FUNCTIONAL ION MEMBRANES SUPPORTED INSIDE MICROPOROUS POLYPROPYLENE MEMBRANES TO TRANSPORT CHROMIUM IONS. DETERMINATION OF MASS TRANSPORT COEFFICIENT

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ABSTRACT

Polypropylene (PP) membranes incorporating interpenetrating polymer networks of poly[(ar-vinylbenzyl) trimethylammonium chloride](P(CIVBTA)) and poly[sodium (styrenesulfonate)] P(SSNa) were modified via an “*in-situ*” radical polymerization synthesis inside the pores. The modified polypropylene membranes were characterized using SEM, ATR/FTIR, DRX, TGA, and Donnan dialysis for the transport of chromium ions. The modified membranes exhibited a percent modification between 2.5% and 4.0% in weight gain and a hydrophilic character with a water uptake capacity between 15% and 20%. The mass transport coefficient was determined using the non-linear fit of the experimental data to the exponential equation. Hexavalent chromium ions were efficiently transported by the modified membranes containing P(CIVBTA). At pH 3.0, the M4Cl.PEI ($11.0 \times 10^{-6} \text{ m s}^{-1}$), and at pH 9.0, the M3Cl ($14.4 \times 10^{-6} \text{ m s}^{-1}$) could transport hexavalent chromium ions efficiently using a 1 mol L^{-1} NaCl extraction agent. In the same way, the transport of trivalent chromium could be performed using membranes modified with P(SSNa). At pH 3.0 and $4.0 \times 10^{-2} \text{ mol L}^{-1}$ trivalent chromium in the food chamber, the M9Na.PVA ($16.3 \times 10^{-6} \text{ m s}^{-1}$) performed efficient transport using $1 \times 10^{-3} \text{ mol L}^{-1}$ HNO₃ as the extraction agent.

Keywords: interpenetrating polymer network, membranes, Donnan dialysis, chromium, ion exchange, and polypropylene.

1. INTRODUCTION

Environmental pollution of water, soil, and air is a serious problem when it includes oxyanions. Some oxyanion water-contaminating species employed in industry are chromate, arsenate, permanganate, hydrogen selenite, and selenate. A particular case is the derivatives of the chromium oxyanions. Chromium ions have two oxidation states in the water, for example, the trivalent chromium Cr(III) and hexavalent chromium Cr(VI).

Cr(VI) produces the oxyanion (chromate) and the polyoxyanion (dichromate). These oxyanions are the more toxic ionic species and cause serious health problems such as cancer. The toxicity depends on the concentration and the exposure period^{1,2}. Cr(VI) oxyanions are water-soluble across all pH ranges and accumulate well in biological systems (bioassimilable), and their speciation depends on the pH and concentration. If the pH is strongly acidic and the Cr(VI) ions are highly concentrated, the chromium ions exist as dichromate ($\text{Cr}_2\text{O}_7^{2-}$), chromic acid (H_2CrO_4), and dichromate acid ($\text{H}_2\text{Cr}_2\text{O}_7$)^{3,4}. However, at weakly acidic pH values above 6.0, a large quantity of chromate (CrO_4^{2-}) ions exists, and in the range of pH values between 4.0 and 6.0, dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and chromate (CrO_4^{2-}) ions can exist. The World Health Organization (WHO) recommends a maximum concentration limit of $0.05 \text{ (mg L}^{-1}\text{)}$ by the hexavalent chromium ions.

However, the Cr(III) ion is an element essential for life⁶. Nevertheless, at certain concentrations, the Cr(III) ion can cause biological damage. The main Cr(III) species that dissolves in water depends on the pH range, and the ions are Cr(OH)_3^+ , Cr(OH)_3^0 , and Cr(OH)_4^- chromyl ions, which prevail at pH values below 3.6⁷. When the pH values are higher, Cr(III) precipitates as $\text{Cr(OH)}_3 \cdot n\text{H}_2\text{O}$ ⁸.

The most common methods developed to remove Cr(VI), and Cr(III) ions from polluted solutions are reduction and precipitation⁹, adsorption¹⁰, and ion exchange^{11,12}. Membrane technologies allow for reverse osmosis, ultrafiltration, nanofiltration, dialysis, diffusion dialysis, Donnan dialysis, membrane electrolysis, and electrodialysis^{4,12-14} (liquid, emulsified and supported)^{13,15,16}. However, it is difficult to eliminate the oxyanions Cr(VI) and the Cr(III) ions selectively from the water. The improvement of the removal methods and the production of new functional polymer materials are very useful in the development of new technologies for removal, retention, and recovery of the chromium ions from aqueous solutions. Donnan dialysis using the ion exchange membranes has been considered as an alternative for the separation process.

The Donnan dialysis technique is based on the employment of the chemical potential differences between the membrane sides to generate ionic transport and to maintain the electro neutrality of the two solutions, and the Donnan dialysis is considered a hybrid process¹⁷. The efficient Donnan dialysis process depends on selecting a suitable working membrane. The main applications are in areas such as chemical analysis for pre-concentration, for extraction processes, for hydrometallurgy¹⁸, for separating acids from their

salts^{19,20}, for deacidification of radioactive flow²¹, for removing copper and zinc using commercial cationic membranes²², for removing inorganic anions such as fluoride, nitrate, bromate, and borate from drinking water^{14,19,23} and for removing Cr(VI) ions using commercial anion exchange membranes such as SB-6470, AFN, ACM, and Raipore 1030^{18,24,25}.

Generally, the Donnan dialysis employs the functional membranes that are ideally developed from chemically stable commercial porous materials. An alternative for the modification of some porous supports is interpenetration of polymer network (IPN) synthesis^{26,27}. Some samples of commercial disposable micro-porous membranes are polypropylene (PP) or polyethylene²³.

The IUPAC classification of an interpenetrating polymer network (IPN) architecture is “Polymer comprising two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken”²⁶⁻²⁸. The goal of the IPN material is the combination of physicochemical properties of individual functional polymers in the same material. The IPNs materials have been used in different scientific areas as; ion exchange materials²⁹, proton exchange membranes³⁰, alkaline fuel cell membranes³¹, functional membranes by the diffusion dialysis³², among others.

