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Surface modification of polyethersulfone membranes with goethite through self-assembly

Ivette G. Sandoval-Olvera[a], Liliana Villafaña-López[a], J. Antonio Reyes-Aguilera[b], Mario Ávila-Rodríguez[a], Teresa A. Razo-Lazcano[a], M. Pilar González-Muñoz[a,*]

[a]*Department of Chemistry, Cerro de la Venada s/n, University of Guanajuato, Mexico, emails: gomupi@ugto.mx (M.P. González-Muñoz), ivette_mx@msn.com (I.G. Sandoval-Olvera), ana_lili_vl@hotmail.com (L. Villafaña-López), avilam@ugto.mx (M. Ávila-Rodríguez), teresarazo@ugto.mx (T.A. Razo-Lazcano)*
[b]*Department of Chemical, Electronic and Biomedical Engineering, Loma del Bosque #103, Lomas del Campestre, 37150, University of Guanajuato, Mexico, email: ja.reyes@ugto.mx*

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ABSTRACT

The use of ultrafiltration membranes for wastewater treatment is a technique that has gained importance in recent decades. Its success is based on the fact that low energy is required for separating species due to low-pressure operating conditions compared with the techniques of nanofiltration and reverse osmosis. The major disadvantages of processes using ultrafiltration membranes for separation are the large pore size and membrane fouling. To overcome these drawbacks, ultrafiltration membranes have been modified by physical and chemical treatment in an attempt to reduce the pore size and change the surface properties of the membrane for specific applications. In this work, the surface modification of polyethersulfone ultrafiltration membranes by sub-microparticles of goethite is presented. The surface modification is achieved through self-assembly by coating the polyethersulfone membranes with goethite sub-microparticles in suspension. The modified membranes were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and fourier transform-infrared (FT-IR). The results obtained display the goethite's interaction with the membranes through hydrogen bonds between the hydroxyl groups of the goethite, and the $–SO_2$ and CO bonds present in polyethersulfone. The membranes obtained were evaluated for retention of chromate ions at pH values of 4 and 8. It was observed that membranes modified with 1 mg of goethite are capable of retaining almost 90% of the Cr(VI) at pH 8. The pH increase ionizes the hydroxyl groups of the goethite and creates a negative charge on the membrane that rejects chromate ions. The modification of the membrane can be achieved by a simple and efficient procedure that achieves the separation of charged species at low pressure (20 psig).

Keywords: Ultrafiltration; PES; Self-assembly; Goethite; Cr(VI)

1. Introduction

Ultrafiltration (UF) is a low-energy membrane separation process. The major application of UF membranes is water treatment, where UF membranes are generally used before nanofiltration (NF) and reverse osmosis (RO) techniques [1]. Because the pore size of the UF membranes is relatively large, this technique cannot be used directly in the separation of small species, such as inorganic ions. For this reason, the number of UF membrane surface modification techniques has increased in recent years. The main objective of membrane modification is to improve the membrane's antifouling performance by making surfaces more hydrophilic or decreasing their pore size, while at the same time keeping their basic characteristic of being a low-energy process.

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* Corresponding author.

One of the most-commonly used membranes is the UF polyethersulfone (PES) membrane due to its high thermal and chemical stability; for this reason, it has been subjected to surface or structural modification through the application of copolymers, surfactants and nanoparticles.

The structural modification of the membrane is usually done directly during membrane preparation by adding copolymers as precursors in the method of synthesis employed. Chakrabarty et al. [2] and Marchese et al. [3] have reported the preparation of UF PES membranes by the method of phase inversion using mixtures of PES and polyvinyl pyrroline (PVP) and solvents such as dimethyl acetamide (DMAc), which give the membranes an asymmetric structure with a dense top layer and a porous sublayer; average pore size, pore number and permeability were obtained using the liquid displacement test. Other authors have used different hydrophilic monomers such as *N*-vinyl-2-pyrrolidinone (NVP), 2-acrylamidoglycolic acid monohydrate (AAG), 2-acrylamido-2-methyl-1-propanesulfonic acid (AAP) and poly(ethylene glycol) methacrylate (PEGMA), which are grafted onto UF PES membranes by dipping them in the monomer solution; copolymerizing heterogeneous grafting is later induced by applying ultraviolet (UV) radiation or low-temperature helium plasma [4–7], yielding modified low-fouling membranes. In other cases, it has also been applied to generate a composite polymer membrane with specific surface properties. Louie et al. [8] modified polyamide (PA) membranes by coating them with a mixture of nylon-6 and polyethylene glycol (PEG). The modification was accomplished by immersing the membranes in the mixture of polymers, and the membranes were tested for 106 days by filtering an oil/surfactant/water emulsion. The modified membranes showed a slower rate of flux decline when compared with unmodified membranes. Polymers like polyethyleneimine (PEI), polyvinyl alcohol (PVA) and polyacrylic acid (PAA) have also been used in membrane surface modification with good results [9,10].

