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Fe^{2+} Removal from Water Using PVDF Membranes, Modified with Magnetite Nanoparticles, by Polyelectrolyte Enhanced Ultrafiltration

Usuwanie Fe^{2+} z wody za pomocą membran PVDF modyfikowanych nanocząstkami magnetytu, wspomagane ultrafiltracją z polielektrolitem

The aim of this study was to show results of Fe^{2+} removal from water by polyelectrolyte enhanced ultrafiltration on polyvinylidene fluoride membranes modified with magnetite nanoparticles. Magnetite nanoparticles were synthesized by the co-precipitation method and stabilized with sodium polyacrylate. At first stage, the surface of PVDF membranes was modified by grafting of polyethylenimine. At the second stage the polyelectrolyte, grafted to the membrane surface, was used as a linker for magnetite nanoparticles immobilization. The modification of membranes was confirmed by IR spectroscopy, scanning electron microscopy and electro kinetic analysis. The dependence of zeta-potential on pH for PVDF membrane modified with PEI has confirmed the modification of the membrane surface as zeta-potential increases with pH decrease. SEM has shown that the surface of modified membrane is densely covered with nanoparticles, which form clusters. The dependence of the volumetric flux on the applied pressure at various concentrations of the carboxymethylcellulose (CMC) has been studied. Polyelectrolyte enhanced ultrafiltration with CMC has been used for iron(II) removal at initial Fe^{2+} concentration of 20 mg/L. The concentrations of iron(II) in permeate using an unmodified membrane has ranged from 0.6 to 1.0 mg/L, whereas for the modified membrane it has been 0.02÷0.08 mg/L.

Keywords: **polyvinylidene fluoride membrane, magnetite nanoparticles, polyelectrolyte enhanced ultrafiltration, carboxymethylcellulose**

Introduction

Polyelectrolyte enhanced ultrafiltration (PEUF) is widely investigated for the removal of low molecular weight pollutants from water. The use of a complex formation with polyelectrolytes allows for reducing costs by decreasing applied pressures, and therefore, by reducing the energy consumption [1]. The main attention is focused on the removal of heavy metals. For example, the use of polyetheleneimine (PEI) and polystyrene sulfonate (PSS) helps to remove copper by varying the pH value. Chou et al. [2] showed that PEI was the most effective for Cu^{2+} removal at pH 3 (94%). On the other hand, the highest copper removal efficiency with PSS (99%) was reached at neutral media and alkaline media. PEI can also bind cadmium-organic ligand complexes, such as Cd-EDTA, Cd-nitrilotriacetic acid, and citric acid for Cd(II) removal. Li and coauthors [3] proved that pH value not only influenced on protonation-deprotonation of PEI, but also had an impact on a complex formation between cadmium and low molecular weight ligands. Moreover, not only synthetic polyelectrolytes are used for PEUF, but also natural humic-substances are successful, e.g. for cobalt removal [4]. Polysaccharides and their derivatives such as chitosan, carboxymethyl cellulose (CMC), starch, dextrans are widely used for treatment of water contaminated by toxic metals (nickel, zinc, lead, copper) [5-8]. Sanli et al. [9] used alginic acid (AA) for iron(III) removal by PEUF on membranes prepared of poly(methyl metacrylate-co-metacrylic acid). They found that time required for complex formation between AA and Fe^{3+} was 5 minutes, and optimum pH value for iron(III) rejection was 3.1. However, authors mentioned the membrane fouling and as a result a flux decline during the process of filtration. Zhu et al. [10] also observed the dramatic flux decline during nitrate removal by ultrafiltration with different polyelectrolytes with quaternary amine groups. They attributed such an effect to changeable gel concentration level of polymers on the membrane surface. Consequently, the main disadvantage of using ultrafiltration in combination with polyelectrolytes is the reduction of the volumetric flux due to concentration polarization.

The surface of the membrane plays an important role in the membrane processes. Therefore, its modification makes the change the membrane hydrophilicity, charge, roughness etc. possible, what can improve the concentration polarization and membrane fouling. Thus, smart systems sensitive to the various factors (temperature, pH, ionic strength, magnetic and electric fields) can significantly influence on the mass transfer through polymeric membranes and improve their properties [11].

