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ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES



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ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES

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Коллективна монографія «Environmental Protection: from Sorbents to Membranes» - під ред. проф. Н. Кабай, докт. хім. наук Ю. С. Дзязько, проф. М. Арда, докт. хім. наук К.О. Каздобіна - 108 с.

Коллективна монографія включає статті за матеріалами українсько-турецького семінару, який було проведено 11 листопада 2016 р. на базі Інституту загальної та неорганічної хімії ім. В. І. Вернадського НАН України за участю фахівців Егейського університету (Турецька республіка) та за підтримки Відділення хімії НАН України, Відділу міжнародних зв'язків НАН України, а також Наукової та Технічної дослідної Ради Турецької республіки TÜBİTAK. У монографії наведено результати досліджень, які направлені на вилучення токсичних і цінних компонентів із розчинів техногенного та природного походження, зокрема з біологічних рідин, із застосуванням сорбційних та мембранних методів. Результати робіт можуть бути застосовані у водопідготовці, хімічній, фармацевтичній, харчовій промисловості. Особливу увагу приділено синтезу нових матеріалів для процесів розділення та впливу структури цих матеріалів на їх функціональні властивості: проникну здатність, електропровідність, каталітичну спроможність тощо.

Монографія є корисною для фахівців в області мембранних та сорбційних технологій, а також для студентів вищих навчальних закладів.

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NANOCOMPOSITE POLYSULFONE MEMBRANES WITH IMPROVED ANTIFOULING PROPERTIES

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Abstract. The immobilization methods of nanoparticles of magnetite and tin oxide on membrane surface have been developed for improving the stability of polysulfone membrane to fouling. SnO₂ nanoparticles were deposited on the membrane by the method of "layer-by-layer" with using polyelectrolyte complexes of polyethyleneimine and carboxymethyl cellulose to provide them photocatalytic properties. Fe₃O₄ nanoparticles were covalently immobilized on the membrane using polyethyleneimine as a polymer spacer. It has been shown that the resulting nanocomposite membranes were characterized by improved transport properties in the ultrafiltration of protein solutions. Membrane resistance to fouling increased by reducing the effect of concentration polarization and increasing mass transfer coefficient.

Keywords: *nanocomposite membrane, membrane fouling, membrane modification.*

Introduction. Surface modification is an effective approach to obtain fouling-resistant membranes [1-5]. Numerous modification methods have been adopted to improve the antifouling properties of polymer membranes [2-3]. Hydrophilic moieties can be introduced on the membrane surface through covalent bonding via grafting or through physical interaction via coating [2]. The grafting method requires caustic chemical treatment or special equipment, which decreases the ease of membrane preparation. In the coating method, the stability of the coated hydrophilic layer on the membrane surface depends strongly on the physical affinity of the coating material with the membrane surface. The coated layer can easily be detached from the membrane surface by changes in the solution pH or by the application of back flushing during the filtration process [3-4]. Blending modification also can avoid the difficulties and short comings mentioned above and provide the ease of one-step modification.

In this work two different approaches were applied to modified polysulfone membrane with improved antifouling resistance. Firstly, photocatalytic membranes were developed by immobilization of SnO₂ nanoparticles (NP) on the polyethersulfone ultrafiltration membranes with "layer-by-layer" (LbL) technic. LbL assembly exploits the surface charge of polyelectrolytes to adhere suspended catalytic nanoparticles to a surface. This process includes two steps: i) applying polyelectrolytes (PE) on the surface, and then ii) exposing the polyelectrolyte-modified surface to a nanoparticle suspension to enable particle adhesion to the polyelectrolyte-coated surface. We have investigated the effect of SnO₂ nanocomposites on membrane performance, morphology, and antifouling properties during milk filtration without UV irradiation applying.

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And secondly radically new method of suppressing fouling during ultrafiltration was developed by grafting a magnetically responsive nanolayer, consisting of hydrophilic polyelectrolyte chains grown from the surface of a thin film composite membrane. The magnetic nanoparticles were attached to the chain ends. In an oscillating magnetic field the chains oscillate. Movement of the magnetically responsive nanobrushes leads to mixing at low Reynolds number at the membrane surface and reduces concentration polarization effect [5].