The main goal of this work was to modify polypropylene membranes for the “*in-situ*” synthesis of the interpenetrating poly[(ar-vinylbenzyl) trimethylammonium chloride], P(CIVBTA) and poly[sodium (styrenesulfonate)], P(SSNa) networks with the capacity to transport Cr(VI) and Cr(III) ions via Donnan dialysis.

1.1. Theoretical

For the Donnan dialysis experiments, the following equations were employed to analyze the data. The different experimental systems can be considered as a pseudo-steady state process where the mass transfer (k_m) across the membrane was assumed to be in a steady state during all experiments. Thus, the Donnan membrane mass transfer dialysis can be described by Fick's first law (see eq. 1). A linear concentration gradient across the membrane was assumed. The flux of ions through exchange membranes can be represented by equation 1:

$$J_i = \frac{H \times K \times \varepsilon \times D_s}{\tau \times \delta} \times \Delta C_i \quad (1)$$

$$k_m = \frac{H \times K \times \varepsilon \times D_s}{\tau \times \delta} \quad (2)$$

Where J_i , is the solute flux, ΔC_i , is the concentration gradient, H , is the fraction of available area, K , is the solute partition coefficient, ϵ , is the porosity of the membrane, D_s , is the solute diffusion coefficient inside the pores of the membrane, τ , is the membrane tortuosity, δ , is the membrane thickness, and k_m , is the mass transfer coefficient (see eq. 2).

$$J_i = k_m \times \Delta C_i \quad (3)$$

Figure 1. Ion mass transfer through a membrane system in the z direction. The mass balance equation over a differential element of width Δz and cross-sectional area A_c for the extraction chamber is given in equation 4 (see Figure 1):

$$V_{e,c} \times \frac{dC_{i,e}}{dt} = A_c \times J_{i,\delta} |_{\delta+\delta\delta} \quad (4)$$

Where $V_{e,c}$, is the volume of the extraction chamber (100 mL), A_c , is the effective membrane area (5 cm²), t is the time (min), and $C_{i,e}$, is the concentration of the (Cr(VI), or Cr(III), or NO₃-) inside the extraction chamber. Combining the equations 3 and 4, integrating by $C_{i,e}$, from time zero to t , and rearranging the combined equation yields equation 5:

$$C_{i,e} = \frac{C_{i,f}^0}{2} \times \left\{ 1 - e^{-\frac{2 \times A_c \times k_m \times t}{V_{e,c}}} \right\} \quad (5)$$

Where $C_{i,f}^0$, is the concentration of the (Cr(VI), or Cr(III), or NO₃-) inside the food chamber at time zero.

2. EXPERIMENTAL

2.1 Reagents and materials

Sodium styrenesulfonate (SSNa, Aldrich), Ar-[(vinylbenzyl) trimethylammonium chloride] (CIVBTA, Aldrich), ammonium persulfate (APS, Merck), and N,N' -methylene bis acrylamide (MBA, Aldrich) were used for the (IPN) synthesis.

Microporous isotactic PP membranes were employed (0.6- μ m pore size, AN06 Merck Millipore) (MPP). The other reagents used were: glutaraldehyde (Ga) (Aldrich), 15 kDa polyvinyl alcohol (PVA, Merck), 15 kDa poly(ethyleneimine) (PEI, Aldrich), divinylsulfone (Aldrich), 200 kDa (P(SSNa), Aldrich), ethanol (Merck), and Type I deionized water from Thermo Fisher TKA Scientific. A stirred-cell filtration unit (Millipore, model 8050) was used to inject the reactive solution pressure into the PP porous membrane. An aluminum flat reactor was used for the radical polymerization. A UB-10 pH/mV meter from Denver Instrument was used to measure the pH solution. A dielectric barrier discharge (DBD) plasma reactor was used to activate the membrane surfaces; the components and operating modes of the DBD have previously been published³³.

K₂Cr₂O₇ (Merck) and Cr(NO₃)₃·9H₂O (Merck) were the chromium sources. NaCl was the extraction reagent, and the NaNO₃ (Merck) was used for the binary system. HCl (Merck), HNO₃ (Merck), and NaOH (Merck) were used to control the pH.

2.2 Synthesis of P(CIVBTA) and P(SSNa) interpenetrating polymer networks

The membranes were washed with an aqueous mixture of 50% w/w ethanol

to eliminate all of the wastes and wet the pores. A stirred-cell filtration unit was employed with nitrogen gas and a pressure of 100kPas. Reaction solution (functional monomer (CIVBTA or SSNa), crosslinking reagent (MBA), and initiator reagent (APS), and 10 mL of water as a solvent) was passed through the membrane. The moisturized membranes with the reactive solution inside the pores were carried to the flat reactor by the free radical polymerization.

Other method is the plasma activation process. Both sides of the polypropylene membrane contacted the argon plasma for 1 min. Then, the active membrane contacted the reactive solution (CIVBTA or SSNa, MBA, and APS), and diffuse inside the pores. This process was performed inside an Erlenmeyer flask under an inert argon atmosphere.

Table 1 shows the experimental design for the IPN formation. The “*in-situ*” free-radical polymerization was performed inside the membrane pores at 70°C for 24 h. Ammonium persulfate (1 mol%) was used as the radical generation reagent. The polymerization reaction was carried out fast due to it is necessary to decrease the drain reactive solution, low yield of reaction, and the phase separation. The samples were dried in an oven at 50°C and stored in a silica dryer for 24 h.

Table 2, shows the modified P(CIVBTA) IPN membranes, that were treated using a functional solution (15 kDa PEI (5% w/w)), at room temperature for 12 h. Then, these membranes were submerged in an aqueous Ga (5% w/w) solution. Additionally, Table 2 shows the modified P(CIVBTA) IPN membranes that were treated using a functional solution (15 kDa PVA (5% w/w)) at room temperature for 12 h. At the next step, the membranes were contacted with a 1 mol L⁻¹ divinylsulfone and sodium carbonate mixture. Both processes occurred over 12 h to produce the polyelectrolyte crosslinking. Finally, the membranes were washed four times with water. The samples were dried in an oven at 50°C and left in silica dryer for 24 h.