There are also papers about the modification of membranes using surfactants as modifiers. Rana and Matsuura [11] reported the use of sodium dodecyl sulfate (SDS) and poly sodium 4-styrene sulfonate (PSS) on PES membranes for the separation of PEGs and dextrans solutions, as well as the use of anionic SDS and cationic tetra decyl trimethyl ammomuim bromide (TTAB) for the separation of natural organic matter; in both cases, the modified membranes showed better anti-fouling performance but also a significant flux decline. Xie et al. [12] used surfactant Tween 20 to modify polypropylene (PP) microfiltration (MF) membranes to increase their surface charge. This charge increase was due to the adsorption of the surfactant, creating a monolayer on the membrane surface and inside the pores. The authors reported that modified membranes present a higher water flux coupled with a lower fouling level in comparison with the unmodified membranes.

In the case of membrane surface modification with inorganic oxides, the use of TiO_2 and Al_2O_3 have been reported [11,13–15]. Nanoparticles are added to obtain membranes with specific characteristics, as a result of interaction between polymeric materials and nanoparticles. There some reports on the modification of PES membranes with TiO_2 nanoparticles [16–18], which are trapped in the pores and over the surface of the membrane. The authors report that this modification extends the hydrophilicity, thermal stability and anti-fouling ability of membranes [18]. Rahimpour et al. [19] have applied TiO_2 nanoparticles to modify UF PES membranes during their synthesis. The modified membranes were used to separate milk proteins.

Other authors have carried out the self-assembly of TiO_2 and Al_2O_3 nanoparticles by immersing the UF PES membrane in a colloidal solution of oxide nanoparticles and applying ultrasound [20,21] or by achieving the membrane during a non-solvent induced phase separation process [22]. The membranes obtained are very hydrophilic, photoactive and practical for a wide variety of environmental applications such as water purification, wastewater treatment and hazardous waste control. However, this modification is not easy to carry out effectively, because the membrane pores are plugged by the sorption of oxide.

There are a few reports on the use of iron oxides in the modification of UF membranes. Bagheripour et al. [23] have reported the modification of PES–NF membranes with nanoparticles of iron-nickel oxide. The addition of mixtures of metal oxides during membrane preparation was evaluated with the rejection of $NaCl/Na_2SO_4$ salts. The rejection of salts increases with the content of metal oxides. The addition of 0.01 wt% of metal oxides was enough to increase the water flux but a higher quantity (1.0 wt%) decreased this parameter again. Rahimi et al. [24] report a method based on membrane bioreactor technology (MBR) for the remediation of wastewater using a mixture of O-carboxymethyl chitosan and ferrosoferric oxide ($OCMCS/Fe_3O_4$). Membranes modified with 0.1 wt% of $OCMCS/Fe_3O_4$ have a better water flux recovery ratio (FRR) than unmodified membranes. Huang et al. [25] used different concentrations of PAA/ferroferric oxide chelates (PAA/Fe_3O_4) to modify UF PES membranes for bovine serum albumin (BSA) separation from aqueous solutions. Modified membranes showed a better anti-fouling performance; however, the synthesis reported to obtain the modified membrane requires a lot of time.

In summary, compounds with charged functional groups or compounds that can be ionized in solution are commonly used as modifying agents. Such modifying agents generate changes on the surface membrane such as the diminution of the pore size, variation in the layer thickness and changes in the surface charge of the UF membranes. In general, the modified membranes present an improvement in the hydrophilic character and superficial charge properties. The difference in the surface-modified membrane is a function of the nature of the modifying agent, its concentration and the contact time of modification. The most commonly reported modifying agents are polymers, surfactants and, recently, nanoparticles [11,13]. The use of iron oxide particles in the modification of PES membranes is poorly documented. This lack of knowledge does not allow for the evaluation of the impact of the use of low-cost iron oxides in the modification of UF membranes and their potential application in separation processes. On other hand, there are drawbacks to each membrane modification method mentioned. Membrane preparation by phase inversion techniques using polymer mixture methodology often requires the application of UV or low-temperature plasma radiation; in addition, other requirements of synthesis such as inert atmosphere are needed. Membrane preparation by phase inversion techniques with the addition of nanoparticles to the casting solution requires nanoparticle pretreatment and UV radiation. The doping of membrane by surfactants or nanoparticulate materials presents difficulties in the uniform distribution of the nanoparticles or surfactant; furthermore, the nanoparticles or the surfactant are sometimes lost when the membrane is applied.

In this work, we report a novel, simple self-assembly method for achieving the modification of commercial UF PES membranes with an accessible and simple material: sub-microparticles of goethite (iron oxide), which is very simple to prepare and does not require stabilization prior to its application to the membrane. The characterization by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and fourier transform infrared-attenuated total reflection (FTIR-ATR) showed evidence of goethite self-assembly on the PES membranes. The membrane's performance was evaluated as stable and efficient through water flux and Cr(VI) retention.