Himstedt et al. proposed novel approach to prevent concentration polarization by grafting magnetically active nanoparticles to membrane surface, which could rotate in the magnetic field and provide mixing in the boundary layer [12]. Such the method allowed for increasing salt rejection and filtrate flux through nanofiltration membrane. This approach is promising for the modification of ultrafiltration membranes to prevent concentration polarization during filtration of high molecular weight substances.

Therefore, the goal of the presented study was to modify ultrafiltration polyvinylidene fluoride membranes with magnetite nanoparticles and to show their applicability for iron(II) removal in the process of CMC-enhanced ultrafiltration.

1. Materials and methods

Polyvinylidene fluoride (PVFD) membranes with cut-off 150 kDa were used for modification (Microdyn Nadir, Germany). Sodium polyacrylate with MW 4.5 kDa, polyethylenimine with 25 kDa (PEI), medium viscous sodium carboxymethylcellulose (CMC), and N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich, USA. All materials were used without further purification.

1.1. Synthesis of magnetite nanoparticles

Magnetite nanoparticles were synthesized by the co-precipitation method using $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ salts in the ratio 1:2 [13]. After synthesis, the magnetite nanoparticles were precipitated with the external magnet and washed with deionized water to neutral pH value. Finally, 20 mL of 1% aqueous solution of low molecular weight sodium polyacrylate was added for suspension stabilization and functionalization of Fe_3O_4 nanoparticles surface with carboxyl groups. The resulted concentration of magnetite nanoparticles in suspension was 8 g/L.

Size and particle size distribution of magnetite nanoparticles were measured by transmission electron microscopy (JEOL JEM 1230, Japan) and dynamic light scattering (Malvern Zetasizer NanoS, UK).

1.2. PVFD membrane modification with PEI and magnetite nanoparticles

At the first step, PVFD membranes were modified according [14], using PEI as a source of amino groups. Dehydrofluorination and the nucleophilic substitution reactions were carried out at the same time. For this purpose, previously washed samples of commercial membranes were immersed in 0.5% solution of PEI in the carbonate buffer at 55°C for overnight. After that modified membranes were washed with distilled water.

At the second stage, the membranes with terminal amino groups were functionalized with magnetite nanoparticles *via* the amide linkage formation. For this case, 20 mL of magnetite nanoparticles and small amount of EDC were added to the dead-end cell with the fixed membrane. Modification was continued at room temperature for 15 hours.

1.3. Membrane characterization

IR spectra of membranes were recorded with IRAffinity-1, Shimadzu in ATR mode. SEM images were recorded using field emission scanning electron microscope JEOL JSM 6700F (Japan). The measurements of the membrane surface zeta-potential were made using Electrokinetic Analyzer (Anton Paar GmbH, Austria) at room temperature at different pH values in 10^{-3} M solution of KCl.

1.4. Ultrafiltration experiment

Ultrafiltration experiments were performed in dead-end cell Amicon 8050 (Millipore, USA) at constant stirring of 350 rpm and at pressure 100÷400 kPa. The membrane separation area was 13.4 cm^2. The recovery rate was 80% for all measurements. Polyelectrolyte enhanced ultrafiltration was used for Fe^{2+} removal from water. For this purpose, solution of $FeSO_4 \cdot 7H_2O$ (20 mg Fe/L) was prepared in the presence of CMC of different concentration (0.1÷0.5%) at pH 4.8. Iron(II) concentration in permeate was measured by atomic absorption spectrometry. Fe^{2+} rejection (R_f, %) was calculated according to equation (1):

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

where C_p is Fe^{2+} concentration in permeate, mg/L; C_f - Fe^{2+} concentration in feed, mg/L.

2. Results and discussion

PVDF membranes has hydrophobic surface, which results in rapid membrane fouling and flux decrease during filtration experiments. In this research, antifouling properties of PVDF membranes were provided by their functionalization with magnetite nanoparticles, which behaved as micromixers on the membrane surface [12].

2.1. Synthesis of magnetite nanoparticles

Magnetite nanoparticles attract attention due to their significant superparamagnetic properties, low toxicity, biocompatibility, and easy fabrication [15]. The co-precipitation method consists of preparing an aqueous solution of Fe^{3+} and Fe^{2+} salts in a molar ratio of 2:1, followed by mixing under vigorous stirring in alkaline solution with $pH > 11$ at room temperature. By using the ammonium hydroxide, it is possible to provide the necessary mild conditions for the reaction, which contributes to the formation of a stoichiometric magnetite $FeO{\cdot}Fe_2O_3$ with an equal content of iron oxides.

