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Removal of Cr(III) from aqueous solutions using P-EAn and P-MAn/PVDF composite membranes

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ABSTRACT

In this work, composite membranes were prepared by chemical polymerization of a thin layer of substitute anilines (methylaniline and ethylaniline) in the presence of an oxidant on the surface polyvinylidenefluoride (PVDF) membrane support sheet. Poly-N-ethylaniline (P-EAn) and poly-N-methylaniline (P-MAn)/PVDF composite membranes were obtained from this polymerization. Scanning electron microscopy, Fourier transform infrared spectroscopy, and atomic force microscopy studies for composite membranes confirmed substitute anilines loading on the PVDF membrane. The membrane thickness and their ion-exchange capacities were also measured. Donnan dialysis experiments were performed using P-EAn and P-MAn/PVDF composite membranes for the removal of chromium (III) from aqueous solution. The flux values (*J*) of Cr(III) were obtained at 25˚C. The flux value of Cr(III) for P-EAn/PVDF composite membranes was higher than the other membrane because of the high ion-exchange capacity.

Keywords: Composite membrane; Cr(III); Donnan dialysis; Poly-*N*-ethylaniline; Poly-*N*-methylaniline

1. Introduction

Chromium is unique among regulated toxic elements in the environment since different oxidation states of chromium, specifically Cr(III) and Cr(VI), have been found to have different toxicities [1]. Trivalent chromium is much less toxic than hexavalent chromium, which is known as a carcinogenic agent [2]. However, Cr(III) can convert into the harmful Cr (VI) via oxidation in the environment. While there are natural sources of chromium in the environment, mostly chromium(III), the majority of chromium(VI) originates from industrial sources. These industrial sources include electroplating, metal finishing, dye, textile, leather tanning, stainless steel production, photography, etc. [1].

Therefore, different processes have been developed and used for the removal or recovery of Cr(III) from wastewater [3]. For removal, processes including thermal, biological, and chemical methods such as coagulation [4], chemical precipitation [5], electrolysis [6], solvent extraction [7], and adsorption [8] have been used. Precipitation and adsorption are two traditional methods for the recovery of Cr(III) contained in

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tanning wastewater [5,8] but they are not commonly utilized and the quality of the recovered solutions is not always optimal due to the presence of metals and lipidic impurities. Therefore, to improve the quality of the recovered Cr(III), membrane processes were studied in the past years. In recent years, membrane-based separation techniques have been developing rapidly as a cleaner technology and without the use of chemicals or thermal energy [9–13].

Chaudry et al. have discussed coupled transport of Cr(III) ions across triethanolamine/cyclohexanone-based supported liquid membranes for tannery waste treatment. The experimental results demonstrated that Cr(III) ions can be removed from aqueous or waste (tannery) solutions without its oxidation to VI state [14].

For the purification and concentration of diluted solutions, Donnan dialysis which is an ion-exchange membrane process can also be used [15,16]. The theory and principles of the Donnan dialysis process are reviewed [17,18].

Lately, conducting polymers have attracted much attention as membrane preparation materials [19–21]. However, few studies were found on using substituted PANI [22]. Conducting polymers are blended with non-functional polymeric materials to improve and modify the membrane properties by different chemical reactions [23,20]. Composite membranes have been gained cation-exchange properties introducing a $-SO_3H$ group on the conducting polymer chains [22]. Ferreira et al. [21] have mentioned the use of composite membranes containing polyaniline for the transport of metallic ions. Dodecylbenzenesulfonic acid, *p*-toluenesulfonic acid, and camphorsulfonic acid have been used in this study as doping agents.

In the present study, composite membranes were prepared by using substitute anilines and used for the removal of Cr(III) ion from aqueous solution for the first time in this work. To prepare composite membranes, the poly-N-ethylaniline (P-EAn) and poly-N-methylaniline (P-MAn) overlayers were deposited on both sides of a porous polyvinylidenefluoride (PVDF) *in situ* by oxidative polymerization of N-ethylaniline and N-methylaniline. These membranes were prepared using o-aminobenzenesulfonic acid (ABS) as dopant and named as P-EAn/PVDF and P-MAn/PVDF.

