Investigation of Electrospun and Film-Cast PVC Membranes Incorporated with Aliquat 336 for Efficient Cd Extraction: A Comparative Study

Lisa Wong,[1] **Wei Shen,**[1] **Yen Bach Truong**[2]

[1]*Department of Chemical Engineering, Australian Pulp and Paper Institute, Monash University, Clayton, Victoria 3800, Australia*
[2]*CSIRO Materials Science and Engineering, Clayton South, Victoria 3169, Australia*

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ABSTRACT: This article was aimed to investigate the cadmium extraction behaviors of the two different poly-vinyl chloride membranes incorporating Aliquat 336—electrospinning and film-casting. An optimal investigation condition for membranes used in the extraction process was produced at 25 kV with 10 cm tip-to-collector distance. Membranes were electrospun for 8 h at 200 μL/h. Membrane extraction studies were carried out using a 127 mg/L Cd(II) solution. Scanning electron microscope (SEM) images revealed differences in fiber diameters and membrane morphology. The addition of Aliquat produced very fine fibers (7–722 nm) resulting Brunauer-Emmett-Teller (BET) surface areas of 4.67–11.3 m^2/g for electrospun membranes and 1.70–5.44 m^2/g for film-casted membranes. Extraction studies using membranes with different levels of Aliquat (0–40% w/w) revealed that the cadmium extraction performance of electrospun membranes was significantly better than conventional film-cast membranes. For 40% Aliquat 336, with an initial concentration of 127 mg/L Cd, the cast membrane extracted down to concentration to 115 mg/L as compared to electrospun membrane, which extracted down to 88 mg/L within 40 h. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 327–335, 2011

Key words: electrospinning; cadmium; Aliquat 336; membrane; poly-vinyl chloride; BET

INTRODUCTION

The accumulation of cadmium (Cd) as an environmental contaminant in our freshwater ecosystems has been of increasing concern, because of its toxicity to aquatic animals through both airborne and dietary routes. The need to establish water quality systems that can help protect our aquatic ecosystems has therefore been of considerable interest.[1–4]

Although various technologies have been used for the extraction of metal ions from aqueous systems, there are disadvantages associated with each. For example, large quantities of solvents used in solvent technology are a disadvantage as they are a major environmental concern.[2]

Polymer fibers have been used in a variety of applications such as textiles, and recent work has looked at the preparation of submicron fibers with good mechanical properties and smooth skin-like fibers.[1,5–7] The electrospinning process has attracted increased interest in recent years due to its unique ability to produce fibers with diameters of 50–500 nm.[1,5] Furthermore, membranes manufactured from a collection of such electrospun fibers have large surface areas and small pore sizes, which are important characteristics for applications such as filtration.

The basic principles of electrospinning are very simple. A polymer in solution is encapsulated within a syringe, which is connected to an anode that connects to a high-voltage power supply. Because of surface tension, the polymer solution forms a hemispherical drop at the end of the capillary tip, and when voltage is applied, the droplet distorts due to an induced charge on the solution surface. At an applied voltage sufficient to overcome this surface tension, an electrostatically driven jet of fiber is produced, which travels between the capillary tip and a grounded cathode-connected metallic collector placed at a certain distance from the capillary tip of the syringe. Under the appropriate conditions, a single jet may undergo solution instability and splay or split, resulting in smaller diameter fibers. Therefore, by controlling the electrospinning parameters, optimal nanofibers can be prepared.

The membranes used in this study incorporated polyvinyl chloride (PVC) and Aliquat 336 (tricaprylylmethylammonium chloride, hereafter referred to as "Aliquat") shown in Figure 1.

Correspondence to: Y. B. Truong (Yen.Truong@csiro.au).

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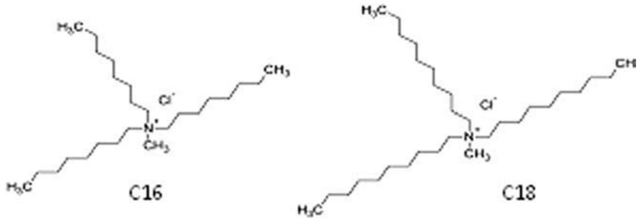

Figure 1 Structure of Aliquat (left showing R-groups as C8 and right showing R-group as C10).

This type of membrane avoids the overuse of solvents, making them more environmentally friendly. In addition, they only require a small amount of extractant or reagent and the metal extracted into the membrane can be analyzed directly using spectrometry, making them economically viable. The disadvantages of PVC/Aliquat membranes are their low mechanical strength, and there is a limit to the amount of Aliquat that can be incorporated (50% for cast membranes).[6,8]

According to Wang et al.,[7] the first event to occur in the extraction process is the complexation of Aliquat with the metal ions at the membrane/aqueous interface, as shown in eq. (1):

$$(A^{+}Cl^{-})_{m} + ([CdCl_{3}]^{-})_{a} = (A^{+}[CdCl_{3}]^{-})_{m} + (Cl^{-})_{a}, \tag{1}$$

where $A^{+}Cl^{-}$ is the Aliquat chloride, $[CdCl_{3}]^{-}$ is the trichlorocadmium(II) ion, and $A^{+}[CdCl_{3}]^{-}$ is the extracted ion pair complex. Finally, the diffusion of Aliquat–metal ion complexes occurs across the membrane.

