Removal of Cr(III) and Cu(II) using poly(2-chloroaniline)/polyvinylidenefluoride composite cation-exchange membranes by Donnan dialysis

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Abstract: P2ClAn/PVDF composite membranes were prepared utilizing cation-exchange groups in the PVDF (polyvinylidenefluoride) membrane matrix by casting method. The poly(2-chloroaniline) (P2ClAn) was chemically synthesized with different dopant anions such as o-aminobenzene sulfonic acid (ABS) and sodium dodecyl sulfate (SDS). P2ClAn/PVDF membranes were extensively characterized for their surface morphology, thickness, ion-exchange capacity, SEM, AFM, and FTIR-ATR measurements. The SEM, AFM and FTIR-ATR pictures, comparing the original PVDF membrane support sheet to P2ClAn/PVDF composite membranes, indicate that the morphologies of the membranes are different. The membrane potential measurements were performed in various electrolyte solutions in order to observe the selectivity and stability of these membranes at different pHs. The P2ClAn/PVDF cation-exchange membranes were then used for the removal of chromium(III) and copper(II) ions from aqueous solution with Donnan dialysis. The flux values (J) of chromium(III) and copper(II) were obtained. The flux value of copper(II) ion was higher than chromium(III) for all of composite membranes because of the hydration volume.

Key words: Conducting polymers, ion exchangers, membranes, modification, polyaniline

1. Introduction

Ion-exchange membranes have mostly been used in various separation processes such as electrodialysis, electrodeionization, electro-dialytic demineralization of saline water, removal of toxic metal ions, and Donnan dialysis.[1−3] Donnan dialysis is an ion-exchange membrane process driven by an electrochemical potential in aqueous solutions and is different from the classical dialysis technique as its theory and principle are reviewed in textbooks.[4,5] Donnan dialysis has been used in the recovery of valuable ions and the removal of undesired ions from waste effluents.[6−8]

Polyaniline, polypyrrole, polythiophene, and polyacetylene have the potential to produce new functional materials due to their unique electrical, optical, and ion-exchange capabilities.[9−11] For example, they have been used in solid electrolyte capacitors,[12] electrochromic devices,[13] and electrochemical sensors.[14] Several reports are available regarding the preparation of a new generation of ion-exchange membranes based on conducting polymers (CPs).[15,16]

The polyaniline (PANI) and substituted PANI are special members of the CP family and have a good affinity for ion-exchange membranes. They can also polymerize in the membrane matrix by chemical oxidation.[17]

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Composite membranes consisting of a microporous polymeric material coated with CP have recently been investigated in detail. One of the main applications of these membranes is in the removal of toxic metal ions.[9,18,19]

Heavy metals are unique among pollutants and they can accumulate in living tissues, causing various diseases and disorders. In particular, chromium is an important toxic element in the environment. Chromium(III) and chromium(VI) are regulated in different ways based on their toxicities.[20] Chromium and its derivatives are widely used in various industries such as metallurgical, manufacture of refractories (chrome and chrome-magnesite) and wood preservatives, and chemical (paint and pigments, electroplating, textile, leather tanning etc.). Due to these industrial processes, large quantities of Cr compounds are discharged into the environment and can ultimately have significant adverse biological and ecological effects.[20−22] The maximum contamination level of chromium in drinking water should be less than 0.05 mg/L.[23]

A number of processes have been used for removal of Cr(III)-containing wastewater such as adsorption,[24] precipitation,[25] conventional ion-exchange,[26] and membrane processes.[27−29] Moreover, copper is a widely used metal in industry in electrical wiring, gear wheels, air conditioning tubing etc. An ultra-trace amount of copper is essential for most life forms as a micronutrient, but is also toxic at high concentrations. For instance, in humans it can cause brain and kidney failure, stomach upsets, ulcers, and so on.[30,31]

This study examined the preparation of P2ClAn/PVDF composite cation-exchange membranes and removal of Cr(III) and Cu(II) ions from aqueous solution with Donnan dialysis. P2ClAn/PVDF composite cation-exchange membranes were prepared using different dopant anions such as o-aminobenzene sulfonic acid (ABS) and sodium dodecyl sulfate (SDS).