2. Experimental

2.1. Chemicals and materials

$CrCl_3{\cdot}6H_2O$, HCl, NaOH, ABS, ammonium peroxydisulfate $(NH_4)_2S_2O_8$, N-methylaniline, and N-ethylaniline of analytical grade were supplied from Merck Co and Fluka. N-methylaniline and N-ethylaniline were distilled repeatedly until a colorless liquid was obtained, and kept in darkness at 4˚C prior to use. All solutions were prepared using ultra-pure water obtained from a Milli-Q (Millipore Corp.). PVDF membrane support sheets (0.45 μm) were purchased from Millipore. In preparation of all solutions, $18.2\,\mu\Omega\,cm^{-1}$ deionized water was used.

2.2. Preparation of P-EAn and P-MAn membranes

In this study, the P-EAn and P-MAn/PVDF composite membranes were prepared with the formation of a thin layer of P-EAn and P-MAn on the surface of PVDF membrane support sheets. For this purpose, the P-EAn and P-MAn overlayers were deposited on both sides of a porous PVDF membrane support sheet *in situ* by oxidative polymerization of substitute anilines. Polymerization solutions are composed of o-aminobenzensulfonic acid as dopant anion, ammonium peroxydisulfate as oxidant and, N-methylaniline or N-ethylaniline. The ratio of dopant to monomer was taken as two. After 24 h, the membranes were taken out from the polymerization solutions and then washed with water. Before usage, the composite membranes were immersed in deionized water at 70˚C for 1 h to remove impurities and residual solvent. Then they were conditioned in 1 mol/L HCl solution for 24 h to ensure complete protonation of the polymers [24].

2.3. Characterizations of composite membranes

The morphology of composite membrane surfaces was assessed with a Field Emission Gun Scanning electron microscope (FEG-SEM, Oxford Instruments-7430) and TESCAN VEGA II LSU model SEMs, respectively. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of membranes were recorded in the range 400–4,000 cm^{-1} using a Shimadzu IR Prestige-21 FTIR spectrometer. The composite membrane surfaces have been structurally characterized by Atomic Force Microscopy (AFM) Nanosurf easy scan instrument. The pH measurements were performed with Seven Multi Mettler Toledo during all the experiments. 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used for pH adjusting. The ion-exchange capacity values of membranes were determined by an acid-base titration as described previously [24]. Membrane thickness was measured by Mitutoyo CD-15 CPX digital micrometer at different points of the sample.

The main characteristics of the composite membranes are listed in Table 1.

Table 1
Properties of the prepared membranes

Property	P-MAn/PVDF	P-EAn/PVDF
Type	Cation-exchange	Cation-exchange
Thickness (μm)	110	110
Ion-exchange capacity (mmol/g)	0.9478 (0.01)	1.1923 (0.01)

2.4. Donnan dialysis

The transport of Cr(III) ion from an aqueous solution was performed by using a cell consisting of two detachable compartments made of Teflon [22]. The membrane was clamped tightly between two compartments of 40 mL capacity, and the surface area of the membrane was 7.07 cm^2. Both phases were stirred at 500 rpm with magnetic stirrer, during the experiment. All of the measurements were carried out at 25°C. The feed phase contained 10^{-1}–10^{-3}°mol/L $CrCl_3$ solutions and the receiver phase contained 0.1 mol/L HCl solution. The sampling of the solution (1 mL) was carried out at certain intervals (each 30 min) and the amount of Cr(III) ions transported across the membrane was determined by the use of an ICP–OES (Perkin Elmer 5300 DV model). The wavelength for the determination of Cr(III) ion by ICP-OES is 267.716 nm. The experiments of Cr(III) have been carried out at optimum pH 3, as stated in the literature for the Cr(III) [25].

3. Results and discussion

Structural surface characterization of P-EAn and P-MAn/PVDF composite membranes was investigated by FTIR, AFM, and SEM. These studies confirmed P-EAn and P-MAn loading on the PVDF membrane support sheet for both types of composite membranes.

FTIR spectrums of composite membranes are given in the Figs. 1 and 2, which have a peak between 1,500–1,800 cm^{-1} because of C=C stretch and it seems that aromatic N-ethylaniline and N-methylaniline are attached to the PVDF membrane support sheet. The new bands and the wavelength shifts indicate the effect of substituent groups on the structure of P-EAn and P-MAn.