Wang et al.[7] also reported that the concentration of Aliquat after extraction increased on the surface of a membrane, suggesting that there was migration of the extractant. Although the evidence is not conclusive, there may also have been a slight leakage of extractant into the aqueous phase, therefore decreasing the actual measured amount of Aliquat contained in the membranes. Wang et al. used X-ray photoelectron spectroscopy to study membrane surfaces after extraction experiment, and found that they had $[N^{+}]$ and $[Cl^{-}]$ ratios twice as high as those prior to extraction.

Xu et al.[1] studied the structure of membranes with various Aliquat loadings in cast membranes, and found that those incorporating 30% Aliquat had good entanglement of the extractant molecules in the polymer chains. They have also reported that it is possible as the extractant acts as a plasticizer to the polymer film, causing it to have low activity due to its reduced mobility. At high Aliquat content (>40%), excess extractant may form microaggregates that prevent the PVC molecular chains forming a complete polymer matrix leading to the formation of micropores or microchannels. It is also possible that the concentration of extractant on the walls of these micropores is much higher than that of the membrane bulk, resulting in greater activity than for the entangled membranes. These microporous passageways could provide a route for Aliquat and Cd(II)–Aliquat ion pairs to diffuse across the membrane.

The aim of the current research is to develop electrospun membranes that have improved metal ion extraction rates compared to film-cast membranes and also increased extraction capacity through optimized electrospinning conditions. It is expected that electrospun membranes will improve the feasibility of membrane technology for the extraction of heavy metal ions on an industrial scale. In this study, electrospun PVC membranes incorporating various amounts of Aliquat were used to extract Cd from 2*M* hydrochloric acid (HCl) solutions.

EXPERIMENTAL

Materials

The Aliquat (straw-colored and viscous in appearance at room temperature), molecular weight of 404.17 obtained from sigma aldrich and high molecular weight PVC (in fine white powder form) obtained from Fluka (Product of Italy, *K* value 69–71). The analytical reagents HCl, cadmium chloride ($CdCl_2.H_2O$) (Cd(II)), HPLC-grade tetrahydrofuran (THF), and 2,5-dimethylformamide (DMF) were obtained from BDH. Distilled water was used for all dilutions.

The Cd(II) solutions used in the experiments were prepared by mixing 127 mg/L ($CdCl_2{\cdot}H_2O$) in 2*M* HCl solution.

Electrospun membranes

Preparation of electrospun membrane is shown in Figure 2. A range of trial solutions were prepared for electrospinning by varying the concentrations of PVC (15–20%), DMF/THF ratio (100/0, 80/20,

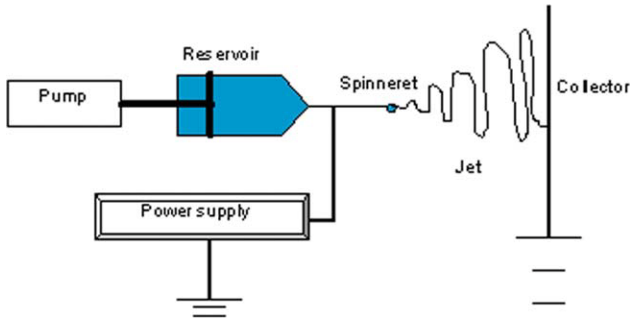

Figure 2 Experimental setup for the electrospinning process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

60/40, 50/50, 40/60, 20/80, and 0/100), and Aliquat (0–40%). These solutions were electrospun for 8 h at 200 μL/h, at different applied voltages (20–30 kV) and at different distances (10–20 cm) between the syringe tip and a glass collector plate for easier collection of membrane fibers. A clean glass slide was placed in front of collector plate to collect membranes used for extraction experiments. SEM, Brunauer-Emmett-Teller (BET) surface area, and extraction studies were then conducted. This made it possible to obtain intact membranes. Collecting membranes on metallic foils allowed for faster production rates due to better conductivity but made it difficult to strip the membrane off the collector plate. A pump rate of 200 μL/h was chosen as a baseline rate to produce the fibers. A collection time of 8 h was necessary to obtain dense enough fibers to be used in the electrospinning process with the flow rate chosen.

Film-cast membranes

Each film-cast membrane used in the extraction studies was prepared by pouring PVC/Aliquat solution into a petri dish containing 18% PVC in 40 : 60 DMF: THF ratio (%w/w) with 10–40% Aliqaut solution. The solvent was allowed to evaporate overnight, before the membrane was peeled from the Petri dish prior to experiment. This yielded a colorless, flexible, transparent, and mechanically strong film. All film-cast membranes were made with the same concentrations as those produced using electrospinning.

Characterisation

Microscopy

The measurement of membrane thickness was performed using stereo optical microscopy (Olympus Mercury Burner). A cross-sectional sample of each membrane was cut using the freeze–fracture technique which involved immersing the membrane in liquid nitrogen and then fracturing it in the desired plane. A sample was carbon taped to a stub, fractured side facing up and imaged at a magnification of 40 times.