2. Experimental

2.1. Materials

Analytical reagent-grade $CrCl_3.6H_2O$, $Cu(NO_3)_2$, HCl, NaOH, ABS, SDS, ammonium peroxydisulfate (($NH_4)_2 S_2 O_8$)), and 2-chloroaniline were obtained from Merck and Fluka. All solutions were prepared using ultra-pure water obtained from a Milli-Q system (Millipore Corp., Billerica, MA, USA). The pH measurements were performed with a Mettler Toledo model pH meter during all of the experiments.

2.2. Synthesis of P2ClAn

The P2ClAn was chemically synthesized using ABS and SDS dopant anions with $(NH_4)_2 S_2 O_8$ as oxidant. In the synthesis of polymers, the ratio of dopants to monomer was taken as 2. Forty-seven grams of ammonium peroxydisulfate was dissolved in 5 mL of deionized water and stirred with a magnetic stirrer for 10 min. The polymerization reaction was continued for 24 h at 4 °C. The polymers were filtered and then washed with deionized water, methanol, and diethylether. The washing of the polymers was continued until a colorless liquid passed across the filter. After that, the polymers were dried under vacuum for about 24 h.

2.3. Preparation of P2ClAn membranes

Polymer solutions were prepared by dissolving a certain amount of P2ClAn synthesized using different dopant anions in methanol. Polyvinylidene fluoride (PVDF) membrane support sheets were used for preparation of P2ClAn/PVDF composite membranes. PVDF membrane support sheets were obtained from Millipore (hydrophilic, filter pore size: 0.45 μm, porosity: 70%).

Polymer solutions were cast on the PVDF membrane support sheets and dried for 24 h at room temperature.[32,33] The P2ClAn/PVDF composite membrane disks in the H^+ form were conditioned by a cycle of equilibrations with HCl, distilled water, NaOH, and finally distilled water; then the membrane disks were pretreated with 1.0 M HCl. The main physical characteristics of the P2ClAn/PVDF composite cation-exchange membranes are listed in Table 1.

Table 1. Characteristics of the studied membranes.

Property	P2ClAn (SDS)	P2ClAn (ABS)
Type	Cation exchange	Cation exchange
Thickness, μm	110	110
Ion-exchange capacity, (meq/g)	1.2346	1.9123

2.4. Characterization of composite membranes

The FTIR-ATR spectra of membranes were recorded in the range 400–4000 cm^{-1} using a PerkinElmer Spectrum 100 FTIR spectrometer. The spectrometer was equipped with a single reflection ATR accessory for reflection mode. The morphology of membrane surfaces was assessed with a field emission gun scanning electron microscope (FEG-SEM), an Oxford Instruments-7430 model.

P2ClAn/PVDF composite membrane surfaces were structurally characterized by an AFM Nanosurf easy scan instrument. Membrane potential measurements were carried out by means of an electrometer (Fluke 87 III True Rms Multimeter) with Ag/AgCl electrodes (Mettler Toledo Inlab Reference Pro).

2.5. Donnan dialysis experiments

Donnan dialysis experiments were performed in a 2-compartment cell made of Teflon.[34] The volume of each cell was 40 mL and it was stirred at 500 rpm. The area of the exposed membrane was 7.07 cm^2.

The feed phase contained 0.01 M $CrCl_3$ or $Cu(NO_3)_2$ solutions, and the receiver phase contained 0.1 M HCl solution. In preparation of all solutions 18.2 MΩ cm deionized water was used. The samples were taken from the receiver phase at certain time intervals and the amounts of Cr(III) and Cu(II) ions transported across the membrane were measured by an ICP-OES (PerkinElmer 5300 DV model). The experiments of Cr(III) were carried out at optimum pH 3 as stated in the literature for Cr(III).[35] All measurements were performed at 25 °C.

The flux values (J) for Cr(III) and Cu(II) were calculated from the time profile of receiver solution concentration of ions by initial rate technique and the results are presented in Table 2. The integration of Eq. (1) has been described by Cengeloğlu et al.[34] The ion flux equation can be defined as follows:

$$J = \left(\frac{V}{A}\right)\left(\frac{dC^{n+}}{dt}\right)_{t\to 0} \tag{1}$$

where V is the volume of the receiver phase, A is the effective membrane area, and C^{n+} is the concentration of Cr(III) or Cu(II) ions in the receiver solution and at t time.