Fig. 3(a–c) shows the corresponding AFM amplitude images of PVDF membrane support sheet and P-EAn/P-MAn/PVDF composite membranes, respectively. The nature of the AFM can be used to estimate changes in roughness and surface morphology variations. Fig. 3(a) shows that PVDF membrane has a relatively flat surface. After the modification, granules or hemispheres in surface topography are observed. It can be seen from Fig. 3(b) and (c) that the P-EAn and P-MAn were coated on the surface of PVDF membrane support sheet.

SEM images of PVDF membrane support sheet and composite membranes were recorded and representative images of these membranes are presented in Fig. 4(a–c). The surface of PVDF is composed of a macro porous structure. When polymerization was carried out on PVDF, the holes of PVDF were filled and coated with polymeric solutions.

The removal of Cr(III) ion from aqueous solution through composite membranes that have cation-exchange properties under Donnan dialysis conditions was studied as a function of pH gradient at 25°C. The flux values of the Cr(III) were calculated from the time profile of receiver solution ion concentration by

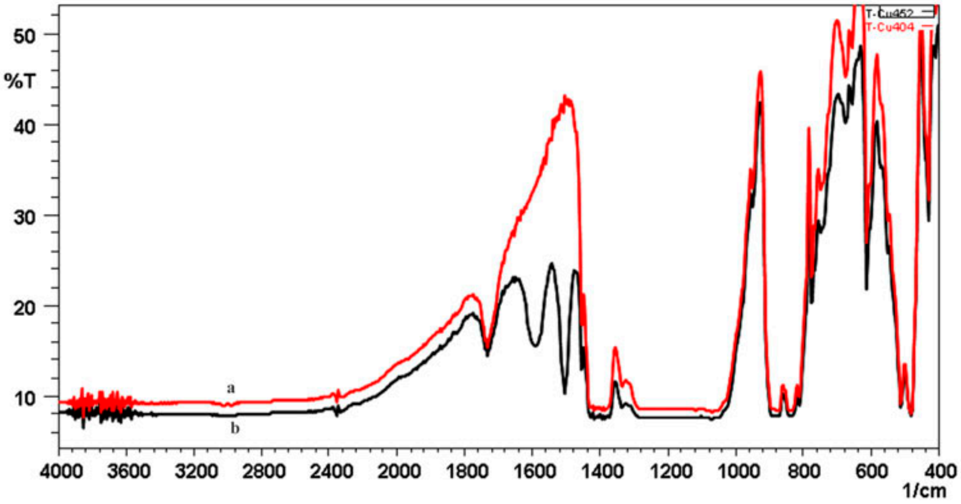

Fig. 1. FTIR spectrum of P-EAn/PVDF composite membrane (a) PVDF and (b) P-EAn/PVDF.

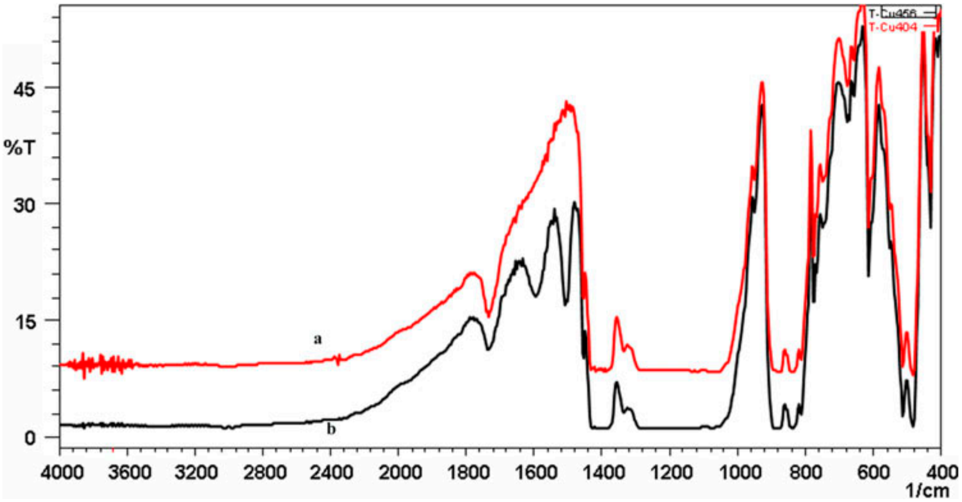

Fig. 2. FTIR spectrum of P-MAn/PVDF composite membrane (a) PVDF and (b) P-MAn/PVDF.