Experimental. *Membrane modification by “layer-by-layer” method.* For membrane modification polyelectrolyte solutions were alternately deposited on the membranes for 15 min each with a water rinse between layers. Sodium polystyrene sulfonate ($0.02 \text{ mol}\cdot\text{L}^{-1}$) was used as the first layer because it adsorbs well to polysulfone surface by hydrophobic interactions. Next layers were assembled of PEI (MW 750 kDa) as a positively charged polyelectrolyte and carboxymethyl cellulose (CMC) as negatively charged ones. They adsorbed to the previous layer via electrostatic interactions and van der Waals forces. The sonicated SnO_2 nanoparticles were used as the top layer, because they had negative charge at pH 6.5 and adsorbed to PEI layer, thus resulting in 3.5 layers.

Membrane modification by magnetite nanoparticles. In the first step of the modification sequence, PES membrane disc were modified by reacting terminal hydroxyl groups with diepoxide EGDGE. The samples were placed into 50 mL of a 0.3 M EGDGE solution in the isopropanol–water azeotrope. After 15 min of incubation (wetting the pore surfaces) the reaction was catalyzed with 50 μL of 1 M KOH solution. The samples were incubated at room temperature for 15 h and then washed five times with deionized water. In the second step the epoxidized PES membranes were modified by polyethyleneimine as a nucleophilic reagent. Membranes were incubated in 0.5 % water solution of PEI for 1 h at room temperature. Nanoparticles were attached to the membrane surface by reacting carboxyl groups on the nanoparticle surface to the primary amine at the PEI chain via an amide linkage. Carbodiimide activated amide formation was used. 10 mg of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide was added to 10 mL of water and pour into a plastic jar containing a membrane disk for 10 min. Next, 5 mL of carboxyl shell Fe_3O_4 nanoparticles (4 g/L) were added and incubated in the dark for 4 h. Then, the membrane was removed, washed in water for 15 h.

Filtration studies. A dead-end stirred cell (Amicon-8050, MA) with a total cell volume of 50 ml and effective membrane area of 13.4 cm^2 was used for filtration experiments. The permeation flux of the membranes was determined by the volume of the permeate during a certain period of time. BSA water solutions with concentration from 0.1 to 5 % were used to study transport properties.

Results and discussion. Ultrafiltration experiments of BSA solutions at different concentrations have been carried out to determine the mass transfer coefficient for unmodified pristine membrane and membrane with immobilized

nanoparticles. Fig. 1 shows the mass transfer coefficient for membrane with immobilized magnetic nanoparticles is $12.3 \cdot 10^{-6}$ m/s, which is a 1.64 times higher than for control membrane without nanoparticles. Mass transfer coefficient is the ratio of solute diffusion coefficient in our case to the BSA diffusion to bounding layer thickness. Since the diffusion coefficient under these conditions does not change, it is obvious that increase of the mass transfer coefficient occurs by reducing the thickness of the diffusion layer, which in turn depends on the criterion of turbulence Reynolds. And, therefore, the movement of magnetic nanoparticles in membranous layer creates additional turbulence, which reduces concentration polarization.

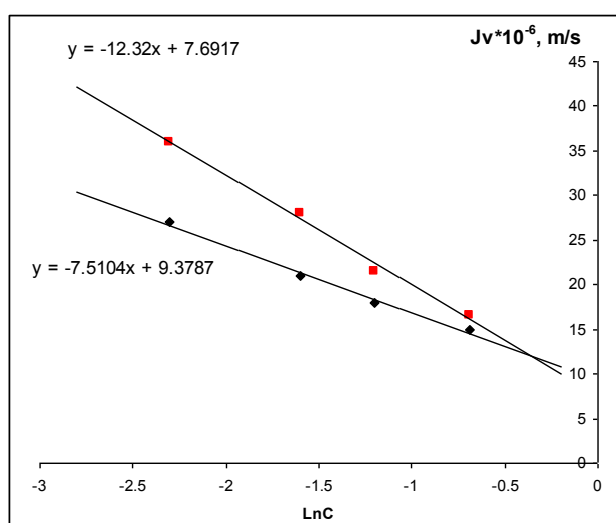


Fig. 1. Determination of mass transfer coefficient by linearization of the concentration polarization equation for control membranes (●) and the membranes with immobilized magnetic NP (■).

