precipitate is seen as a web-like patina (Fig. 5). At the same time, the outer surface of the organic-inorganic membrane remains clean.

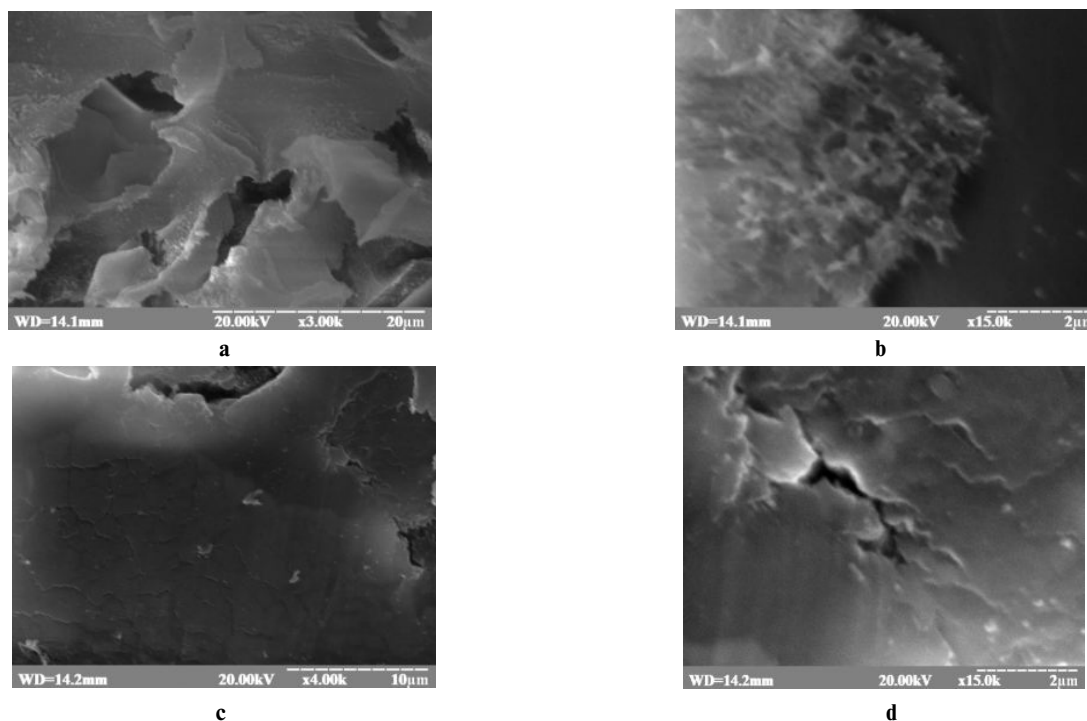


Fig. 5. SEM images of the samples after filtration of sugar beet juice: pristine PAN membrane (a, b), membrane modified with HZD (c), HZD and MNT (d)

Conclusions

When hydrated zirconium dioxide is deposited in ultrafiltration polymer membranes, the aggregates of the nanoparticles are formed both in the macroporous support and in the active layer. MNP provides formation of smaller HZD particles. Fractal analysis shows the DLA model of particle formation. The function of MNP is assumed to accelerate diffusion of HZD nanoparticles being precipitated. This depresses enlargement of the aggregates. Due to the modification, the composite membrane shows slight improvement of rejection of hardness ions and much higher rejection of vegetable proteins comparing with pristine membranes. The modifying effect is most expressed for the PAN polymer membrane, which is characterized by smaller pores through its active layer comparing with the PS membrane. The composites also demonstrate stability against fouling by organics due to additional hydrophilization of polymer support. The membranes can be recommended for water treatment and processing of feedstock and wastes of food industry.