The size of the obtained nanoparticles was investigated by the TEM method. Fe_3O_4 nanoparticles had spherical hexagonal shape typical for magnetite nanoparticles. The size of the nanoparticles was about 10÷20 nm.

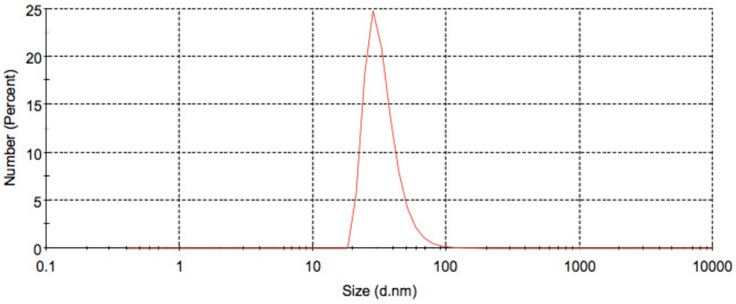


Fig. 1. Particle size distribution by number for magnetite nanoparticles, functionalized with sodium polyacrylate

The investigation of the hydrodynamic diameter of magnetite nanoparticles, functionalized with sodium polyacrylate, was carried out by the dynamic light scattering (Fig. 1). The spectrum of particle size distribution by the number was characterized by the presence of a one high peak, indicating on a narrow distribution of nanoparticles with mean hydrodynamic diameter about 30 nm.

2.2. Polyvinylidene fluoride membranes modification

Polyvinylidene fluoride membranes were modified by grafting polymers with amino groups, i.e. PEI, according to Figure 2. The grafting was carried out through the formation of double bonds in the process of PVDF degradation in alkali medium due to HF elimination at 55°C [16]. As a result, membranes colour changed from white to dark brown due to polyene formation.

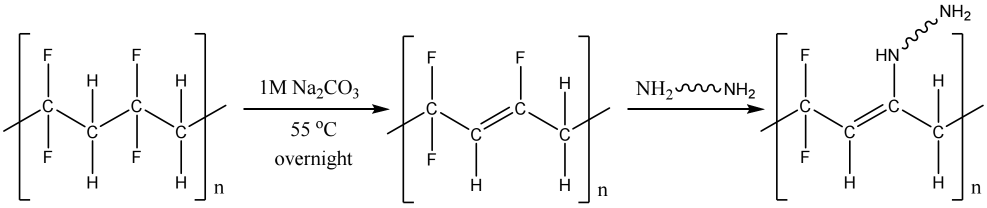


Fig. 2. Modification of PVDF membranes with PEI

After that, Fe_3O_4 nanoparticles stabilized with sodium polyacrylate were immobilized on the membrane surface *via* the peptide bond formation (Fig. 3).

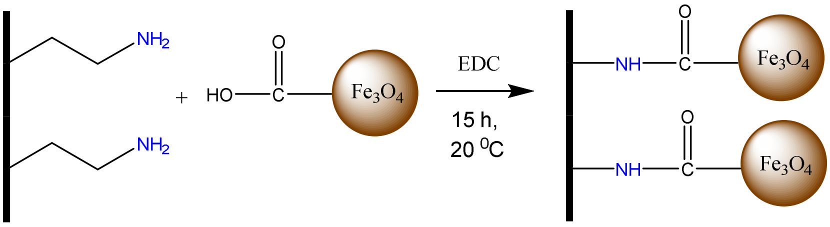


Fig. 3. Immobilization of Fe_3O_4 nanoparticles covered by sodium polyacrylate on the surface of PVDF membranes with grafted PEI

Membranes modification with PEI was confirmed by IR spectroscopy. As can be seen in Figure 4, in the IR spectrum of the unmodified PVDF membrane the most intense and wide absorption bands were in the range of 1500÷800 cm^{-1} due to the stretch and deformation vibrations of bonds ν(C-H), ν(C-C), ν(C-F), and δ(C-H). As well, the absorption bands at 877, 1174 cm^{-1} corresponded to stretching vibrations of the C-F bonds, absorption bands at 838, 1420 cm^{-1} were deformation vibrations of the C-H bonds, 1070 cm^{-1} belonged to stretching vibration of C-C bonds, and 2976 cm^{-1} corresponded to stretching asymmetric vibration of C-H bonds of the $-CH_2-$ group.

