Composite ultrafiltration membrane incorporated with dispersed oxide nanoparticles

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Introduction

Ultrafiltration technology is widely used for removal of colloidal particles from ground and brackish water, wastewater, sea water. This stage of water treatment is before reverse osmosis to prevent membrane fouling. Ultrafiltration is also applied to beverage industry, for instance, for milk skimming and effluents treatment etc. The main problem of filtration is a decrease of membrane permeability due to fouling with 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 time 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. As a rule, nanoparticles of inorganic ion-exchangers are used for modification of polymers. A number of inorganic compounds are applied to modifying: zirconium hydrophosphate (the attempt to use these materials as a filler for electromembrane processes is known, moreover, they are used for modifying of ion exchange resins), silica, hydrated zirconium or iron oxide. This approach allows one to enhance liquid permeability and anti-fouling ability without sufficient changes of membrane structure.

Magnetic particles are another type of modifier that improves functional properties of polymer membranes. The membrane containing magnetic Fe_3O_4 nanoparticles and graphene oxide particles shows high flow of pure water and high degree of rejection (up to 83.0%). Membranes containing iron nanoparticles can be used to remove copper and lead ions from wastewater. Adsorption capacity increases due to improved hydrophilicity on the one hand and nucleophilic functional groups on the surface of nanoparticles on the other hand. 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 shows an increase in water flow due to changes in the average pore radius, porosity and hydrophilicity of the membranes. The membrane surface roughness and hydrophilicity are considered to be main factors, which minimize membrane fouling.

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

Experimental details

Membrane modifying

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

Magnetic nanoparticles (MNP) $BaFe_{12}O_{19}$ were synthesized according to [1]. In order to provide their fixation in membrane pores, hydrated zirconium dioxide (HZD) was used. First of all, sol of insoluble zirconium hydroxocomplexes was obtained from a 0.25 M $ZrOCl_2$ solution similarly to [2]. MNP 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 0.1M NH_4OH solution. The membrane was dried at 50°C and cleaned with ultrasound to remove the precipitate from its outer surface. For comparison, the membranes containing only HZD were obtained. 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 with methods of cube counting, triangulation, and power spectrum analysis.

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.

Membrane testing

The experimental set-up for filtration consisted of typical elements for baromembrane separation (magnetic pump, manometer, rotameter). A divided two-compartment flow-type cell was used. An effective area of the membrane was 2.82˙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 and 0.2 mol dm-3 Ca2+ and Mg2+ respectively was used for testing. The content of ions in permeate was determined by means of atomic absorption technique.

Filtration was carried out at 2 bar. Sugar beet juice (PC "Salyvonkivskyy sugar factory") was also applied to investigations. Before testing, juice was diluted in 10 times. The content of vegetable proteins was determined in permeate using such dye as Coomassie brilliant blue G-250. Selectivity of membranes, i.e. rejection of species was estimated via [3]:

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

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

Results

Morphology of membranes

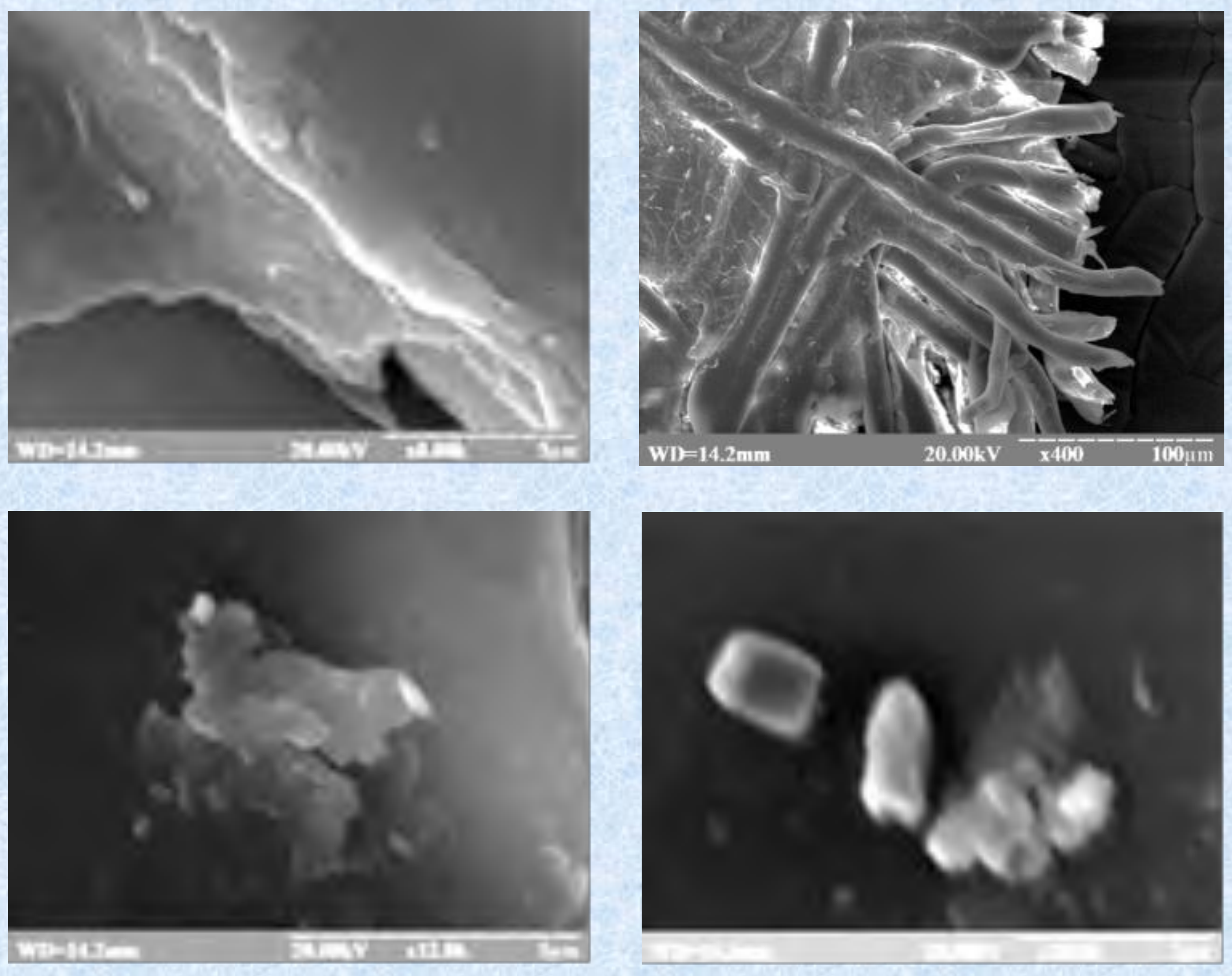

Fig. 1. SEM image of pristine (a, b) and modified (c, d) PAN membrane: active layer (a) and macroporous support (b-d). One-component HZD (c) and HZD containing MNP (c. d) were used as a modifier.