Acknowledgments

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REFERENCES

1. *A comprehensive review on polymeric nano-composite membranes for water treatment* / Zahid M., Rashid A., Akram S., Rehan Z.A., Razzaq W. // *J. Membr. Sci. Technol.* – 2018. – Vol.8. – Article No. 179.
2. *Organic-inorganic membranes for filtration of corn distillery* / Myronchuk V.G., Dzyazko Yu.S., Zmievskaia Yu.G., Ukrainets A.I., Bildukevich A.V., Kornienko L.V., Rozhdestvenskaya L.M., Palchik A.V. // *Acta Periodica Technologica.* – 2016. – Vol.47. – P.153-165.
3. *Dzyaz'ko Yu.S., Rozhdestvenskaya L.M., Pal'chik A.V. Recovery of nickel ions from dilute solutions by electro dialysis combined with ion exchange* // *Russ. J. Appl. Chem.* – 2005. – Vol.78. – No. 3. – P.414-421.
4. *Ion-exchange resin modified with aggregated nanoparticles of zirconium hydrophosphate. Morphology and functional properties* / Dzyazko Yu.S., Ponomaryova L.N., Volfkovich Yu.M., Trachevskii V.V., Palchik A.V. // *Micropor. Mesopor. Mater.* – 2014. – Vol.198. – P.55-62.
5. *Preparation and characterization of PES–SiO₂ organic–inorganic composite ultrafiltration membrane for raw water pretreatment* / Shen J., Ruan H., Wu L., Gao C. // *Chem. Eng. J.* – 2011. – Vol.168. – P.1272-1278.
6. *Magnetic field induced orderly arrangement of Fe₃O₄/GO composite particles for preparation of Fe₃O₄/GO/PVDF membrane* / Huang Y., Xiao C., Huang Q., Liu H., Hao J., Song L. // *J. Membr. Sci.* – 2018. – Vol.548. – P.184-193.
7. *Polyethersulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: application of new functionalized Fe₃O₄ nanoparticles* / Ghaemi N., Madaeni S.S., Daraei P., Rajabi H., Zinadini S., Alizadeh A., Heydari R., Beygzadeh M., Ghouzvand S. // *Chem. Eng. J.* – 2015. – Vol.263. – P.101-112.
8. *The ferrite permanent magnet ac motor – a technical and economical assessment* / Richter E., Miller T.J.E., Neumann T.W., Hudson T.L. // *IEEE Trans. Ind. Appl.* – 1985. – Vol.IA-21. – No. 3. – P.644-650.
9. *Mossbauer study and magnetic properties of M-type barium hexaferrite doped with Co + Ti and Bi + Ti ions* / Belous A.G., V'yunov O.I., Pashkova E.V., Ivanitskii V.P., Gavrilenko O.N. // *J. Phys. Chem. B.* – 2006. – Vol.110. – P.26477-26481.
10. *Composite inorganic membranes containing nanoparticles of hydrated zirconium dioxide for electro dialytic separation* / Dzyazko Y.S., Volfkovich Y.M., Sosenkin V.E., Nikolskaya N.F., Gomza Y.P. // *Nanoscale Res. Lett.* – 2014. – Vol.9. – Article No. 271.
11. *Modification of ceramic membranes with inorganic sorbents. Application to electro dialytic recovery of Cr(VI) anions from multicomponent solution* / Dzyazko Yu.S., Rudenko A.S., Yukhin Yu.M., Palchik A.V., Belyakov V.N. // *Desalination.* – 2014. – Vol.342. – P.52-60.
12. *Fractal character of cold-deposited silver films determined by low-temperature scanning tunneling microscopy* / Douketis C., Wang Z., Haslett T.L., Moskovits M. // *Phys. Rev. B.* – 1995. – Vol.51. – P.11022-11031.
13. *Protein determination – method matters* / Maehre H.K., Dalheim L., Edvinsen G.K., Elvevoll E.O., Jensen I.J. // *Foods.* – 2018. – Vol.7. – No. 1. – Article No. 5.
14. *Meakin P. Progress in DLA research* // *Physica D.* – 1995. – Vol.86. – P.104-112.
15. *Holysz L., Szczech A., Chibowski E. Effects of a static magnetic field on water and electrolyte solutions* // *J. Colloid Interface Sci.* – 2007. – Vol.316. – P.996-1002.

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МОДИФІКУВАННЯ УЛЬТРАФІЛЬТРАЦІЙНИХ МЕМБРАН ДИСПЕРСНИМИ ОКСИДНИМИ НАНОЧАСТКАМИ

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Одержано органо-неорганічні мембрани, що містять наночастки гідратованого цирконій діоксиду та магнітні наночастки $BaFe_{12}O_{19}$. Ці наночастки інкорпоровані в полімерній матриці. Як полімерну підкладку для досліджень використовували ультрафільтраційні мембрани. Ці мембрани складаються з макропористого шару (нетканий поліефір) та ультра тонкого активного шару (полісульфон або поліакрилонітрил). Морфологію мембран досліджували з використанням скануючого електронного мікроскопа. Було встановлено, що неорганічні часточки утворюють агрегати розміром 20 нм (в активному шарі) та 2 мкм (в макропористій волокнистій підкладці полімеру). Більш великі агрегати утворюються у відсутності магнітної складової (до 5 мкм). Згідно з даними фрактального аналізу ці часточки формуються відповідно до моделі дифузійно обмеженої агрегації. Неорганічні часточки утворюють вторинний активний шар всередині полімерних пор, і цей шар визначає швидкість потоку та затримуючу здатність мембран. Більш тонкий вторинний шар утворюється в полімерній матриці з меншим розміром пор. Одержані мембрани тестували при фільтрації соку цукрового буряка. Внаслідок меншого розміру частинок мембрана, що містить $BaFe_{12}O_{19}$, демонструє потік перміату при 2 бар, рівний $4,3 \cdot 10^{-7}$ – $5,7 \cdot 10^{-7} \text{ м}^3 \text{ м}^{-2} \text{ с}^{-1}$, а затримуюча здатність щодо рослинного білку досягала 55–87%. Що стосується мембран, що не містять магнітних наночастинок, то ці величини становили $8,0 \cdot 10^{-7}$ – $5,5 \cdot 10^{-7} \text{ м}^3 \text{ м}^{-2} \text{ с}^{-1}$ і 38–77%, відповідно.