2. Materials and methods

2.1. Materials

UF PES membranes with a molecular weight cutoff of 10 kDa were purchased from Millipore Corp., USA.

The goethite sub-microparticles (α-FeOOH) were provided by the Institute of Materials Science of Madrid (CSIC). The sub-microparticles present an acicular morphology, and a size of 250 nm.

The Cr(VI) solutions were prepared from potassium dichromate (MERCK, Denmark) using deionized water; the solutions were adjusted to different pH values using HCl 0.1 M and NaOH 0.1 M. 1,5-diphenyl carbazide (KARAL, Mexico), acetone (KARAL, Mexico), sulfuric acid (KARAL, Mexico) and standard of Cr(VI) 1,000 mg/L (KARAL, Mexico) were also used. All the reagents were of analytical grade.

2.2. Experimental procedure

Prior to the modification of the PES UF membranes, the commercial membrane was rinsed with 75 mL of water, and then washed with a 0.1 N NaOH solution; finally, the membrane was rinsed again with distilled water until the pH of the permeate was neutral. The membrane was stored in distilled water to keep it hydrated until use.

For better dispersion, the goethite was placed in a vial with 5 ml of ethanol and then suspended in an ultrasonic bath (BRANSON Ultrasonic Cleaner model 2510-MTH, frequency: 40 KHz) for 10 min; temperature was controlled at 25°C. The membrane was fixed on an acrylic frame, and the active layer was coated with the goethite suspension dropwise over the membrane's entire surface; then the ethanol was allowed to evaporate for a few minutes until the goethite was deposited on the membrane. The procedure was repeated until the goethite suspension was used up. Finally, the modified membrane was dried for 18 h in a room with the temperature controlled at 20°C.

The evaluation of the modified membrane was performed by filtration in an Amicon model 8200 dead flow cell (Millipore Copr., USA) with nitrogen gas. The filter cell has a capacity of 200 mL and an effective membrane area of 28.7 cm^2. The functional performance of the membrane was evaluated on the basis of permeate obtained from filtration (10 fractions of 10 mL). All experiments were made in triplicate. The standard deviation and the permissible uncertainty limits, for a confidence level of 95%, were calculated using a Student's t-distribution with t = 2.9200 [26].

The membranes were characterized by infrared spectroscopy (FTIR-ATR) using a FT-IR spectrometer (PerkinElmer, USA), SEM using a Sigma field emission scanning electron microscope (Zeiss, Germany) and confocal microscopy with an Olympus U-TVO.5XC-3 microscope.

The functional performance of the membranes was evaluated in terms of water flux and Cr(VI) retention (%R). Cr(VI) quantification was performed by UV-Vis spectrophotometry using a colorimetric technique based on complex formation between Cr(VI) and 1,5-diphenylcarbazide in an acid medium [27]. A Cary 50 model Varian UV-Vis PROBE spectrophotometer was used for this purpose.

The relative flux reduction (RFR) was calculated as follows:

$$\mathrm{RFR}(\%) = \left(1 - \frac{J_M}{J_0}\right) \times 100 \tag{1}$$

where J_M represents the flux of the ultrapure water through the modified membrane, and J_0 the flux of the ultrapure water through the unmodified membrane. All the experiments were conducted at a constant stirring speed of 180 rpm and a nitrogen pressure of 20 psig. Finally, the percentage of retention was calculated using the permeate concentration (C_p) and retentate concentration (C_r) in the following equation:

$$\%R = \left(1 - \frac{C_p}{C_r}\right) \times 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of modified and unmodified membranes

3.1.1. Structural characterization

The membrane modification was carried out with 1 and 1.5 mg of goethite suspended in solution; subsequently, the characterization was performed.

3.1.1.1. Microscopies

Differences in the superficial morphology of the membrane were evaluated using confocal microscopy and scanning electron microscopy (SEM) images. Fig. 1 shows the confocal microscopies (Objective 20X) of the unmodified and goethite modified (1 and 1.5 mg) membranes.

The confocal microscopy of the unmodified membrane shows a homogeneous and smooth surface (Fig. 1(A)). On the modified membrane, the presence of the goethite can be observed on its surface. The membrane modified with the goethite suspension of 1 mg presents a uniform distribution of the sub-microparticles; goethite agglomeration can be seen, however, in some areas (Fig. 1(B)). By employing a larger amount of goethite (1.5 mg) to modify the membrane, a greater number of areas with sub-particle agglomeration can be observed, as well as some areas without goethite (Fig. 1(C)).

Fig. 2 shows the SEM images of the unmodified membranes (Figs. 2(a1), (a2) and (a3)) and the goethite modified membranes: 1 mg (Figs. 2(b1), (b2) and (b3)) and 1.5 mg (Figs. 2(c1), (c2) and (c3)). 1000X (1), 5000X (2) and 10000X (3) amplifications were used.

It can be observed in Fig. 2 that the goethite sub-microparticles on the membrane increase in direct proportion to the mass in the suspension (1.5 mg), presenting a higher agglomerate presence.