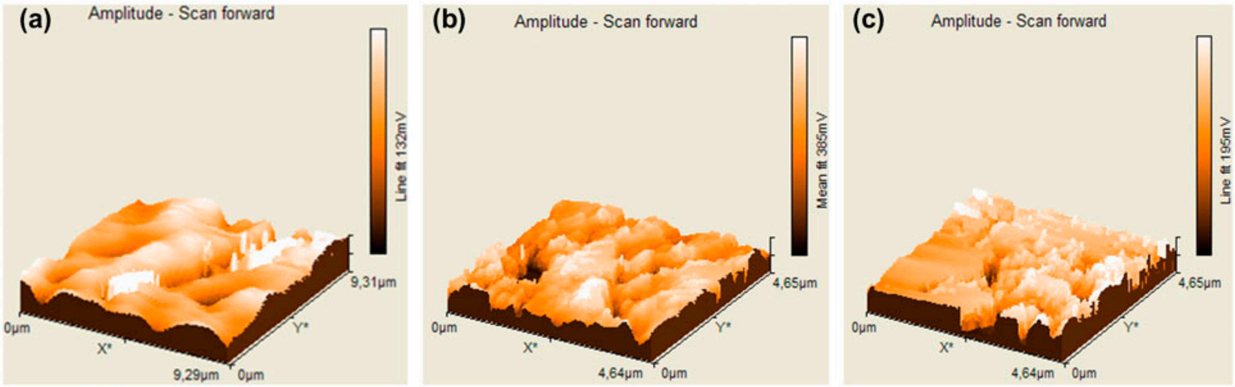

Fig. 3. AFM photograph of (a) PVDF, (b) P-EAn/PVDF composite membrane, and (c) P-MAn/PVDF composite membrane.

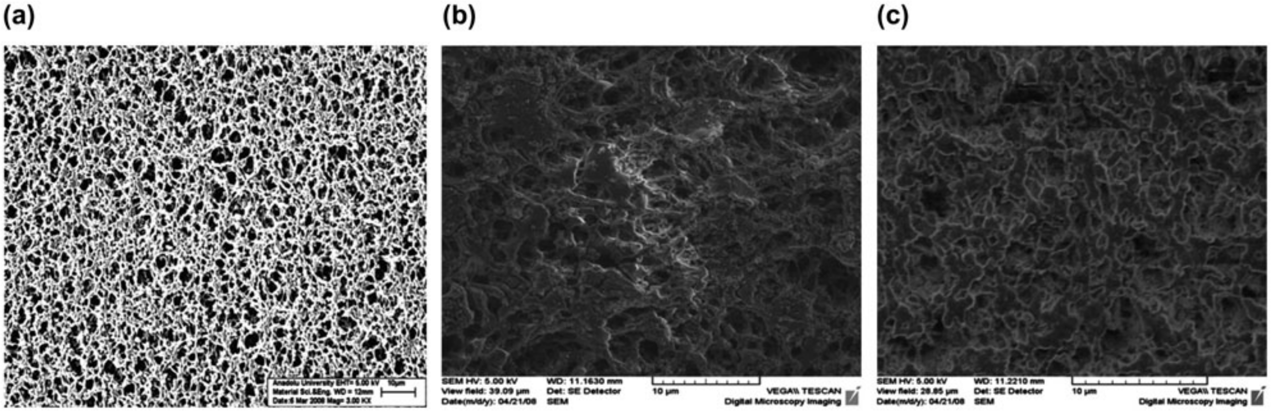

Fig. 4. SEM photograph of (a) PVDF, (b) P-EAn/PVDF composite membrane, and (c) P-MAn/PVDF composite membrane.