Ключові слова: наночастки, мембранне розділення, магнітні наноконізати, гідратований цирконій діоксид, барій феррат.

MODIFICATION OF ULTRAFILTRATION POLYMERIC MEMBRANES WITH DISPERSED OXIDE NANOPARTICLES

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REFERENCES

1. Zahid M., Rashid A., Akram S., Rehan Z.A., Razzaq W. A comprehensive review on polymeric nano-composite membranes for water treatment. *Journal of Membrane Science & Technology*, 2018, vol. 8, article no. 179.
2. Myronchuk V.G., Dzyazko Yu.S., Zmievskii Yu.G., Ukrainets A.I., Bildukevich A.V., Kornienko L.V., Rozhdestvenskaya L.M., Palchik A.V. Organic-inorganic membranes for filtration of corn distillery. *Acta Periodica Technologica*, 2016, no. 47, pp. 153-165.
3. Dzyaz'ko Yu.S., Rozhdestvenskaya L.M., Pal'chik A.V. Recovery of nickel ions from dilute solutions by electrodialysis combined with ion exchange. *Russian Journal of Applied Chemistry*, 2005, vol. 78, pp. 414-421.

4. Dzyazko Yu.S., Ponomaryova L.N., Volkovich Yu.M., Trachevskii V.V., Palchik A.V. Ion-exchange resin modified with aggregated nanoparticles of zirconium hydrophosphate. Morphology and functional properties. *Microporous and Mesoporous Materials*, 2014, vol. 198, pp. 55-62.
5. Shen J., Ruan H., Wu L., Gao C. Preparation and characterization of PES-SiO₂ organic-inorganic composite ultrafiltration membrane for raw water pretreatment. *Chemical Engineering Journal*, 2011, vol. 168, pp. 1272-1278.
6. Huang Y., Xiao C., Huang Q., Liu H., Hao J., Song L. Magnetic field induced orderly arrangement of Fe₃O₄/GO composite particles for preparation of Fe₃O₄/GO/PVDF membrane. *Journal of Membrane Science*, 2018, vol. 548, pp. 184-193.
7. Ghaemi N., Madaeni S.S., Daraei P., Rajabi H., Zinadini S., Alizadeh A., Heydari R., Beygzadeh M., Ghouzivad S. Polyethersulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: application of new functionalized Fe₃O₄ nanoparticles. *Chemical Engineering Journal*, 2015, vol. 263, pp. 101-112.
8. Richter E., Miller T.J.E., Neumann T.W., Hudson T.L. The ferrite permanent magnet ac motor – a technical and economical assessment. *IEEE Transactions on Industry Applications*, 1985, vol. IA-21, no. 3, pp. 644-650.
9. Belous A.G., V'yunov O.I., Pashkova E.V., Ivanitskii V.P., Gavrilenko O.N. Mossbauer study and magnetic properties of M-type barium hexaferrite doped with Co + Ti and Bi + Ti ions. *Journal of Physical Chemistry B*, 2006, vol. 110, pp. 26477-26481.
10. Dzyazko Y.S., Volkovich Y.M., Sosenkin V.E., Nikolskaya N.F., Gomza Y.P. Composite inorganic membranes containing nanoparticles of hydrated zirconium dioxide for electro dialytic separation. *Nanoscale Research Letters*, 2014, vol. 9, article no. 271.
11. Dzyazko Yu.S., Rudenko A.S., Yukhin Yu.M., Palchik A.V., Belyakov V.N. Modification of ceramic membranes with inorganic sorbents. Application to electro dialytic recovery of Cr(VI) anions from multicomponent solution. *Desalination*, 2014, vol. 342, pp. 52-60.
12. Douketis C., Wang Z., Haslett T.L., Moskovits M. Fractal character of cold-deposited silver films determined by low-temperature scanning tunneling microscopy. *Physical Review B*, 1995, vol. 51, pp. 11022-11031.
13. Maehre H.K., Dalheim L., Edvinsen G.K., Elvevoll E.O., Jensen I.J. Protein determination – method matters. *Foods*, 2018, vol. 7, no. 1, article no. 5.
14. Meakin P. Progress in DLA research. *Physica D: Nonlinear Phenomena*, 1995, vol. 86, pp. 104-112.
15. Holysz L., Szczes A., Chibowski E. Effects of a static magnetic field on water and electrolyte solutions. *Journal of Colloid and Interface Science*, 2007, vol. 316, pp. 996-1002.