Table 2. Chromium(III) and copper(II) flux values for different membranes.

Membranes	$J \times 10^{11}$ (mol cm^{-2} s^{-1})	
	Cr(III)	Cr(III)
P2ClAn (SDS)	139.00 ($\pm$ 0.62)	228.00 ($\pm$ 0.38)
P2ClAn (ABS)	148.00 ($\pm$ 0.52)	244.00 ($\pm$ 0.46)

These results are obtained at 95% confidence level (N = 3).

2.6. Properties of membranes

Ion-exchange capacity values were determined by leaving the membranes in 0.1 M HCl solution for 24 h to transform the membrane samples to H$^+$ form. These membranes were then washed with deionized water to remove excess acidity. The ion-exchange capacity was determined by acid–base titration as described previously.[15] Membrane thickness was measured with a Mitutoyo CD-15CPX digital micrometer at different points of the sample.

3. Results and discussion

P2ClAn/PVDF composite membrane surfaces were structurally characterized by FTIR-ATR, AFM, SEM, and membrane potential. Figures 1 and 2 show FTIR-ATR spectra of P2ClAn/PVDF composite membranes. The FTIR-ATR spectrum was used to characterize the molecular structure of the resulting different membranes. As can be seen from these spectra, between 1600 and 1800 cm^{-1}, the C=C double bond stretch showed that the bonding of P2ClAn on the membrane support sheet (PVDF) completed successfully. The new bands and the wavelength shifts indicate the effect of substituent group on the structure of P2ClAn.
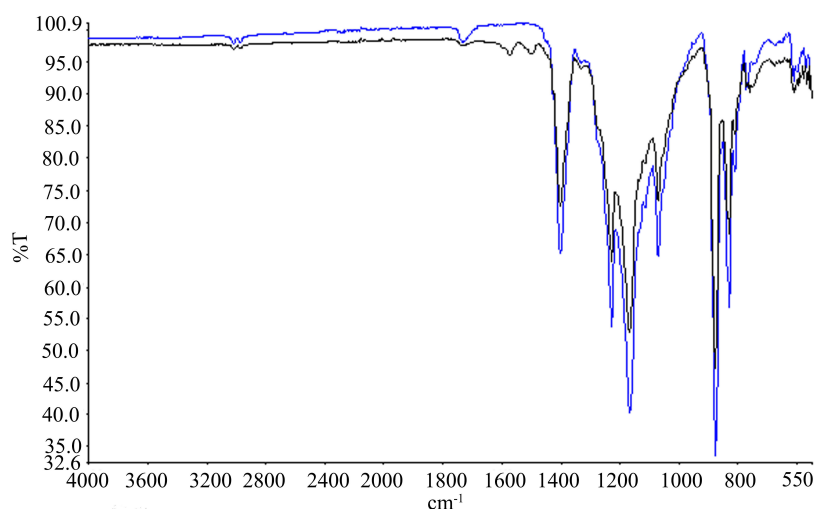

Figure 1. FTIR-ATR spectrum of poly(2-chloroaniline) (SDS) composite membrane.