The membranes were characterized by EDS analysis before and after their modification (Fig. 3). The elemental analysis of the unmodified PES membrane shows C, S and O peaks. On the modified membranes, Fe peaks from the goethite were also found.

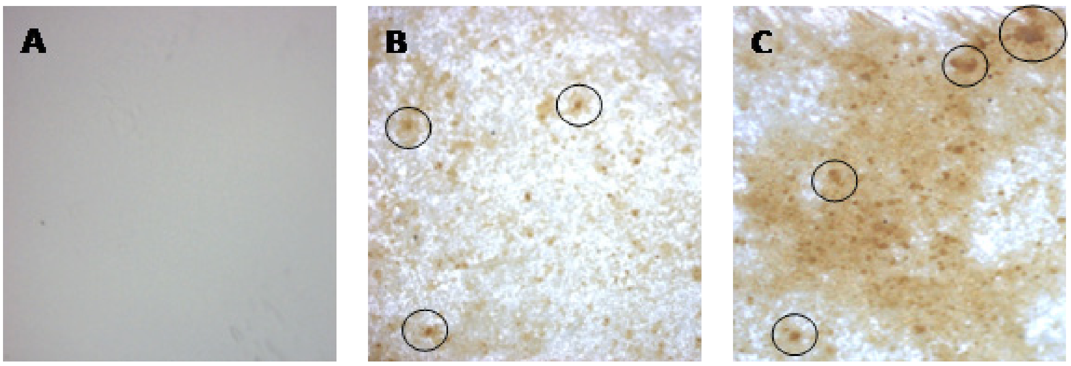

Fig. 1. Confocal microscopy of the PES unmodified membrane (A), goethite modified membranes: 1 mg (B) and 1.5 mg (C). Objective 20X.