2.3 Characterization

The percent modification (% P_{Mi}) was gravimetrically measured and determined from equation 6. The dry membrane samples (unmodified and modified IPNs) were weighed again after the modification process. This method quantitatively calculated the mass percent of the hydrophilic IPN.

$$\%P_{Mi} = \frac{(w_f - w_0)}{w_0} \times 100\% \quad (6)$$

Where w_f is the dry IPN membrane weight (g), and w_0 is the unmodified membrane weight (g).

The water uptake percent (% W_{wi}) was calculated from equation 7. The weights of the dry modified IPN membrane samples were measured before wetting with distilled deionized water for 24 h at room temperature.

$$\%W_{wi} = \frac{(w_{wet} - w_{dry})}{w_{dry}} \times 100\% \quad (7)$$

Where w_{wet} is the wet IPN membrane weight (g), and w_{dry} is the dry IPN membrane weight (g).

Microstructural analysis. The surface analysis of the modified and unmodified membranes were analyzed by the Fourier transform infrared spectroscopy coupled to attenuated total reflectance (ATR/IR) (Nicolet FTIR equipment with a DTGS-KBr detector (Omnic 5.2 Nicolet instrument Corp.)), and the scanning electron microscope (SEM) (20,000 KV JEOL microscope (JSH 6380LV model)) to identify the main functional groups and morphological and structural changes.

Change of phases. The modified and unmodified membrane phases were characterized by X-ray diffraction (XRD), using a Bruker AXS D4 Endeavor diffractometer (Germany), with Cu K α radiation ($\lambda=1.5406$ Å), a scan rate of 0.4°/min, and operated at 40 kV and 20 mA.

Thermal gravimetric analysis (TGA). This method was developed using the thermobalance TG209 Iris F1® model equipment. All experiments were performed under a nitrogen gas atmosphere with a heating rate of 10°C/min, in a temperature range between 30°C to 550°C, employing a 250 mL/min flow rate of nitrogen gas. The membrane samples weighed between 5 to 10 mg, and an aluminum saucer was used as a reference. This technique was employed to determine the decomposition temperature of the membranes.

Cr(VI) and Cr(III) ion mass transport and Donnan dialysis evaluation.

The mass transfer of Cr(VI) ions through the modified IPN pore membranes at pH 3.0 and 9.0 was examined. A two-chamber diffusion cell (feed and extraction phases) was used, and the chambers were separated by a membrane. Each chamber had a 100 mL capacity and was filled with 50 mL of

the working solution for the tests. The diffusion cell used in this study is described in Figure 1. The concentration polarization effect was neglected because of a sufficiently high stirring speed in each cell chamber.

Table 1. Experimental design of the interpenetrating polymer networks (IPN) synthesis inside pores polypropylene membranes.

Sample code	N° of Injections	Plasma activation	Monomer mol L ⁻¹	MBA %	Polymer Network
M1Cl	3	---	1.9×10 ⁻¹	2	P(CIVBTA)
M2Cl	3	---	3.8×10 ⁻¹	2	
M3Cl	1	---	5.7×10 ⁻¹	2	
M4Cl	1	---	3.8×10 ⁻¹	6	
M5ClP	1	---	3.8×10 ⁻¹	8	
M6ClP	1	---	3.8×10 ⁻¹	6	
M7Clplasma	---	1	3.8×10 ⁻¹	6	
M8Na	3	---	3.8×10 ⁻¹	2	P(SSNa)
M9Na	1	---	3.8×10 ⁻¹	6	
M10NaP	1	---	3.8×10 ⁻¹	8	
M11NaP	1	---	3.8×10 ⁻¹	6	
M12NaP	1	---	3.8×10 ⁻¹	4	
M13Naplasma	---	1	3.8×10 ⁻¹	6	

Table 2. Experimental design of the superficial layer formed on the P(CIVBTA), and P(SSNa) membranes.

Surface layer	Membranes
PEI	M1Cl, M2Cl, M3Cl, M4Cl, M5ClP, M6ClP, M7Clplasma
PVA	M8Na, M10NaP, M11NaP, M12NaP, M13Naplasma

Table 3. Experimental conditions to evaluate the Cr(VI) and Cr(III) ions transport.

Experiment	[Cr(III)] mol L ⁻¹	[Cr(VI)] mol L ⁻¹	pH _{feedphase}	pH _{extractionphase}	Extraction agent mol L ⁻¹	
P(CIVBTA)					NaCl	
1	---	5×10 ⁻⁴	3.0	3.0	1	
2	---	5×10 ⁻⁴	9.0	9.0	1	
P(SSNa)					HNO₃	NaCl
3	1×10 ⁻²	---	2.0	2.0	1×10 ⁻²	---
4	4×10 ⁻²	---	2.0	1.0	1×10 ⁻¹	---
5	4×10 ⁻²	---	2.0	3.0	1×10 ⁻³	---
6	4×10 ⁻²	---	2.0	2.0	1×10 ⁻²	1

Table 3 shows the experimental conditions for the transport study. The modified P(CIVBTA) IPN membranes were used for Cr(VI) ion transport, together with the P(CIVBTA) IPN modified membranes with a superficial PEI layer. The Cr(VI) solution was put in the feed chamber, and the extraction chamber was filled with a 1 mol L⁻¹ NaCl solution. Every 60 min for 18 to 24 h, 3 mL was extracted from the extraction chamber and was returned to the extraction chamber after reading the Cr(VI) ion concentration. The Cr(VI) concentration is suitable for interacting with the fixed charges in the P(CIVBTA) membrane³⁴. Additionally, a binary Cr(VI)/NO₃⁻ solution (1:1) was prepared. The transport was analyzed using the P(CIVBTA) IPN membranes. The feed chamber was filled with 5×10⁻⁴ mol L⁻¹ K₂Cr₂O₇ and 1×10⁻¹ mol L⁻¹ NaNO₃, and the solution pH was 9.0. The extraction reagent was 1×10⁻¹ mol L⁻¹ NaCl at pH 9.0. The extraction reagent was 1×10⁻¹ mol L⁻¹ NaCl at pH 9.0. Every 60 min for 18 to 24 h, 3 mL of the solution was extracted from the extraction chamber.

The transport was analyzed using the P(CIVBTA) IPN membranes.