The permeate fluxes vs. applied pressure data obtained in the ultrafiltration experiments are shown in Fig. 2.

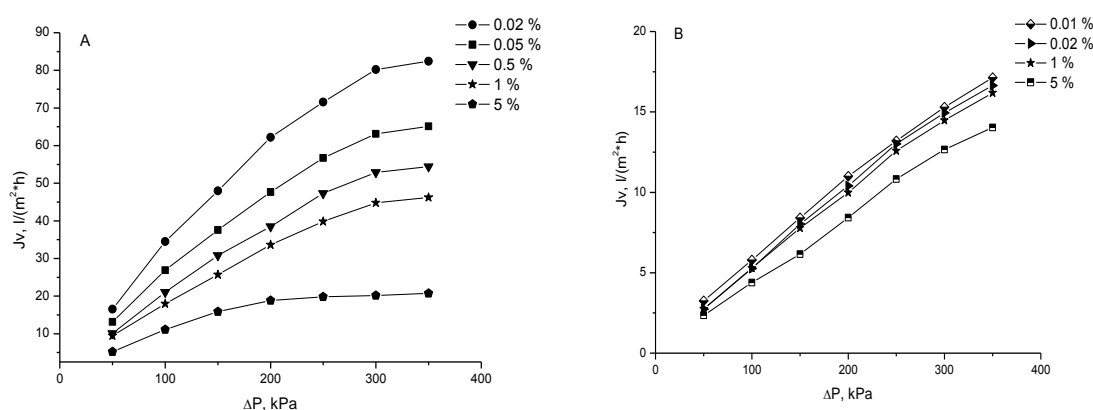


Fig. 2. Permeate flux through (A) unmodified membrane, and (B) membrane with immobilized SnO_2 nanoparticles as function of the applied pressure and different BSA concentrations.

For unmodified polysulfone membrane the permeate fluxes vs. applied pressure have well-known shapes. Permeate flux does not increase and the

maximum flux is achieved at pressure equal to ca. 200 kPa (Fig. 2A) due to the formation of a concentration polarization boundary layer. Additionally, the maximum permeate flux decreases with an increase of bulk BSA concentration.

It is interesting, that for membranes with the immobilized SnO₂ NP the flux dependencies on applied pressure have different shape than for the unmodified membrane (Fig. 2B). It can be observed that membrane flux increased almost linearly with increasing pressure. It can be also noticed that for membrane with immobilized NP, the maximum permeate flux J_{∞} is not achieved and does not depend on BSA concentration. It can be concluded, that the immobilization NP on the membrane surface reduces the concentration polarization effect due to photocatalytic reaction on the membrane surface.

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НАНОКОМПОЗИТНІ ПОЛІСУЛЬФОНОВІ МЕМБРАНИ З ПОКРАЩЕНОЮ СТІЙКІСТЮ ДО ЗАБРУДНЕННЯ

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Резюме. З метою покращення стійкості полісульфонових мембран до забруднення розроблені методи іммобілізації наночастинок оксиду стануму та магнетиту на їх поверхні. Наночастинки SnO₂ наносили на мембрану методом “layer-by-layer” з використанням поліелектролітного комплексу поліетиленімін-карбоксиметилцелюлоза для надання їм фотокаталітичних властивостей. Наночастинки Fe₃O₄ були іммобілізовані на мембрані ковалентно за допомогою полімерного спейсеру поліетиленіміну. Показано, що отримані нанокompatитні мембрани характеризуються покращеними транспортними властивостями у процесі ультрафільтрації білків. Стійкість мембран до забруднення збільшується за рахунок зменшення ефекту концентраційної поляризації та зростання коефіцієнту масопереносу.

Ключові слова: нанокompatитні мембрани, модифікування мембран, забруднення мембран.