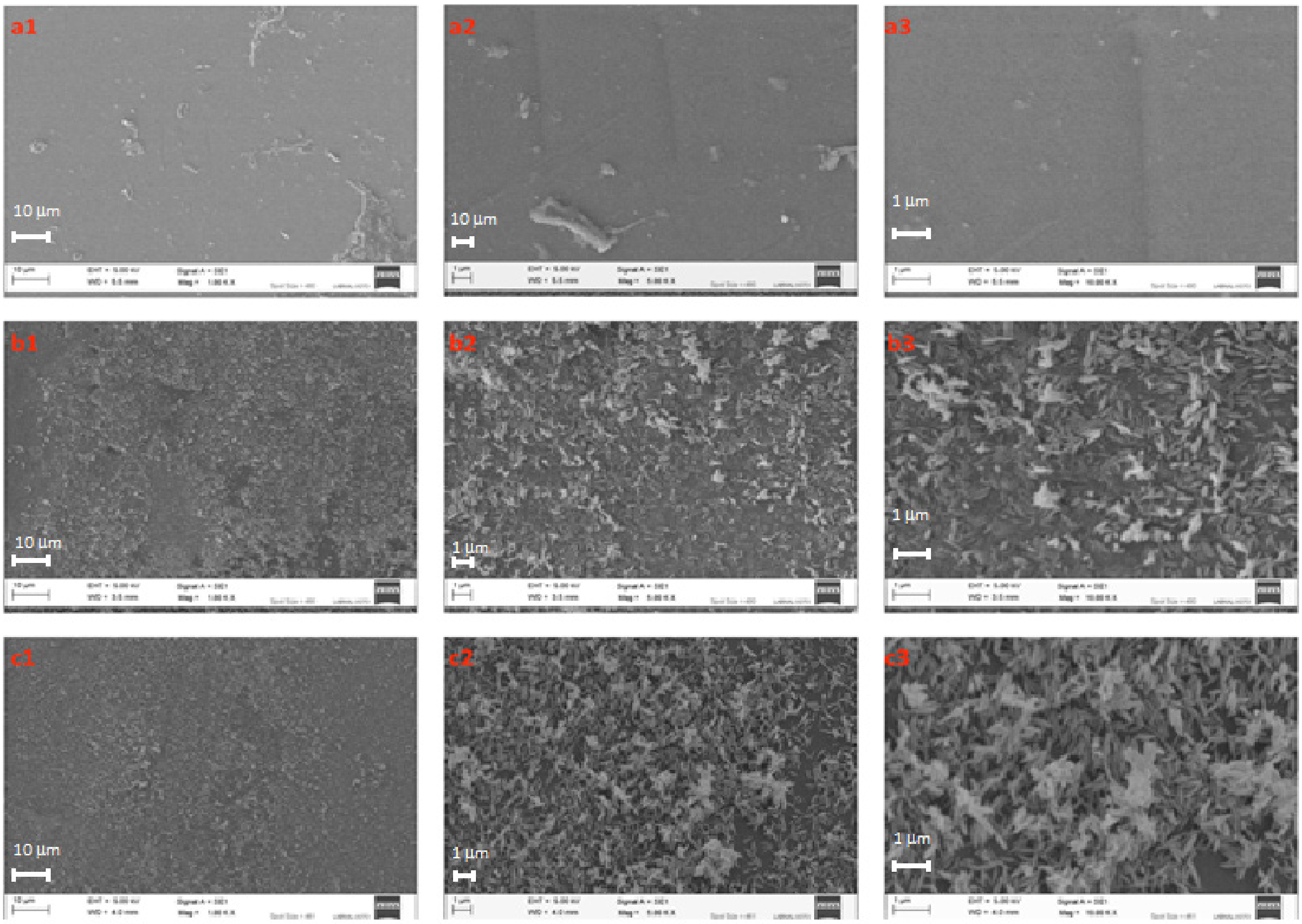

Fig. 2. SEM images (1000x (1), 5000x (2) and 10000x (3)): unmodified membrane (a), modified with goethite: 1 mg (b) and 1.5 mg (c).

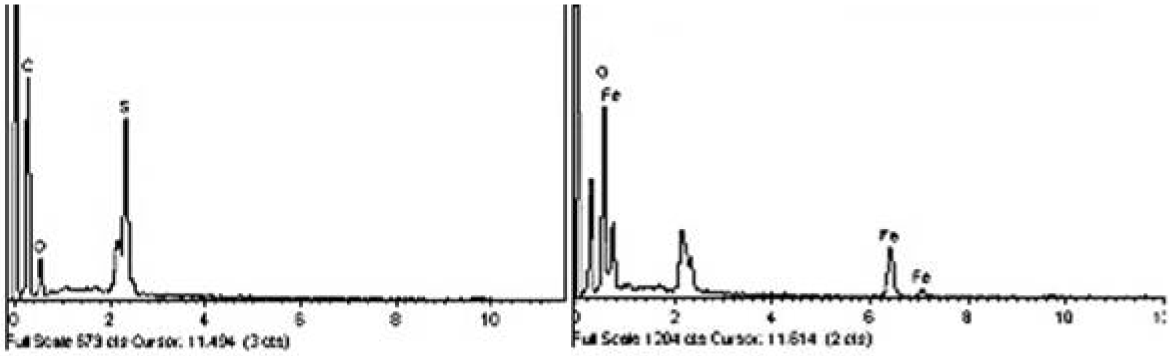

Fig. 3. EDS microanalysis of the PES membranes: unmodified (left) and modified (right).

3.1.1.2. FTIR-ATR

The membranes were also characterized by FTIR-ATR. Fig. 4 shows the spectrum of the unmodified PES membrane; the stretching vibrations of the =C–H groups corresponding to the 1,4-disubstituted benzene ring are present around 3,000 cm^{-1}. The peaks located at 1,585 and 1,588 cm^{-1} correspond to the stretching vibration of the C=C bond. The oxygen attached to the phenyl presents an intense band due to the stretching of the single C–O bond and is located in the range of 1,275–1,200 cm^{-1}. The stretching vibration bands of the sulfone group (–SO$_2$) appear between 1,250–1,290 cm^{-1} and 1,165–1,120 cm^{-1}, but when the sulfone group is linked to the phenyl group, the bands move to lower frequencies. The vibration band of the C–S bond is located at 689 cm^{-1}, and finally, the signals around 800 cm^{-1} are out-of-plane vibrations of the C–H bond [28,29].

The infrared spectrum of the goethite is very representative, due to the bands corresponding to the hydroxyl groups. Ruan et al. [30] reported that synthetic goethite shows two bands of enlargement belonging to the hydroxyl group at ~3,450 and ~3,206 cm^{-1}, two intense hydroxyl stretching bands at ~1,687 and ~1,643 cm^{-1}, two hydroxyl bands of deformation at ~888 and ~798 cm^{-1}, a hydroxyl translation band at ~619 cm^{-1} and a vibration band of Fe–O at ~461 cm^{-1}. Fig. 5 shows the infrared (IR) spectrum of goethite obtained with potassium bromide pellets; the spectrum presents the characteristic peaks reported elsewhere [30].

In the FTIR-ATR spectrum obtained from the PES membrane modified with goethite (Fig. 6), it can be observed that the two signals corresponding to goethite at 3,419 and 3,179 cm^{-1} disappear, and that a wider single peak of lower intensity is detected. This can be attributed to a stretching band signal of polymer association corresponding to the –OH group, which is located between 3,400 and 3,230 cm^{-1}; this signal is broad due to its overlapping with the signal of the =C–H group near 3,000 cm^{-1}. The goethite signals at 1,662 and 1,552 cm^{-1} also disappear on the modified membrane. After the modification, a single signal at 1,665 cm^{-1} is observed, which corresponds to the basic bending vibration of the OH bond; this new signal is less intense than the two original signals that are on the original goethite spectrum. Normally, the fundamental bending signal of the –OH group is located around ~1,636 cm^{-1}. The signal of the C–O is wider once the membrane is modified, and the second signal of the sulfone group, which is present in the 1,165–1,120 cm^{-1} range, becomes more intense.