The modified P(SSNa) IPN membranes were used to study the Cr(III) ion transport, together with the P(SSNa) IPN membranes with a superficial PVA layer. The Cr(III) acid solution was put in the feed chamber, and the extraction chamber was filled with the HNO₃ solution. Table 3 shows the experimental conditions. Samples were taken from the extraction chamber to measure the Cr(III) ion concentration. A 3 mL sample was taken every 60 min for 4 and 6 h and was returned to the extraction chamber after reading the Cr(VI) ion concentration. In other experiments, 1×10⁻² mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaCl were put in the extraction chamber. The Cr(III) concentration is suitable for interacting with the fixed charges in the membrane³⁴.

All Donnan dialysis experiments were conducted at room temperature. A Cary 100 scan UV-visible spectrophotometer from Varian was used to measure the Cr(VI) and Cr(III) ion concentrations directly³⁵. The Cr(VI) ion was

measured at 350 nm in a pH 3.0 solution and at 372 nm in a pH 9.0 solution³⁵. The Cr(III) ion concentration was measured at the wavelengths 407 nm and 573 nm for an acid pH³⁵. A wavelength of 301 nm was used to determine the NO₃⁻ ion concentration.

The transport of Cr(III), Cr(VI), and NO₃⁻ ions was evaluated based on the mass transfer coefficient (k_m) indicated in equation 2. The mass transfer coefficient (k_m) was calculated using the non-linear curve method. The equation 2 was approximated by the non-linear exponential curve as equation 8:

$$y = y_0 \pm A \times e^{R_0 \times t} \quad (8)$$

Where R_0 , is the $(-2 \times \Delta C / V_e \times c) \times k_m$, y_0 , is the $C_{0i,f}$, A , is the $C_{0i,f}/2$, and y is the $C_{i,e}$, of equation 2. $C_{i,e}$, is the concentration of Cr(VI), Cr(III), or (NO₃)⁻ in the extraction chamber during the time. $C_{0i,f}$, was the ion concentration in the feed chamber at time 0 and could be Cr(VI), Cr(III), or NO₃⁻. The aim

of nonlinear fitting is to estimate the parameter values which best describe the data. This method is also called chi-square minimization. It was used the Levenberg-Marquardt (L-M) algorithm to adjust the parameter values in the iterative procedure. This algorithm combines the Gauss-Newton method and the steepest descent method.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of the functionalized microporous PP membranes.

Table 4 shows the results of the micro-pore evaluation of the IPN modified and unmodified PP membranes that were developed from changing the percent modification (% ΔP_{Mi}) and the water uptake percent (% W_{wi}). These results were compared with unmodified PP membrane sample. The M1Cl, M2Cl, and M3Cl membranes showed increasing percent modifications, whereas the water uptake percent decreased for these membranes because the functional IPNs produced resistance to the water.

Table 4. Optimum values of modified degree percentage, water uptake percentage, and mass transport coefficient of Cr(VI) and Cr(III) ions.

Membranes code	% ΔP_{Mi}	% W_{wi}	$k_m \times 10^{-6} \text{ m s}^{-1}$ [Cr(VI)]		$k_m \times 10^{-6} \text{ m s}^{-1}$ [Cr(III)]	
			pH 3.0	pH 9.0	pH 1 HNO ₃	pH 2 HNO ₃ /NaCl
M1Cl	2.6	22.79	0.85	1.2	---	---
M2Cl	3.99	20.3	1.4	1.6	---	---
M3Cl	5.27	15	4.2	14.4	---	---
M4Cl	3.5	15.04	2.0	1.8	---	---
M5ClP	4.38	13.20	6.6	2.0	---	---
M6ClP	3.38	22.54	1.6	1.2	---	---
M7Clplasma	4.1	12.5	2.3	6.9	---	---
M8Na	3.36	28.4	---	---	2.3	2.4
M9Na	2.74	19.1	---	---	8.2	7.8
M10NaP	3.19	18.57	---	---	2.2	2.0
M11NaP	2.81	16.7	---	---	3.4	3.7
M12NaP	3.52	19.53	---	---	10.1	13.4
M13Naplasma	3.53	20.4	---	---	11.9	11.3
MPP	---	---	0.4	0.8	0.1	0.1

The percent modification for the M8Na (P(SSNa) IPN) membrane was similar to the percent modification for the M2Cl (P(CIVBTA) IPN) membrane. However, the water uptake percentages were different. Additionally, other comparisons between the percent modification of the M2Cl and M9Na membranes were similar values, whereas the percent water uptake was smaller for higher quantities injected (see Table 4).

The highest value for all of the synthesized membranes was achieved by M6ClP and M12NaP semi-IPNs. These differing results occurred because of the P(SSNa) IPN morphology in the shape of the layer, and the P(CIVBTA) IPNs formed agglomerated amorphous particles (see SEM analyze). The P(SSNa) IPNs went deeper into the PP membrane structure than the P(CIVBTA) IPNs. The P(CIVBTA) IPNs agglomerated in large quantities on the surface, which makes accessing the quaternary ammonium groups easier.

The semi-IPN membranes (M6ClP and M12NaP) exhibited percent modifications and percent water uptake very similar to the membranes synthesized via a superficial activation plasma technique (M7Clplasma and M13Naplasma) (see Table 4). The internal pore structure of polypropylene membrane modified by the “*in-situ*” synthesis of the functional polymeric network can be considered as an IPN or semi-IPN depending on the cross-linking of the new polymeric network. Generally, the modifications of the polypropylene membranes depend of the percent modification completely. These results do not exceed 5%, due to that they have 30% of porosity, and the polypropylene fibers which shape the membrane are very compacts. However, the hydrophilic properties of the membranes were changed. Phase separation

is expected during the IPN formation due to that the CIVBTA, and SSNa monomers are hydrophilic and polypropylene membrane is very hydrophobic. This behavior can explain the low values of the percent modification.

3.2 Microstructure analysis

The microstructure of the modified IPN and unmodified PP membranes was determined using the ATR/FTIR absorption bands of the functional groups. The measurement was performed in the range between 400 cm⁻¹ and 5000 cm⁻¹. Figure 2 shows the ATR/FTIR results for the membranes.