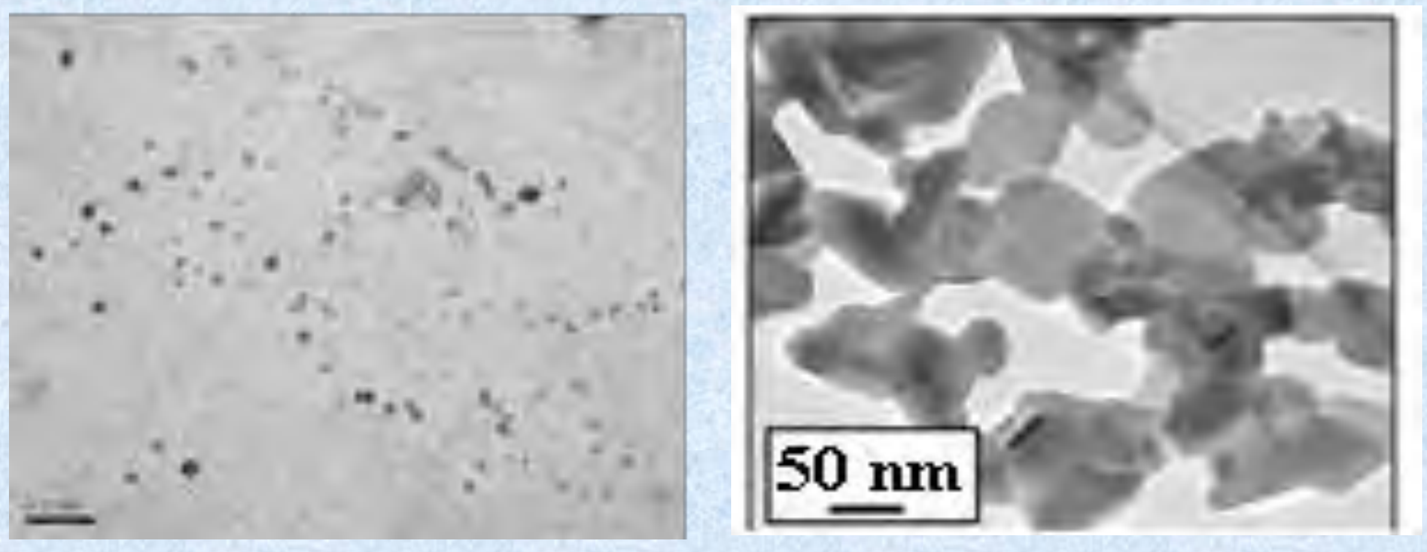

Fig. 2. TEM image of active layer of PAN membrane containing HZD and MNP (a). The image of MNP that are outside the membrane is also given (b).