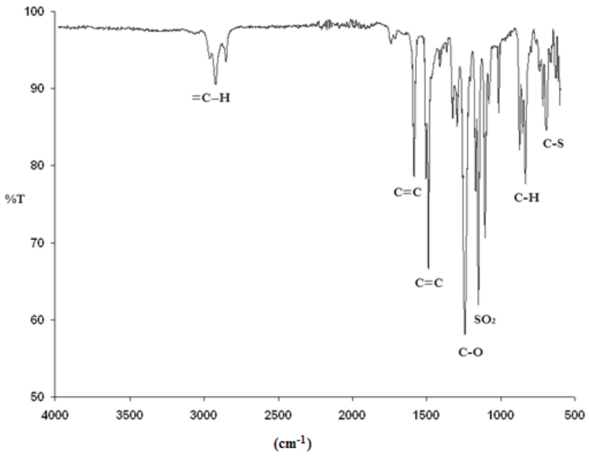

Fig. 4. FTIR-ATR spectrum of the unmodified PES membrane.

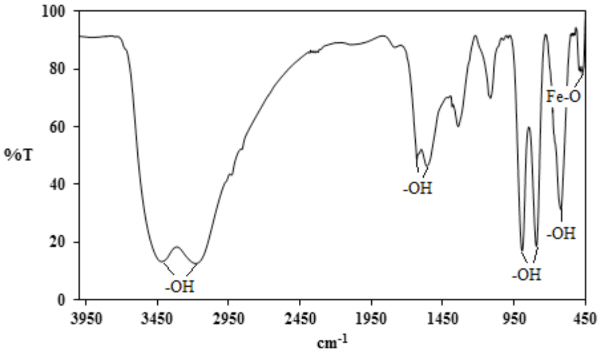

Fig. 5. Goethite IR spectrum obtained with potassium bromide pellet.

3.2. PES–goethite interaction

Based on the FTIR-ATR spectrum, the possible PES–goethite interaction is proposed. Due to the hydroxyl signals of the goethite as well as the changes to the C–O and S–O bonds of the PES in the infrared spectrum after the modification, it is very likely that the membrane–goethite interaction occurs with these groups. Several authors have proposed the interaction between an inorganic oxide and a polymeric membrane, such as titanium dioxide and the PES, by coordination bonds of the oxygen of the sulfone and ether groups with the Ti^{4+} or by a hydrogen bond between the sulfone and ether groups with the hydroxyl of the TiO_2 [31,32]. Considering the above and the fact that the hydroxyls are the most affected groups on the PES–goethite spectrum, the interaction must be through hydrogen bonds rather than a coordination bond between Fe(III) and the sulfone or ether groups. Fig. 7 shows the possible interaction between the PES membrane and the goethite.

3.3. Functional characterization of the modified membranes

The functional performance of the membranes was evaluated by water flux before and after their modification, and the percentage of RFR (%RFR was calculated. Fig. 8 shows the results of a flux of water (J_w) passed across the membrane as a function of time, in the case of the unmodified membrane (Fig. 8(A)) and when the membrane has been modified with 1 mg of goethite.

The fluxes obtained for unmodified membranes were close to 250 Lm^{-2} h^{-1}. The membrane modified with 1 mg of goethite has a decrease in the water flux of 72% (J_w close to 60 Lm^{-2} h^{-1}). This diminution of J_w serves as evidence of the membrane's modification, and the result is the diminution of water flux, which can be attributed to a pore reduction due to the self-assembly of goethite with the membrane surface and inside the pores. When 1.5 mg of goethite is employed, no water flux is detected, indicating that the RFR is 100%. This can be attributed to complete blockage of the membrane's pores [19].

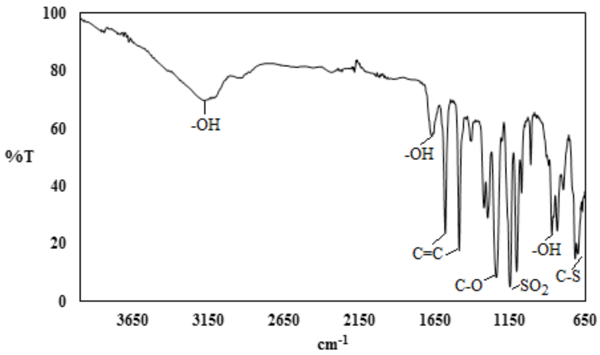

Fig. 6. FTIR-ATR spectrum of a PES membrane modified with goethite.