Figure 2a shows the ATR/FTIR MPP spectra. The MPP sample had absorption bands at 2970-2800 cm⁻¹ resulting from the stress and asymmetric stretching of C-H (δ_{as}) bonds in the methyl (-CH₃) groups, and the signals at 1480-1380 cm⁻¹ resulting from the C-H (δ_{as}) of CH₂ bond flexion vibrations because these bonds have asymmetric scissor deformations. The peak at 1300-700 cm⁻¹ represents the changing isotactic polypropylene microstructural characteristics^{36,37}. However, the absorption signals (δ_{as} (-CH₂), δ_{as} (-CH₂) and δ_s (-CH₂)) were stronger in the modified IPN samples than in the unmodified PP membrane signals (see Figure 2a, b, and c).

Figure 2b shows the characteristic absorption bands of the P(CIVBTA) IPN membrane (M5ClP). The signals from 1400-1600 cm⁻¹ represent the aromatic C=C absorption signals. The absorption peaks of the quaternary ammonium group are placed at 1581 cm⁻¹ for the N-H bond and C-N vibration and 1483 cm⁻¹ for the (-N⁺-(CH₃)) group bond flexion.

Figure 2. ATR/FTIR spectra of P(CIVBTA) and P(SSNa) IPNs and unmodified MPP membranes. a. MPP. b. M5CIP. c. M10NaP.

Figure 2c shows the characteristic absorption bands of the P(SSNa) IPN membrane (M10NaP). The absorption peaks of the SO_3^- from the sulfonate group are observed at 1042 cm^{-1} (S=O) and 1175 cm^{-1} , and the peaks at $1400\text{--}1600\text{ cm}^{-1}$ correspond to the aromatic (C=C) carbons.

The morphologic changes were determined using SEM analysis. Figures 3 and 4 show the morphological analysis.

Figure 3. SEM images of the modified and unmodified polypropylene membranes to $50\text{ }\mu\text{m}$ and $\times 300$ magnifications. a. MPP surface membrane. b. MPP cross-sectional area membrane. c. M4Cl surface membrane. d. M4Cl cross-sectional area membrane. e. M9Na surface membrane. f. M9Na cross-sectional area membrane.

Figures 3a and b show the morphology and fibers of a unmodified MPP membrane as determined by SEM, and the membrane face had an intertwined fiber structure, low porosity, and a smooth superficial aspect. These results are characteristic of an anisotropic membrane^{38,39}. Comparing Figure 3c, 3e with Figure 3a, the structure of the membrane has been modified by the incorporation of P(CIVBTA) and P(SSNa) IPNs.

Figure 3c shows the superficial face SEM image of the M4Cl, and two different phases were observed. Figure 3d shows the cross-sectional area membrane. This result indicates a change in the microstructural homogeneity comparing the M4Cl image with respect to the MPP image.

Figure 3e shows the morphology from the superficial face SEM image of the M9Na. Figure 3f shows the cross-sectional area membrane. Two phases

can be identified: a phase of the PP fibers and the other phase to ion IPNs of the sulfonate group. The decrease of surface homogeneity of the M4Cl, and M9Na (see Figures 3c and e) can be explained as a result in the possible pore size decrease since the IPN were mainly formed in the inside of the pores. The free volume of the unmodified polypropylene membrane was occupied, at least in good part by the P(CIVBTA), and P(SSNa) IPN⁴⁰⁻⁴².

Figures 3d, and 3f of cross-section images, as the mass gain increases respect to the unmodified MPP, the grain-like structure, which indicates the incorporation of P(CIVBTA) and P(SSNa) IPN, becomes denser structure. But due the compact polypropylene fibers the incorporation of P(CIVBTA) and P(SSNa) throughout the whole thickness were not uniform⁴².

The polypropylene fibers making up the membranes are very compact, and the cross-sectional area cut indicated that the P(CIVBTA), and P(SSNa) IPN presented of something protuberances that came from inner part of IPN structure which showed interconnected pores. These results are the microphase separation from the synthesis.

Figure 4. SEM images of the modified and unmodified polypropylene membranes to $10\text{ }\mu\text{m}$ and $\times 1000$ magnification. a. MPP surface membrane. b. MPP cross-sectional area membrane. c. M7Cl plasma surface membrane. d. M7Cl plasma cross-sectional area membrane. e. M13Na plasma surface membrane. f. M13Na plasma cross-sectional area membrane.

Besides, it was analyzed the membrane morphology of M7Cl plasma, and M13Na plasma, and they were compared with the membrane morphology MPP (see Figure 4). A decrease of the surface homogeneity was showed from SEM images.

Figures 4a, and b show the MPP membrane morphology. This morphology is smooth fibers. Figures 4c and d show the M7Cl plasma membrane morphology. On the surface of membrane was formed the P(CIVBTA) IPN, and this material covered the entire PP fiber surface like agglomerated small spheres. The P(CIVBTA) IPN material was more better distributed than the P(CIVBTA) IPN on the M4Cl. Figures 4e and 4f show the M13Na plasma membrane morphology. The IPN material in the M13Na plasma is more distributed in all fibers than the M9Na. The P(SSNa) IPN covered the entire PP fiber surface like a paint in the M13Na plasma and M9Na (see Figure 4e). The P(SSNa) IPN particle sizes were smaller and less agglomerated in the M13Na plasma, and the M9Na showed smaller particle sizes and appeared less agglomerated than the P(CIVBTA) IPN (M4Cl). The PP fibers provide support and mechanical resistance to the amorphous IPN materials, and the IPN materials produce the ion exchange. The (P(CIVBTA) and P(SSNa)) IPN former could be the cluster particles formation as a result of the relatively high (MBA) crosslinked concentration^{43,44}.

Similar results were obtained when a polypropylene film was superficially modified with P(SSNa), and a polyethylene film was modified with P(SSNa). The main results showed a structural surface change where small particles with small pores appeared⁴⁵. The grafted and copolymerized 4-vinylpyridinium monomer appeared within the PP membranes with $0.5\text{-}\mu\text{m}$ pores⁴⁶. Poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) was grafted and crosslinked onto the PP membrane surface. The membrane had an 80% porosity with a $0.20\text{-}\mu\text{m}$ pore size⁴⁷.

Figure 5. X-Ray diffraction analysis of unmodified and modified IPN membranes. a. MPP. b. M11NaP. c. M6CIP.