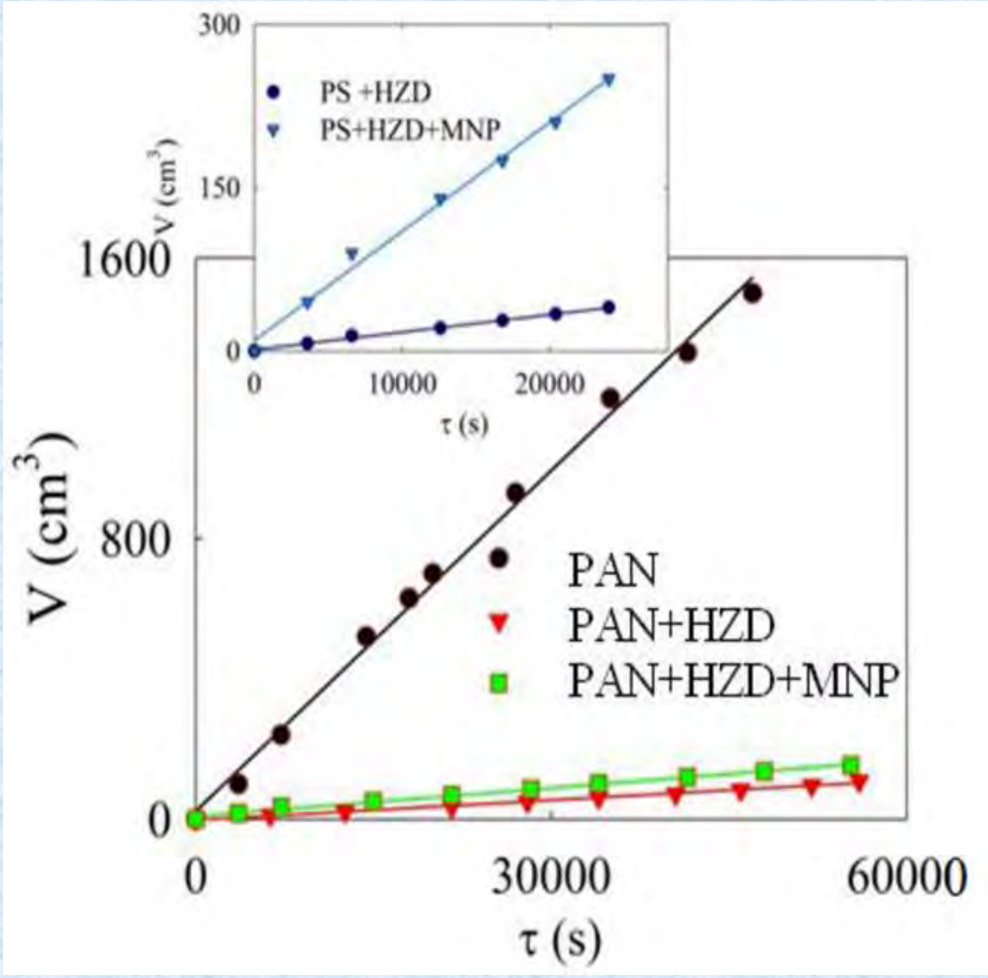

Fig. 3. Permeate volume as a function of time of water filtration through the PAN membrane. Insertion: it is the same for the PS membrane

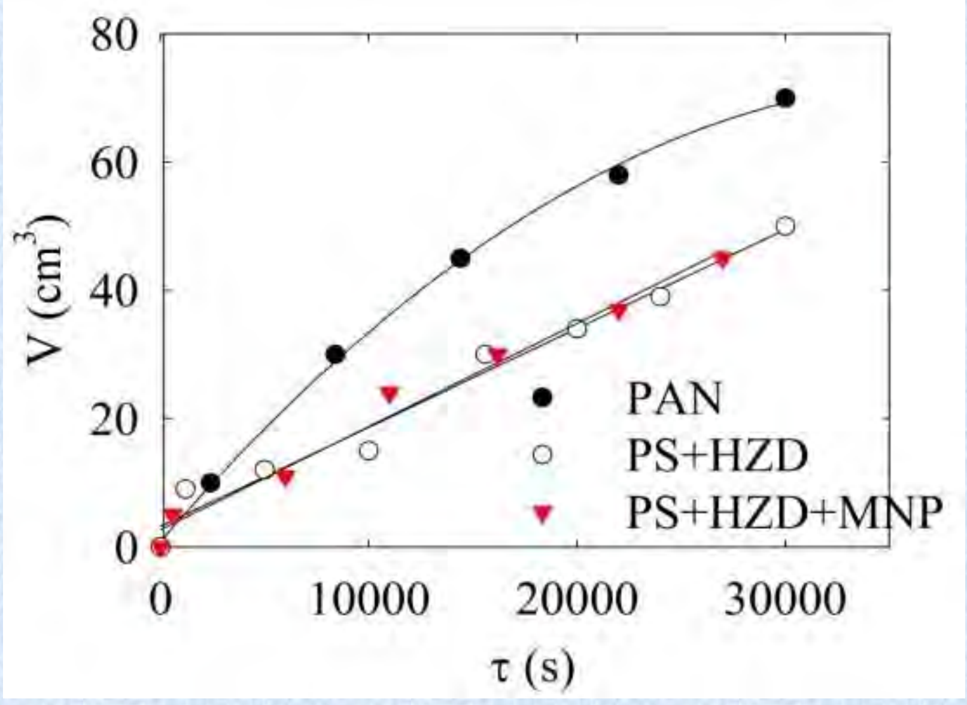

Fig. 4. Permeate volume vs time of filtration of sugar beet juice.