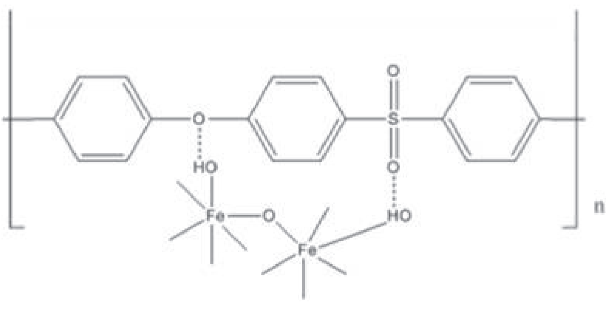

Fig. 7. Interaction between the goethite sub-microparticles and the PES membrane.

In accordance with these results, the modification of membranes for ion retention tests was carried out using 1 mg of goethite in the modification solution.

The functional performance of the modified and unmodified membranes was evaluated using the Cr(VI) species at two different pH values (4 and 8), in order to evaluate the effect of the retention percentage due to ion charge. Fig. 9 shows the species distribution diagram of H_2CrO_4: at pH 4 the $HCrO_4^-$ is the predominant ion, while at pH 8 the CrO_4^{2-} predominates.

The %RFR of Cr(VI) solutions are shown in Table 1. It can be seen that the %RFR is greater at pH 4: the flux reduction

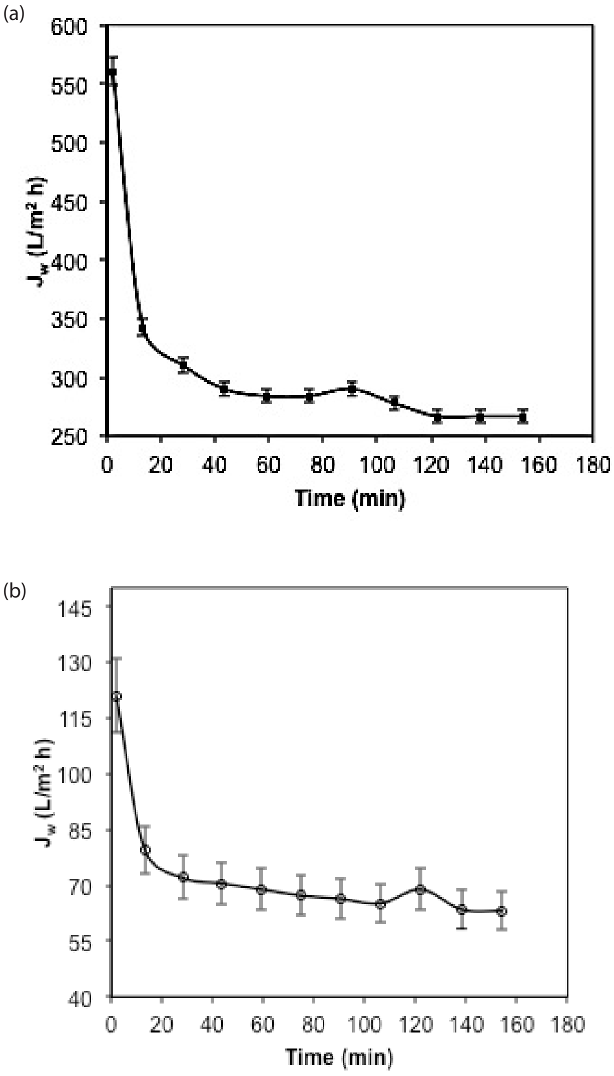

Fig. 8. Water flux variation (J_w) as a function of time: (A) unmodified membrane and (B) modified membrane: $P = 20$ lb/in^2.

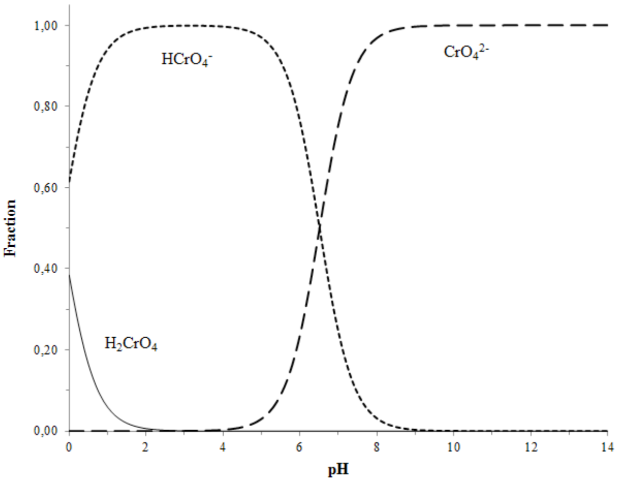

Fig. 9. Species distribution diagram of chromic acid.

Table 1
Cr(VI) relative flux reduction by modified membranes at pH 4 and 8

Cr(VI) solution pH	%RFR
4	87.2
8	67.7

observed was greater than that observed with pure water. This can be due to the adsorption of Cr(VI) ions on the membrane surface, resulting in a decreased flux. At pH 8 it was observed that the %RFR was similar to that observed with pure water; this may be caused by the absence of adsorption of Cr(VI) ions on the membrane surface at this pH.

Fig. 10 shows the results of %R of Cr(VI) as a function of the permeate volume for the unmodified and modified membranes at different pH values (4 and 8).