The scanning mode AFM images can be used to study the surface morphology of composite membranes. Figure 3a–c shows the corresponding AFM amplitude images of P2ClAn/PVDF composite membranes. After the modification, changes in surface topography are observed. The AFM amplitude image of the PVDF membrane support sheet exhibits wider peaks (i.e. roughness) in comparison with P2ClAn/PVDF composite membranes. It can be seen from Figure 3 a,b that the PCl2An was coated on the surface of PVDF because of forming smaller granules.
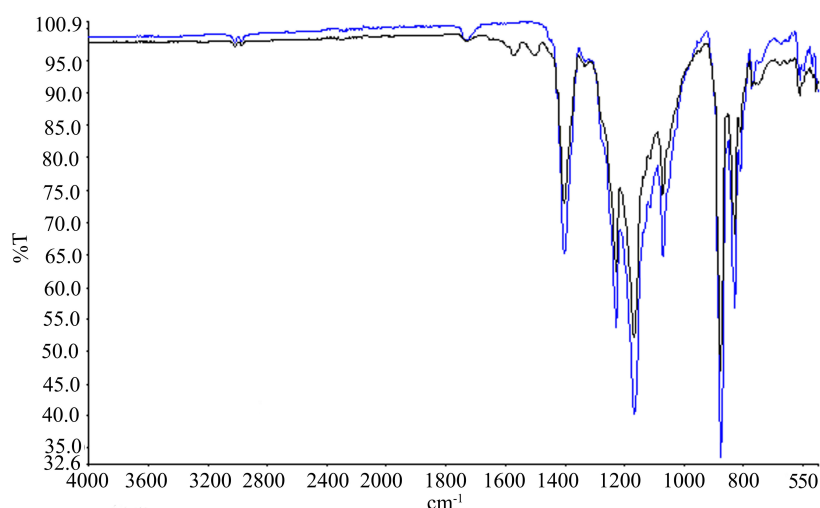
Figure 2. FTIR-ATR spectrum of poly(2-chloroaniline) (ABS) composite membrane.
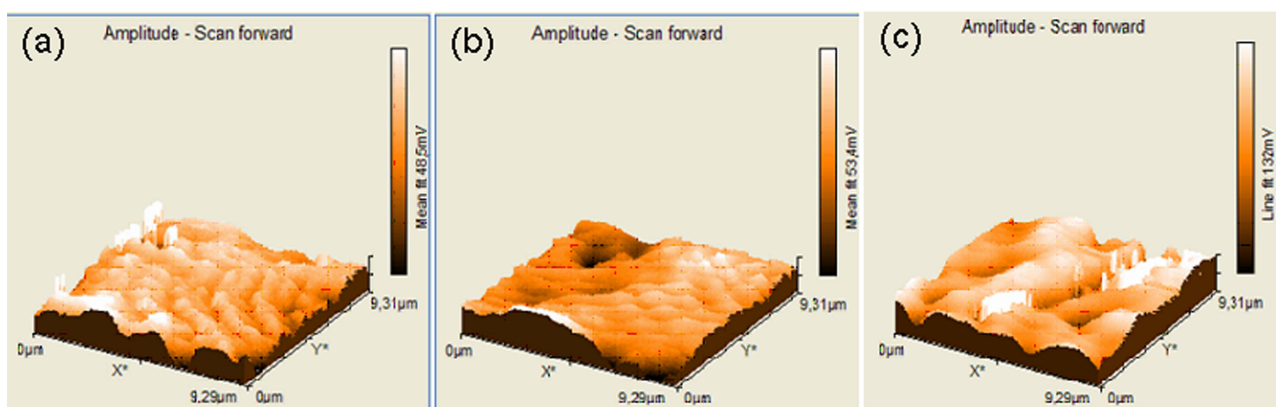

Figure 3. (a) AFM image of poly(2-chloroaniline) composite membrane (SDS), (b) AFM image of poly(2-chloroaniline) composite membrane (ABS), (c) AFM image of membrane support sheet (PVDF).

Scanning electron micrographs (SEMs) of P2ClAn/PVDF composite membranes with different dopants and PVDF membrane support sheet were recorded and representative micrographs of these membranes are presented in Figure 4a–c. It can be seen that the structures of the PVDF and P2ClAn/PVDF composite membranes are different. The surface of the PVDF is composed of a macroporous structure. When P2ClAn polymeric solution was cast on PVDF, the holes in the PVDF were filled and coated with the P2ClAn polymers. The ion-exchange capacity of the membranes strictly depends on the content of sulfonic acid group incorporated into the polymer structure.[36] The ion exchange capacity and thickness of the P2ClAn/PVDF composite membranes are shown in Table 1. The results showed that the ion-exchange capacity of P2ClAn (ABS) is higher than that of P2ClAn (SDS). The increase in the ion-exchange capacity of the P2ClAn (ABS) composite membrane in comparison with that of the P2ClAn (SDS) composite membrane is probably due to the presence of sulfonic acid groups.