After PEI modification of the membrane surface, a broad absorption band appeared in the region of 3500÷3100 cm^{-1}, which corresponded to stretching vibrations of N-H bonds of polyethyleneimine. It should be noted that weakly absorption bands at 1540 and 1643 cm^{-1} belonged to stretching vibrations of both conjugated C=C bonds and isolated ones, respectively. Also after modification, the intensity of absorption bands at 877 and 1174 cm^{-1} decreased, which indicated the successful dehydrofluorination of the PVDF membrane.

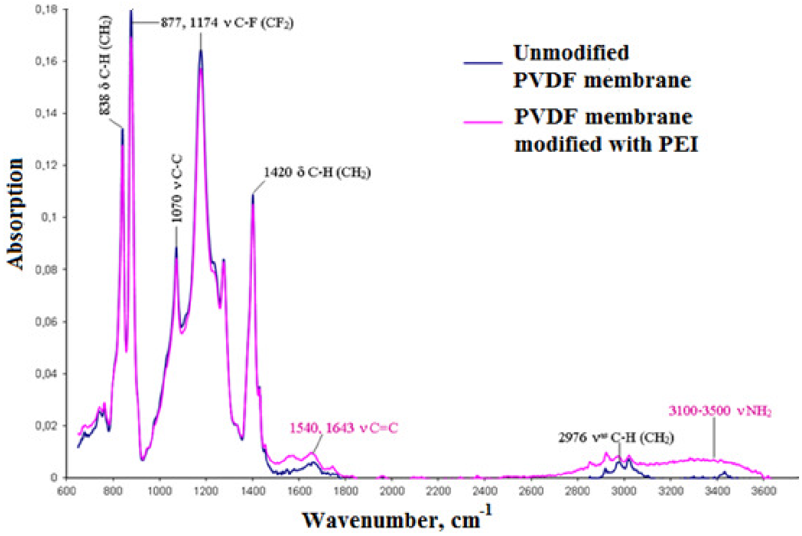


Fig. 4. IR spectra of unmodified PVDF membrane and membrane modified with PEI in alkali medium

The measuring of zeta-potential is an informative method for studying the membrane surface properties, since this parameter is very sensitive to any charge changes. The dependence of zeta-potential on pH for PVDF membrane modified with polyethyleneimine confirmed the modification of the membrane surface (Fig. 5). The unmodified PVDF membrane was negatively charged in all pH range (–17…–27 mV). As a comparison, a modified membrane surface was slightly negatively charged in alkali medium and its zeta-potential increased with pH decrease. The isoelectric point of the modified membrane was observed at pH 6.0. This behaviour could be explained by protonation of amino group in acidic medium.

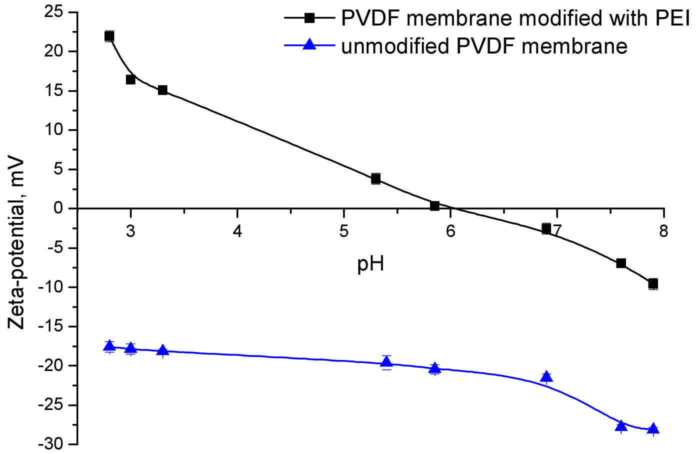
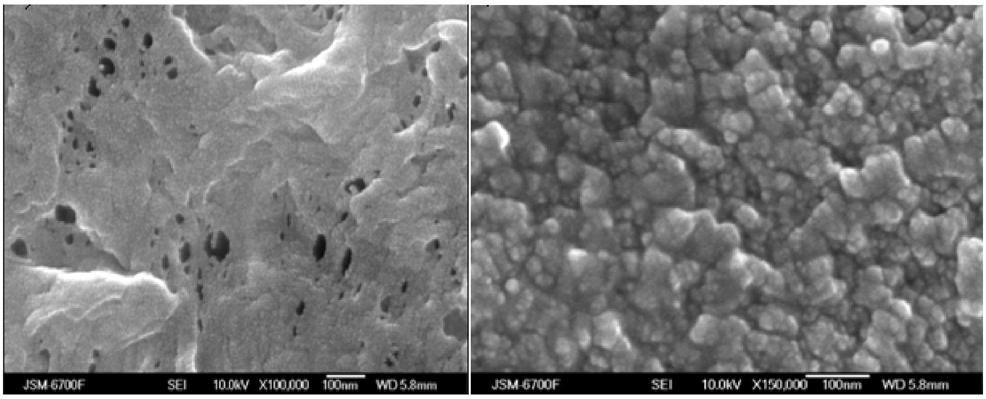