It can be seen that the %R of the unmodified membrane at both pH values (4 and 8) is lower than 20%, indicating that the pH of the feed solution does not affect the %R. Those results were as expected because the ion size is smaller than the pore size, and the size exclusion is the phenomenon that controls the retention mechanism.

The retention of Cr(VI) by the modified membranes presents an important increase in comparison with the unmodified membranes. At pH 4, the retention is 40%, while the retention is almost 90% at pH 8.

The increase in the anion retention can be explained if it is considered that during the retention process three phenomena can be present: (1) charge exclusion generated by the electrostatic interactions; (2) the sorption of anions on the membrane and (3) molecular exclusion due to the decrease in the pores' size due to the incorporation of the goethite sub-microparticles. Xie et al. [33] studied the absorption of Cr(VI) onto the surface of goethite finding that the adsorption of chromates is directly proportional to their concentration. Absorption is high at low pH values (3–5) and decreases strongly with increasing pH, with minimal adsorption at pH = 8. Therefore, it can be said that charge exclusion is the most important factor for the rejection of Cr(VI) because the charge of the anion increases (from 1 to 2 for pH 4 to 8). The charge exclusion is caused by the hydroxyl groups of the goethite, which can be ionized and create a negative charge on the surface of the modified membrane. This negative charge is determined by goethite's pI. Some authors [34,35] report isoelectric point values from 6.2 to 7.7, which differ due to the medium used for the synthesis of goethite. However, it is important to note that the pI of goethite can be affected by interaction with the membrane. For that reason, at pH 4, the membrane would be positively charged, and at pH 8, it could present a negative charge. Thus, at pH 4, the predominant separation mechanism is the adsorption of Cr(VI) ions, while at pH 8 the electrostatic rejection between the modified membrane and the chromates is the main mechanism. This behavior supports the %RFR results obtained, which are similar for the solutions at different pH values.

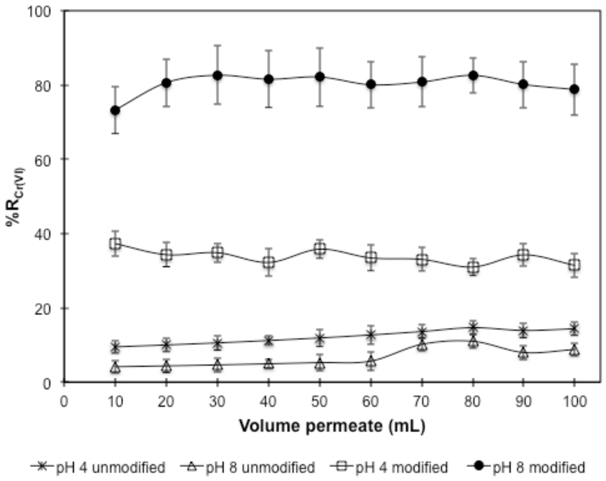

Fig. 10. Cr(VI) percentage of retention obtained by the unmodified and modified membranes (pH of 4 and 8): Cr(VI) = 40 mg/l, P = 20 lb/in^2.

3.4. Membrane stability

The modified membrane was left immersed in water for 4 weeks. Every week, water flux and Cr(VI) retention were evaluated. The results show that the %RFR is maintained at 70%, while the retention of Cr(VI) is about 80% (100 ml of chromate solution were permeated). From these results, we can say that modified membranes exhibit good stability at least for 4 weeks.

4. Conclusions

A modification technique was developed through the self-assembly of sub-microparticles of iron oxyhydroxide (goethite) on PES UF membranes. The microscopies show the presence of goethite on the membrane surface, as well as the formation of agglomerates when a higher goethite concentration is used in the suspension. The FTIR-ATR characterization showed evidence of the interactions between the goethite and the PES membrane. This evidence includes the disappearance of the signals located at 3,419 and 3,179 cm^{-1}, producing a wider signal of lower intensity. Moreover, the two signals at

1,662 and 1,552 cm^{-1} of the goethite spectrum disappear after modification, and a signal appears at ~1,655 cm^{-1}. The signal of the C–O interaction is wider on the modified membrane, and the second signal of the sulfone group from 1,165 to 1,120 cm^{-1} becomes more intense. Goethite–PES self-assembly was achieved through the formation of hydrogen bonds between the oxygen of the membrane's ether and sulfone groups, and the hydrogen of the goethite's hydroxyl groups. Cr(VI) was retained on the modified membranes. A better percentage of retention, close to 90%, was registered with 1 mg of goethite and pH 8. The separation mechanism proposed takes into account the contribution of both the sieve effect and repulsive electrostatic interactions between the modified membrane and the chromate anion.

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Symbols

%RFR – Percentage of relative flux reduction
J_s – Permeate flux of Cr(VI)
J_0 – Initial flux of the ultrapure water
%R – Percentage of retention
C_p – Permeate concentration
C_r – Retentate concentration

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