Figure 5a shows the characteristic crystalline phases of the MPP membranes, and the monoclinic alpha phase with the reflection on $\alpha(110)$, and $\alpha(040)$, perpendicular to each other⁴⁸. The $\alpha(110)$ intensity values of the M11NaP (3893.28) and the M6CIP (4480.58) are less than the alpha plane intensity values of the MPP. Similarly, the $\alpha(040)$ intensity values of the MPP samples are higher than the M11NaP (3628.61) and the M6CIP (3965.32) (see Figure 5b and 5c).

The order of the 2θ values is as follows: MPP(14°)>M11NaP(13.73°)>M6CIP(13.71°) by the $\alpha(110)$ plane, and the MPP(16.79°)>M11NaP(16.53°)>M6CIP(16.51°) by the $\alpha(140)$ plane. The modified IPNs produce a decrease of the 2θ value phases in comparison with the MPP.

These results suggested that the P(CIVBTA) and the P(SSNa) IPNs are producing changes in the crystallinity of the PP support⁴⁹. It is possible that the

P(CIVBTA) and the P(SSNa) were grafted on the polypropylene fibers.

Previous research has shown similar results using DRX analysis. For example, PP and polyethylene films were modified using a polystyrene graft, followed by the sulfonation process. This modified method produces a decrease in the crystallinity of the film⁵⁰.

3.3 Thermogravimetric(TGA)analysis.

Figure 6 shows the thermogravimetric curves of the modified IPNs and unmodified PP membranes. All thermogram curves produce a simple thermal decomposition form. These results were produced by the drying process of the samples before being analyzed. The thermal decomposition of the isotactic PP started in the range between 150°C and 220°C ^{51,52} (see Figure 6a). The residual mass percentage was 0.089%.

Figure 6. Thermogravimetric analysis (TGA) of the modified IPNs and unmodified MPP membranes. a. MPP. b. M13Naplasma. c. M4Cl. d. M7Clplasma.

Figure 6b shows the thermal decomposition of the M13Naplasma membrane, produced in the range between 220°C to 340°C . This temperature range corresponds to the decomposition of the sulfonate group and of the aromatic ring^{53,54}. The residual mass percentage was 1.46%, higher than the

MPP value.

Figures 6c and 6d show the thermal decomposition of the M4Cl and M7Clplasma membranes, produced in the range between 310°C to 380°C . The temperature ranges correspond to the decomposition of the quaternary

ammonium group and of the aromatic ring^{55,56}. The residual mass percentage was 1.4% for the M4Cl and 1.9% for the M7Clplasma. The residual mass percentage values are higher than the MPP value.

The cationic and anionic IPNs produce a thermal resistance of the MPP membranes because the decomposition temperature (T_d) value (M13Naplasma, M4Cl and M7Clplasma) was increased to a point higher than the (T_d) of the MPP.

3.4 Determination of membrane mass transport coefficient for Cr(VI) and Cr(III) ion transport evaluation.

The membrane capacity permeability for Cr(VI) ions through P(CIVBTA) IPNs, semi-IPNs and PP membranes was determined. The percent modification effects on the permeability, together with an acidic pH medium and a basic pH medium have been investigated.

The mass transport coefficient values decreased from M4Cl.PEI ($11.0 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP ($6.60 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma.PEI ($5.25 \times 10^{-6} \text{ m s}^{-1}$) > M3Cl ($4.15 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP.PEI ($3.76 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma ($2.32 \times 10^{-6} \text{ m s}^{-1}$) > MPP ($0.35 \times 10^{-6} \text{ m s}^{-1}$) at pH 3.0. The M7Clplasma membrane exhibited a lower mass transport coefficient value (as determined by the injection method) than the membranes containing P(CIVBTA) (IPN)s.

Figure 7. Cr(VI) extraction profile. At pH 3.0: a. M4Cl.PEI, b. M6CIP. At pH 9.0: c. M7Clplasma, d. M7Clplasma.PEI. Extraction profile for binary system at pH 9.0 for Cr(VI) ions, e. M3Cl.PEI, f. M6CIP. For NO_3^- ions, g. M3Cl.PEI, h. M3Cl.

Some values are shown in Table 4. Figure 7a shows the Cr(VI) concentration profile by the M4Cl.PEI membrane, and Figure 7b shows the M6CIP in the extraction cell. The red line indicates the mathematical exponential non-linear curve fit for both membranes. The Donnan equilibrium was achieved after 500 min by the M4Cl.PEI and after 875 min by the M6CIP. The PEI was absorbed on the surface of the membrane to form a monolayer⁵⁷. The membranes with the PEI layer achieved values higher than the values for the P(CIVBTA) IPN membranes without a PEI superficial layer. At a pH of 3.0, Cr(VI) exists mainly in the form of HCrO_4^- at $5.0 \times 10^{-4} \text{ mol L}^{-1}$ and under these conditions, the PEI monolayer becomes charged with a hydrogen ion that reinforces the Cr(VI) ion interactions with the cationic groups. The PEI monolayer obstructs the smallest pores and partially obstructs the pores due to the electrostatic repulsion between the protonated amines and the quaternary ammonium groups⁵⁷.

Cr(VI) ion transport under such conditions depends on the P(CIVBTA) network concentration inside the pores because at an acid pH, the influence of the percent modification is mainly due to the variation of the porosity. In the same way, a strong quaternary ammonium group (P(CIVBTA) networks and PEI protonated) interacts with the Cr(VI) ions, which decreases the ion transport velocity and increases the ion exchange relationship⁵⁷.