Fig. 5. The dependence of zeta-potential of unmodified PVDF membrane and membrane, modified with PEI, on pH

To confirm the immobilization of magnetite nanoparticles on the membrane surface, scanning electron microscopy (SEM) of modified and unmodified membranes was performed. As it can be seen in Figure 6, membrane surfaces significantly differed.

The surface of the unmodified PVDF membrane had the classical structure of a polymer film obtained by the phase inversion. The surface was penetrated with pores with wide size distribution. The surface of modified membrane was densely covered with a layer of nanoparticles. The size of the nanoparticles varied from 10 to 20 nm. Nanoparticles formed clusters on the surface of PVDF membrane. These clusters could not indicate on the heterogeneity of the surface coating, but they may have been formed due to the complex samples preparation prior to analysis.



A B

Fig. 6. SEM microphotographs of unmodified PVDF membrane (A) and PVDF membrane, modified with magnetite nanoparticles (B)

2.3. Fe^{2+} removal from water by CMC enhanced ultrafiltration

Iron substances can cause a lot of problems such as turbidity, odor and taste of water, and formation of sediments in water pipes. Due to WHO, regarding the health effect the level of iron in water should not exceed 2 mg/L. But even iron content of 0.3 mg/L (i.e. the level recommended) can cause the mentioned problems [17]. For drinking water taste, threshold of iron in water is 0.1 mg/L for iron(II) [18]. Thus, iron removal is a challenge in water treatment. To solve this problem, we proposed iron(II) removal by CMC enhanced ultrafiltration, as it formed cellulose-Fe coordination complexes [19].

At the first stage, for studying the phenomenon of concentration polarization in the process of CMC ultrafiltration, the dependence of the volumetric flux on the applied pressure was investigated (Fig. 7). Thus, for unmodified membrane, there was no significant volumetric flux increase with the pressure increase at CMC concentrations of 0.1÷0.3%, what indicated on the formation of a dense layer on the membrane surface during ultrafiltration. At CMC concentration of 0.5%, even a flux decrease was observed with pressure rising due to the formation of a cake and the blocking of membrane pores. For membrane modified with magnetite nanoparticles, it could be seen that the dependence of the volumetric flux on the applied pressure was linear in the range of CMC concentrations of 0.1÷0.2% and tended to the plateau at concentration of 0.3÷0.5%. The critical flux was 1.8÷2.0 times higher for modified membrane compared with unmodified one. This difference could be explained by magnetite nanoparticles rotation in the boundary layer in a magnetic field.