Table 1. Filtration of liquids at 2 bar

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

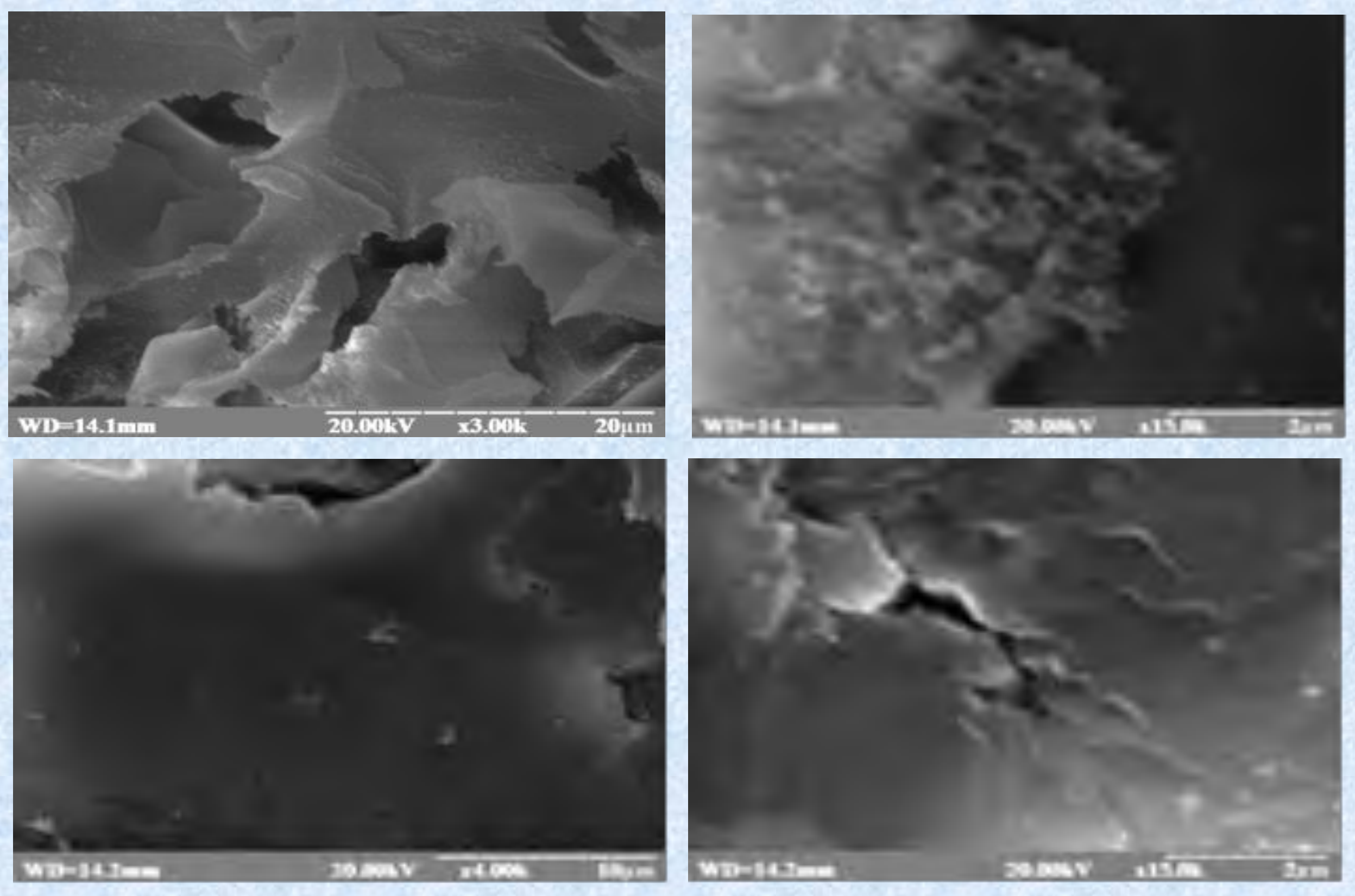

Fig. 5. SEM images of the samples after filtration of sugar beet juice: pristine PAN membrane (a, b), membrane modified with HZD (c), HZD and MNT (d).

Conclusions

When hydrated zirconium dioxide is deposited in ultrafiltration polymer membranes, aggregates of the nanoparticles are formed both in macroporous support and 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, As a result of modifying, 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 with 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.