Mass transport coefficient values at pH 9.0 decrease in the order M3Cl% ($14.4 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma ($6.86 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma.PEI ($5.15 \times 10^{-6} \text{ m s}^{-1}$) > M4Cl.PEI ($3.93 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP ($2.03 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP.PEI

($0.95 \times 10^{-6} \text{ m s}^{-1}$) > MPP ($0.79 \times 10^{-6} \text{ m s}^{-1}$). At a pH of 9.0, most of the Cr(VI) ions are CrO_4^{2-} . The high concentration of the initial monomer membrane (M3Cl%) and the plasma membrane exhibited a higher mass transport coefficient value than the other membranes containing P(CIVBTA) (IPN)s. Some values are shown in Table 4. Figure 7c shows the Cr(VI) concentration profile of the M7Clplasma membrane, and Figure 7d shows the M7Clplasma.PEI in the extraction cell. The red line indicates the mathematical exponential non-linear curve fit by both membranes. The Donnan equilibrium was achieved after 700 min by the M7Clplasma and after 1000 min by the M7Clplasma.PEI. PEI at pH 9.0 was not protonated, and produced a chelating effect due to the concentration gradient when the Cr(VI) ions and quaternary ammonium groups or Cr(VI) ions and amine groups interacted during the diffusion. The Cr(VI) ions compete against hydroxyl ions during ion exchanges within the membrane with the quaternary ammonium group P(CIVBTA) networks.

The Cr(VI) ion at pH 9.0 yielded a higher mass transfer coefficient value than at pH 3.0. At acid pH, the Cr(VI) ions and the P(CIVBTA) IPN membranes, and P(CIVBTA) IPNs + PEI layer membranes are in their ionized forms, resulting in the retention of the Cr(VI) through the membranes by the strong ionic interactions. At basic pH, the Cr(VI) ions are ionized, but the P(CIVBTA) IPN membranes and the P(CIVBTA) IPNs + PEI layer membranes are in the partially ionized form. Thus, the transport of Cr(VI) is accelerated by the partially ionized P form (CIVBTA) IPN membranes due to the chelating effect and the electrostatic force. The Stokes radii hydration of Cr(VI) at pH

3.0 (HCrO_4^- , 0.375 nm) and pH 9.0 (CrO_4^{2-} , 0.240 nm) produces one effect in the transport through the membranes because the size difference causes friction during the movement and a strong electrostatic force during the ion exchange. All of these features produce a retention effect.

A binary system of Cr(VI)/NO_3^- in the mass transport through the IPN membranes was analyzed. The extraction reagent was 1 mol L^{-1} NaCl. The mass transport coefficient values of the Cr(VI) in the binary system decreased in order M3Cl ($21.0 \times 10^{-6} \text{ m s}^{-1}$) > M3Cl.PEI ($17.7 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP ($8.6 \times 10^{-6} \text{ m s}^{-1}$) > M4Cl.PEI ($8.1 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP.PEI ($7.8 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma.PEI ($4.3 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma ($3.2 \times 10^{-6} \text{ m s}^{-1}$) > M4Cl ($2.5 \times 10^{-6} \text{ m s}^{-1}$) at pH 9.0. Figure 7e shows the Cr(VI) concentration profile of the M3Cl.PEI membrane, and Figure 7f shows the M6CIP in the extraction cell. The red line indicates the mathematical exponential non-linear curve fit by both membranes. The Donnan equilibrium was achieved after 300 min by the M3Cl.PEI and after 625 min by the M6CIP.

The mass transport coefficient values of the NO_3^- in the binary system decreased in the order M3Cl.PEI ($39.8 \times 10^{-6} \text{ m s}^{-1}$) > M3Cl ($35.1 \times 10^{-6} \text{ m s}^{-1}$) > M4Cl ($13.6 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP ($10.4 \times 10^{-6} \text{ m s}^{-1}$) > M6CIP.PEI ($9.7 \times 10^{-6} \text{ m s}^{-1}$)

s^{-1}) > M7Clplasma ($6.9 \times 10^{-6} \text{ m s}^{-1}$) > M7Clplasma.PEI ($5.8 \times 10^{-6} \text{ m s}^{-1}$) > M4Cl.PEI ($1.1 \times 10^{-6} \text{ m s}^{-1}$) at pH 9.0. Figure 7g shows the NO_3^- concentration profile of the M3Cl.PEI membrane, and Figure 7h shows the M3Cl in the extraction cell. The red line indicates the mathematical exponential non-linear curve fit by both membranes. The Donnan equilibrium was achieved after 125 min by both membranes.

These results may be due to the differences between the Stokes radii and the Gibbs free-energy for hydration (NO_3^- , 0.2 nm and CrO_4^{2-} , 0.240 nm). The NO_3^- ions are smaller and less hydrated than the CrO_4^{2-} ion, which provides more movement through the membranes. The quaternary ammonium groups preferred the CrO_4^{2-} ions because they are divalent and need a greater quantity of charge-fixed groups.

The capacity permeability for Cr(III) ions through P(SSNa) IPN, semi-IPN, P(SSNa) IPN plus PVA layer, and unmodified MPP membranes was determined. The Cr(III) concentration is suitable for interacting with the fixed charges in the membrane³⁴. Cr(III) can exist in the forms CrOH^{2+} and Cr(OH)_2^+ at $4.0 \times 10^{-2} \text{ (mol L}^{-1}\text{)}$ ^{58,59}. The acidity guarantees the total dissolution and Cr(III) ionization, avoiding the formation of metallic hydroxyls⁶⁰.

Figure 8. Cr(III) extraction profile. The extractor agent was $1 \times 10^{-1} \text{ mol L}^{-1} \text{ HNO}_3$, with a Cr(III) food concentration of $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cr(III)}$ with pH 2.0. a. M13Naplasma, b. M12NaP, c. M9Na. At pH 2.0 and $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cr(III)}$ in the food chamber, the extractor agent was $1 \times 10^{-3} \text{ mol L}^{-1} \text{ HNO}_3$. d. M9Na.PVA, e. M13Naplasma, f. M12NaP. At pH 2.0 with $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cr(III)}$ in the food chamber, using a mixture of $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HNO}_3$ and 1 mol L^{-1} NaCl as the extractor. g. M9Na.PVA, h. M13Naplasma, i. M12NaP.