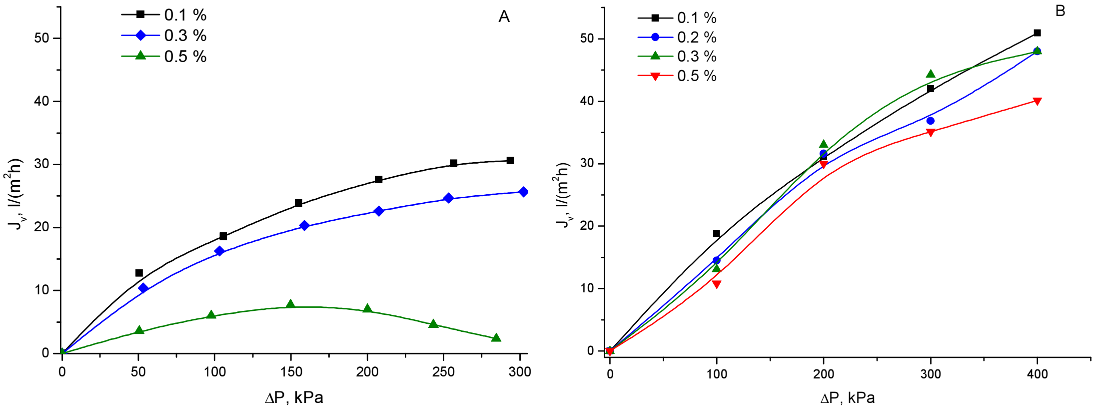


Fig. 7. Dependence of volumetric flux on the applied pressure at different CMC concentration: A) unmodified PVDF membrane; B) PVDF membrane modified with magnetite nanoparticles

Subsequently, the iron(II) rejection in the process of CMC enhanced ultrafiltration was investigated. The Fe^{2+} concentration in permeate is given in the Table 1.

Table 1. **Influence of CMC concentration on the Fe^{2+} amount in permeate**

CMC concentration %	Fe^{2+} concentration in permeate mg/L	
	Unmodified membrane	Membrane modified with Fe_3O_4 nanoparticles
0.1	0.6	0.08
0.2	1.0	0.02
0.3	0.6	0.02
0.5	0.8	0.03

[*] Feed Fe^{2+} concentration was 20 mg/L

The concentration of iron(II) in the permeate after ultrafiltration on the unmodified membrane far exceeded the permissible concentrations for drinking water. Whereas the Fe^{2+} concentration in the permeate after ultrafiltration on the membranes modified with Fe_3O_4 nanoparticles was significantly lower in comparison with the unmodified membrane and definitely fulfilled the requirements. Even at CMC concentration of 0.1% iron(II) amount in permeate was 0.08 mg/L, which was much lower than the maximum recommended level. Consequently, the CMC concentration of 0.1% was sufficient for PEUF.

In Figure 8 the dependence of the volumetric flux and the Fe^{2+} concentration in permeate (C_p, mg/L) on the recovery rate by ultrafiltration on modified membranes is shown.

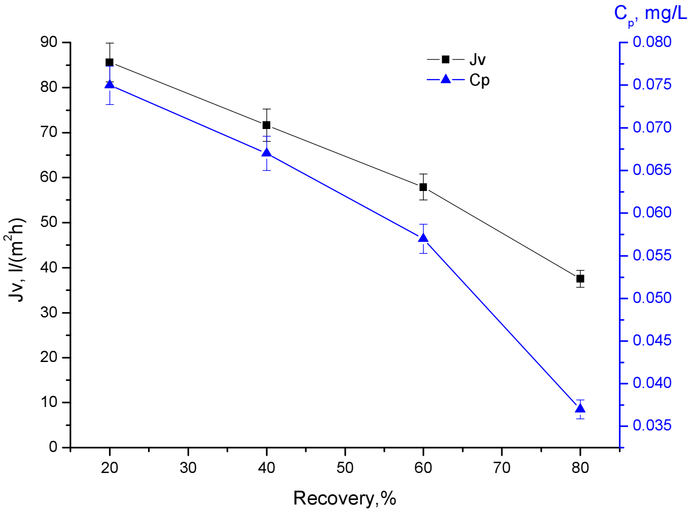


Fig. 8. **Dependence of volume flux and iron(II) content in permeate on the recovery rate at CMC concentration 0.1% after ultrafiltration on PVDF membranes modified with magnetite nanoparticles**

The results showed that at the recovery up to 60% volumetric flux decline was admissible in the range from 80 to 50 L/(m^2·h). With the recovery increase up to 80% there was a significant decrease of flux as the polyelectrolyte concentration increased 4 times due to its concentration at the feed site. However, the increase of the recovery did not affect the iron(II) amount in the permeate. Moreover, the Fe^{2+} concentration in the permeate decreased with the recovery increase. This indicated on the stability of the CMC-Fe complex, and also made the reduction of the polyelectrolyte concentration possible.