The membrane potential measurements were recorded and calculations of concentration potential (Ec) were carried out according to the equation given by Sardohan et al.[37] Figure 5 shows the variation in the pH dependence of membrane potential for 2.0×10^{-4} mol/L and 1.0×10^{-4} mol/L NaCl solutions. The

potentials of the composite membranes were between 19.51 and –0.1823 mV in NaCl solution. There was no significant difference in potential values obtained for P2ClAn/PVDF (ABS) and P2ClAn/PVDF (SDS) composite membranes. The membrane potential values (mV) of composite membranes decreased because the charge of the membrane becomes negative with increasing pH.[38]
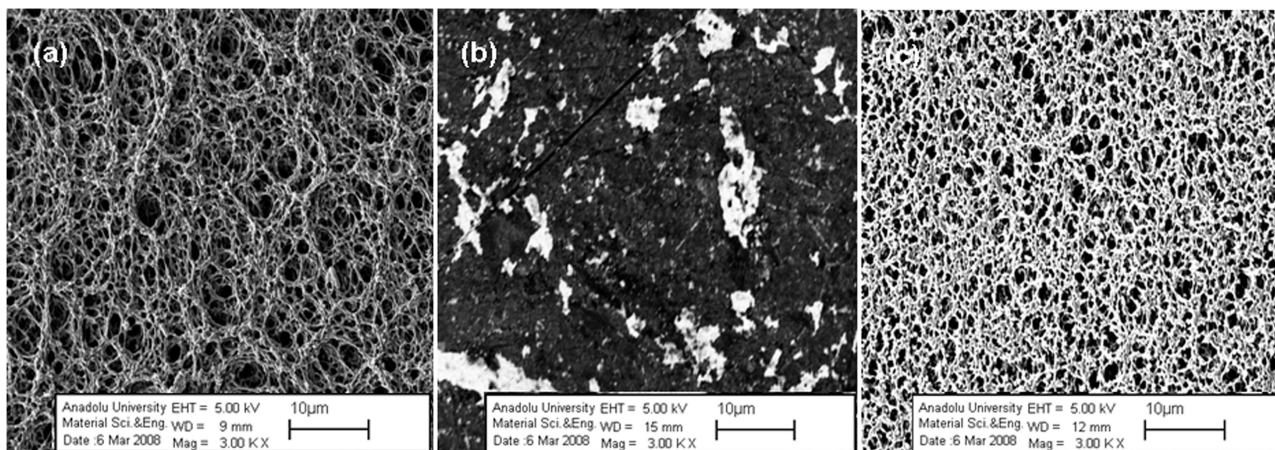

Figure 4. (a) SEM micrograph of poly(2-chloroaniline) composite membrane (SDS), (b) SEM micrograph of poly(2-chloroaniline) composite membrane (ABS), (c) SEM micrograph of membrane support sheet (PVDF).
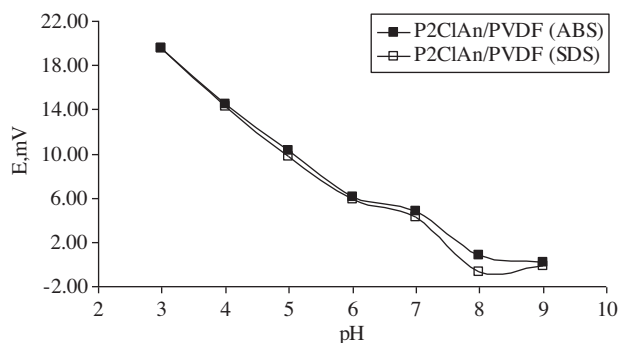

Figure 5. Variation in the pH dependence of membrane potential.