The mass transport coefficient values decreased from M13Naplasma ($11.9 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP ($10.1 \times 10^{-6} \text{ m s}^{-1}$) > M9Na ($8.95 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP.PVA ($8.62 \times 10^{-6} \text{ m s}^{-1}$) > M8Na ($8.18 \times 10^{-6} \text{ m s}^{-1}$) > M11NaP.PVA ($1.44 \times 10^{-6} \text{ m s}^{-1}$) > MPP ($0.1 \times 10^{-6} \text{ m s}^{-1}$) at pH 1.0. The extractor agent was $1 \times 10^{-1} \text{ mol L}^{-1} \text{ HNO}_3$. These results may depend on the strong ionic interactions between the Cr(III) ions and the membrane sulfonate groups. The porosity did not decrease in the superficial PVA layer. The PVA was adsorbed on the

membrane surface to form a monolayer⁵⁷. Some values are shown in Table 4. Figure 8a shows the Cr(III) concentration profile in the M13Naplasma membrane. Figure 8b shows the M12NaP, and Figure 8c shows the M9Na, in the extraction cell. The Donnan equilibrium was obtained after 300 min. The red line indicates the mathematical exponential non-linear curve fit by both membranes.

At pH 2.0 and $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cr(III)}$ in the food chamber, the mass

transport coefficient values decreased from M9Na.PVA ($16.3 \times 10^{-6} \text{ m s}^{-1}$) > M13Naplasma ($12.7 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP ($10.9 \times 10^{-6} \text{ m s}^{-1}$) > M8Na ($10.1 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP.PVA ($9.18 \times 10^{-6} \text{ m s}^{-1}$) > M9Na ($8.86 \times 10^{-6} \text{ m s}^{-1}$) > MPP ($0.5 \times 10^{-6} \text{ m s}^{-1}$), and the extractor agent was $1 \times 10^{-3} \text{ mol L}^{-1} \text{ HNO}_3$. The PVA improved the hydrophilicity of the P(SSNa) network membranes. The pH 3.0 produces a higher pass of the Cr(III) through the IPN membranes than pH 1.0. Figure 8d shows the Cr(III) concentration profile in the M9Na.PVA membrane, Figure 8e shows the M13Naplasma, and Figure 8f shows the M12NaP in the extraction cell. The Donnan equilibrium was obtained after 250 min by the M8Na.PVA, and after 300 min by the M13Naplasma and M12NaP. The red line indicates the mathematical exponential non-linear curve fit by both membranes.

The low pH in the extractor solution may exchange with the Cr(III) ions more rapidly and stimulates diffusion of both ions due to the concentration gradient^{61,62}. However, the mass transport coefficient is higher in the pH 3.0 extractor solution than in the pH 1.0 extractor solution.

At pH 2.0 with $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Cr(III)}$ in the food chamber and using a mixture of $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HNO}_3$ and $1 \text{ mol L}^{-1} \text{ NaCl}$ as the extractor as the M8Na.PVA ($13.4 \times 10^{-6} \text{ m s}^{-1}$) > M13Naplasma ($11.3 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP ($9.62 \times 10^{-6} \text{ m s}^{-1}$) > M8Na ($8.28 \times 10^{-6} \text{ m s}^{-1}$) > M12NaP.PVA ($8.27 \times 10^{-6} \text{ m s}^{-1}$) > M9Na ($7.76 \times 10^{-6} \text{ m s}^{-1}$) > MPP ($0.1 \times 10^{-6} \text{ m s}^{-1}$). Figure 8g shows the Cr(III) concentration profile in the M8Na.PVA membrane, the Figure 8h shows the M13Naplasma, and Figure 8i shows the M12NaP in the extraction cell. The Donnan equilibrium was obtained after 275 min by the M8Na.PVA and after 300 min by the M13Naplasma and M12NaP. The red line indicates the mathematical exponential non-linear curve fit by both membranes. The H^+ (0.030 nm in size) ion has a higher movement capacity during the membrane phase because of its small size relative to the Cr(III) (0.062 nm in size). This mixture did not improve the Cr(III) transport relative to using HNO_3 alone at pH 3.0. The high sodium ion concentration in the extractor mixture may exchange with the Cr(III) ions and stimulate ion diffusion due to the concentration gradient^{61,62}, but this exchange did not occur.

The test at pH 1.0 with a mixture of $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HNO}_3$ and $1 \text{ mol L}^{-1} \text{ NaCl}$ as the extractor reagent produces a retention effect in the P(SSNa) IPN membranes because the mass transport coefficients are lower than the test at pH 3.0. The test at pH 3.0 produced a Donnan transport through the P(SSNa) IPN membranes with a higher mass transport coefficient.

CONCLUSIONS

Microporous P(CIVBTA) and P(SSNa) interpenetrating polymer networks (IPNs) polypropylene membranes with ion exchange capacities can be obtained using radical polymerization. The control of the functional network density was made by the functional monomer and crosslinked MBA concentrations.

The P(CIVBTA) and P(SSNa) IPN membranes were tested via ATR/FT-IR, SEM, DRX, TGA, and their hydrophilicity with the mass transport coefficient. These results demonstrated the IPNs form within the pores.

The transport properties for the Cr(VI) at pH 3.0, pH 9.0, and in a binary system of Cr(VI)/ NO_3^- was evaluated using the Donnan dialysis principle. The mass transport coefficient was determined by non-linear curve fit of the experimental data. The M4Cl.PEI membrane was selected because the obtained Cr(VI) ions mass transport coefficient results ($11.0 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.97) were used at pH 3.0. The M7Cl.plasma membrane was selected due to its transport capacity ($6.86 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.98) for Cr(VI) ions at pH 9.0. And, the M3Cl.PEI membrane was selected due to its transport velocity ($21.0 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.97) for Cr(VI) ions at pH 9.0 in a binary system.

Besides, the transport properties for the Cr(III) ions at pH 1.0, pH 3.0, and a mixture of $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HNO}_3$ and $1 \text{ mol L}^{-1} \text{ NaCl}$ as the extracting reagent was evaluated using the Donnan dialysis principle. The M13Naplasma ($11.9 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.99) was selected for the $1 \times 10^{-4} \text{ mol L}^{-1} \text{ HNO}_3$ extraction reagent, the M9Na.PVA ($16.3 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.98) was selected for the $1 \times 10^{-3} \text{ mol L}^{-1} \text{ HNO}_3$ extraction reagent, and the M8Na.PVA ($13.4 \times 10^{-6} \text{ m s}^{-1}$, R^2 0.99) membrane was selected when the extraction agent was a $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HNO}_3$ and $1 \text{ mol L}^{-1} \text{ NaCl}$ mixture.

The Cr(VI) and Cr(III) extraction results were also important because the starting material was initially hydrophobic, and the wetting properties improved upon modification.

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