Conclusions

In summary, we had successfully removed Fe^{2+} from water by polyelectrolyte enhanced ultrafiltration with CMC on polyvinylidene fluoride membranes modified with magnetite nanoparticles. Magnetite nanoparticles were synthesized by the co-precipitation method and stabilized with sodium polyacrylate. Their average diameter, measured by TEM, was 10÷20 nm and hydrodynamic diameter was about 30 nm. At the first stage, the surface of PVDF membranes was modified by grafting of polyethylenimine. At the second stage, polyelectrolyte grafted to the membrane surface was used as a linker for magnetite nanoparticles immobilization. Modification of membranes was confirmed by IR spectroscopy, scanning electron microscopy and electro kinetic analysis. IR spectroscopy confirms PEI modification of the membrane surface. A broad absorption band appeared in the region of 3500÷3100 cm^{-1}, which corresponded to stretching vibrations of N-H bonds of PEI. Moreover, weakly absorption bands at 1540 and 1643 cm^{-1} belonged to stretching vibrations of both conjugated C=C bonds and isolated ones, respectively. Also after modification, the intensity of absorption bands at 877 and 1174 cm^{-1} decreased, what indicated on the successful dehydrofluorination of the PVDF membrane. The dependence of zeta-potential on pH for PVDF membrane modified with PEI confirmed the modification of the membrane surface as zeta-potential increased with pH decrease. SEM showed that the surface of modified membrane was densely covered with nanoparticles, which formed clusters. The dependence of the volumetric flux on the applied pressure at various concentrations of the carboxymethylcellulose (CMC) demonstrated the reduction of concentration polarization due to the presence of magnetite nanoparticles layer on the membrane surface. The volumetric flux did not reach the plateau for polysaccharide concentrations 0.1÷0.2%, what indicated on the absence of gel layer in the diffusion region near membrane surface. Polyelectrolyte enhanced ultrafiltration with CMC was used for iron(II) removal at initial Fe^{2+} concentration of 20 mg/L. The concentration of iron in permeate using an unmodified membrane ranged from 0.6 to 1.0 mg/L, whereas for the modified membrane it was 0.02÷0.08 mg/L.

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Streszczenie

Celem pracy było przedstawienie wyników badań dotyczących usuwania Fe^{2+} z wody za pomocą ultrafiltracji wspomaganej polielektrolitem na membranach z fluorku poliwinylidenu modyfikowanych nanocząstkami magnetytu. Nanocząstki magnetytu zostały zsyntetyzowane z wykorzystaniem metody strąceniowej i ustabilizowane poliakrylanem sodu. W pierwszym etapie powierzchnia membran PVDF została poddana modyfikacji polietylenoiminą. W drugim etapie polielektrolit, umieszczony na powierzchni membrany, został wykorzystany do immobilizacji nanocząstek magnetytu. Modyfikacja membran została potwierdzona badaniami spektroskopowymi, elektronową mikroskopią skaningową i analizą elektrokinetyczną. Wpływ pH na potencjał zeta membrany PVDF potwierdził jej modyfikację membrany, gdy potencjał zeta wzrasta z obniżeniem się wartości pH. Elektronowa mikroskopia skanningowa wykazała, że powierzchnia modyfikowanej membrany jest gęsto pokryta nanocząstkami, które tworzą klastry. Badano również wpływ wartości stosowanego ciśnienia na objętościowy strumień permeatu dla różnych stężeń karboksymetylocelulozy (CMC). Ultrafiltracja wspomagana polielektrolitem z CMC została wykorzystana do usuwania żelaza(II) przy początkowym stężeniu Fe^{2+} wynoszącym 20 mg/l. Stężenie żelaza(II) w permeacie w przypadku membrany niepoddanej modyfikacji uległo zmianie z 0,6 do 1,0 mg/l, podczas gdy w przypadku modyfikowanej membrany stężenie to było w zakresie 0,02÷0,08 mg/l.

Słowa kluczowe: **membrany z fluorku poliwinylidenu, nanocząstki magnetytu, ultrafiltracja z polielektrolitem, karboksymetyloceluloza**