The membrane stability through membrane potential measurement was also examined.[39] Membrane potential values indicated that the charge selectivity of composite membranes is the same as that of commercial cation exchange membrane.[37]

The flux values of the Cr(III) and Cu(II) ions were calculated from the slope of the amount of transported quantity time curves[34] and the results obtained are given in Table 2. The effects of the membrane structure at initial concentration in the receiver phase with transport time for Cr(III) and Cu(II) ions are presented in Figures 6 and 7. It can be seen that the flux value of Cu(II) ion was higher than that of Cr(III) for both composite membranes. Because of the smaller hydration volume, the mobility and transport of the Cu(II) ion were higher than those of the Cr(III) ion. The hydration volumes of Cu(II) and Cr(III) ions are 147.8 and 219.5 cm^3/mol, respectively.[40] As known, the transport of ions through the ion-exchange membrane is influenced by various factors including the size, charge and hydrated radius of ions, the properties and

structures of the membrane, and the ionic concentration within the membrane. Many studies concerning ion-transport phenomena in membrane-electrolyte solution systems have been done. There is agreement within the literature.[3,41,42] Motion of monovalent and bivalent ions in a cation-exchange membrane was discussed in detail by Miyoshi,[42] who compared the fluxes of mono- and bivalent ions and found that the monovalent ions were larger than the bivalent ions. In our experiment, the data obtained were in agreement with this explanation. Moreover, the fluxes of Cr(III) and Cu(II) ions through P2ClAn/PVDF (ABS) membrane were higher than those through the other membrane. This result showed that the ion-exchange capacity of P2ClAn/PVDF (ABS) membrane was higher than that of P2ClAn/PVDF (SDS) membrane.
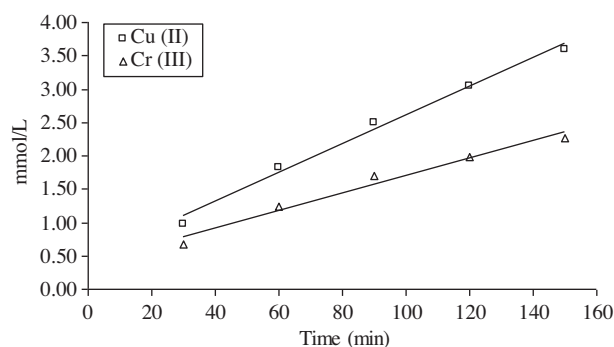

Figure 6. Time dependence of the concentration of Cr(III) and Cu(II) in the receiver solution with P2ClAn (SDS).
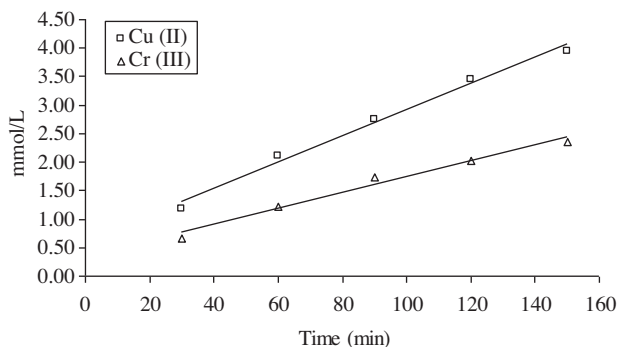
Figure 7. Time dependence of the concentration of Cr(III) and Cu(II) in the receiver solution with P2ClAn (ABS) composite membrane.

4. Conclusion

In the present study, poly(2-chloroaniline) was prepared by chemical oxidation using ABS and SDS dopant anions. P2ClAn/PVDF composite membranes were obtained from chemically synthesized poly(2-chloroaniline) by casting method.

The FTIR-ATR, AFM, and SEM images, comparing PVDF membrane support sheet to P2ClAn/PVDF composite membranes, indicate that the surface morphologies of the membranes are different. The membrane thickness and their ion-exchange capacities were also measured. The ion-exchange capacity value of P2ClAn/PVDF (ABS) composite membrane was higher than of P2ClAn/PVDF (SDS) composite membrane due to dopant anion.

Membrane potential values were obtained for P2ClAn/PVDF composite membranes and these membranes were more negatively charged in NaCl. Donnan dialysis was carried out for transport of Cr(III) and Cu(II) ions from aqueous solution using P2ClAn/PVDF composite membranes. The flux value and transport quantity of Cu(II) ion was higher than of Cr(III) ion for P2ClAn/PVDF (ABS) composite membrane. The obtained results showed that the transport of Cr(III) and Cu(II) ions depends on the hydration volume and charge of ions.

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