Table 2
Cr(III) fluxes for two composite membranes

Membranes	$J \times 10^{11}$(mol cm^{-2} s^{-1})	
	P-EAn	P-MAn
Cr(III)		
1.0×10^{-1} mol/L	1,514 (5.66)	1,450 (1.24)
1.0×10^{-2} mol/L	136 (0.40)	115 (0.29)
1.0×10^{-3} mol/L	104 (0.30)	20.1 (0.026)

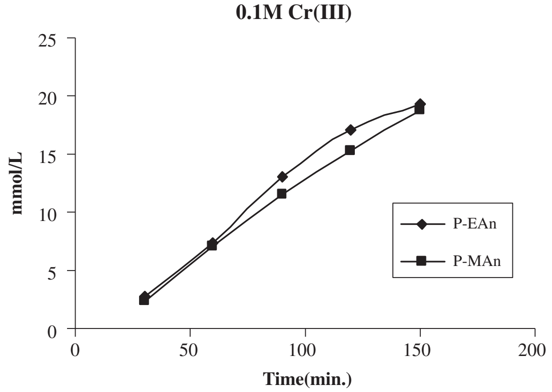

Fig. 5. Time dependence of the 0.1 mol/L concentration of Cr(III) in the receiver solution with composite membranes.

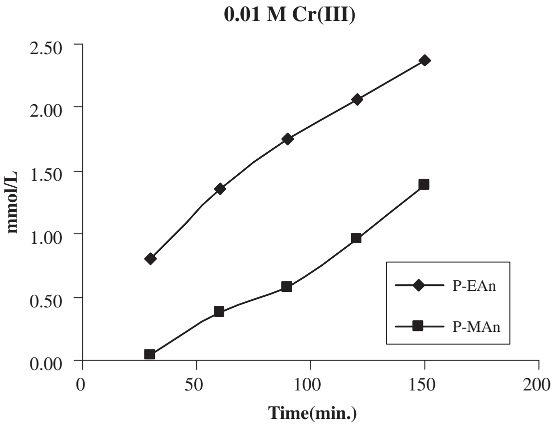

Fig. 6. Time dependence of the 0.01 mol/L concentration of Cr(III) in the receiver solution with composite membranes.

initial rate technique [24] and the results are given in the Table 2. These results are obtained at 95% confidence level ($N = 3$). LOD value of Cr (III) ion is found to be 3 ppb.

J values increased with the increasing of initial Cr (III) concentration for both composite membranes as seen in Table 2, which are in good agreement with literature [26–28]. Besides, the flux value of Cr(III) ion through P-EAn membrane was higher than the other membrane. The IEC is one of the most important parameters of ion-exchange membranes [29]. The IEC value of the P-EAn composite membrane was higher than that of the P-MAn membrane.

The effect of the membrane structure at 10^{-1}–10^{-3} mol/L Cr (III) ion concentrations in the receiver phase, with transport time for Cr (III) ion, is presented in Figs. 5–7. Because of the increasing ion-exchange capacity of the P-EAn/PVDF composite membrane, the transport of Cr(III) ion has been increased. Cr(III) amount increased with the increasing of initial Cr(III) concentration for both composite membranes.

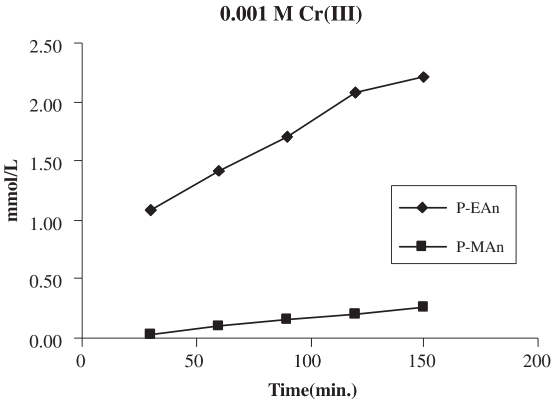

Fig. 7. Time dependence of the 0.001 mol/L concentration of Cr(III) in the receiver solution with composite membranes.

4. Conclusion

The synthesis of P-EAn and P-MAn on the surface of PVDF membrane support sheet has been accomplished using a chemical polymerization.

These composite membranes were used for the removal of Cr(III) ion from aqueous solution as cation-exchange membranes. The experimental results show that removal of Cr(III) depends on the surface morphology and IEC of composite membranes.

The morphologic and spectroscopic investigation (SEM, AFM, and FTIR) showed that the surfaces of composite membranes were different from that of PVDF membrane and therefore they can be considered as a new type of membranes.

The flux values of Cr(III) ion were obtained, and it was found that the J values increased with the increasing of initial Cr(III) concentration.

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