After carbon sputtering all the samples using a Joel JFC-1200 fine coater, the surface morphology of the electrospun membranes was observed using a Philips XL30 Field Emission Scanning Electron Microscope operating at 5.0 kV.

BET surface area

Prior to measurement, samples were cut into roughly into 1 × 1 cm^2 square pieces and were degassed overnight under vacuum at 423 K. High-purity N_2 (99.9999%) was used. Adsorption of N_2 at 77 K was measured using a Micromeritics Tristar 3000 under a wide range of relative pressures (0.001–1). BET surface area determines the quantity of nitrogen (N_2) adsorption for a single layer was used to gain insight into the properties of the fibrous membranes at different Aliquat concentrations.

ImageJ software, a freehand tool, was used to outline the collected membrane fibers on aluminium foil due to electrospinning. The freehand outline of the image was scanned and then imputed into the software for calculation of surface areas. The use of the software allowed collected surface areas to be measured at different electrospinning conditions.

Cd extraction studies

Cd extraction studies were carried out in a one-compartment cell with a liquid capacity of 150 mL. The test membrane was tightly clamped in a Teflon frame with an effective area of 7.1 cm^2, and the stirring rate of the compartment was kept at a constant speed.

One-milliliter pipette Cd solute/ions were collected at times 0.17, 1, 2.5, 5, 8, 23.5, 28, 32.5, and 48 h; then concentrations were determined using flame atomic absorption spectrometry (FAAS) (Varian SpectraAA-20) at a wavelength of 326.1 nm and slit width of 0.5 nm. A lamp current of 4 mA and acetylene and air were used as fuel and support, respectively.

RESULTS AND DISCUSSION

Electrospinning results

Light microscopy revealed the presence of beaded fibers, as shown in Figure 3 for 15 and 18% PVC membranes. These are typical characteristics of low-viscosity samples.[8] Bead formation can also be affected by the electric field and the incorporation of additives such as Aliquat. Voltage changes may have the greatest effect on fiber morphology as it determines the electric field strength and therefore jet initiation. Aliquat addition may act to increase conductivity of the solution and therefore faster flow rates of the polymer jet.

Using the ImageJ software, the surface area of electrospun membranes was measured. An expected, increasing the tip-to-collector distance resulted in larger surface areas. The results are summarized in Figure 4. At longer tip-to-collector distance, the collected membrane area was larger but less dense (see Fig. 5). Longer working distances also favored the formation of thinner fibers due to enhanced solvent evaporation from longer path lengths. As a result, shorter working distance was therefore used to obtain denser fibers.

Voltage is also an important factor in the electrospinning process as it determines the average strength of the electric field. It has been reported[8]

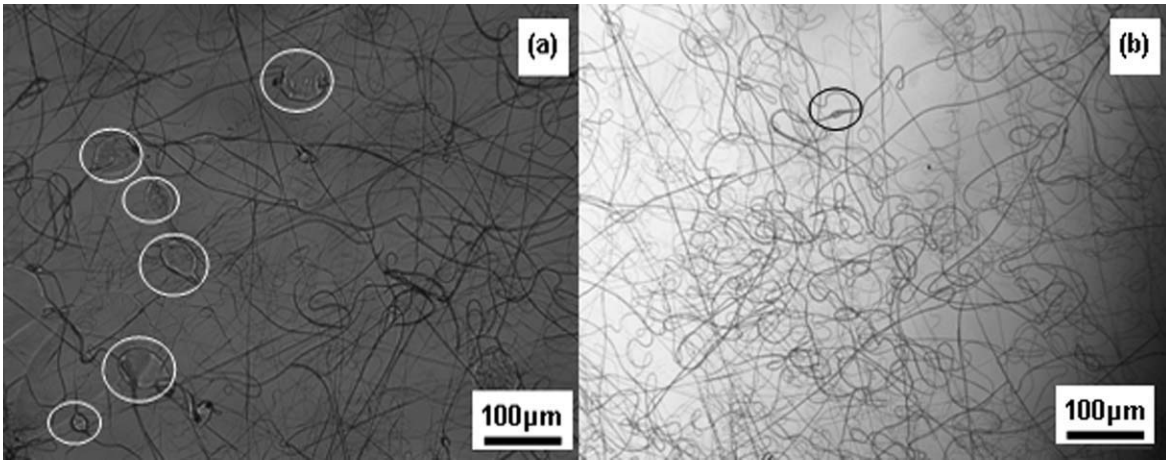

Figure 3 Microscope images show beaded fibers (circled) in (a) 15% and (b) 18% PVC membranes.

an increase in voltage also favors the formation of thicker fiber, due to the higher electrostatic forces on the jet. Although thinner fibers may be obtained with lower voltages, smaller collected areas of the membrane and longer production times result. In this case, membrane size only needed to be within 7.1 cm^2 to fit into the Teflon membrane holders for extraction processes. Lower voltages were used to obtain small fiber diameters with enough surface area for use. The use of 25 kV allowed for these conditions to be met in production times.

As summarized in Figure 6, the average fiber diameters of electrospun membranes varied

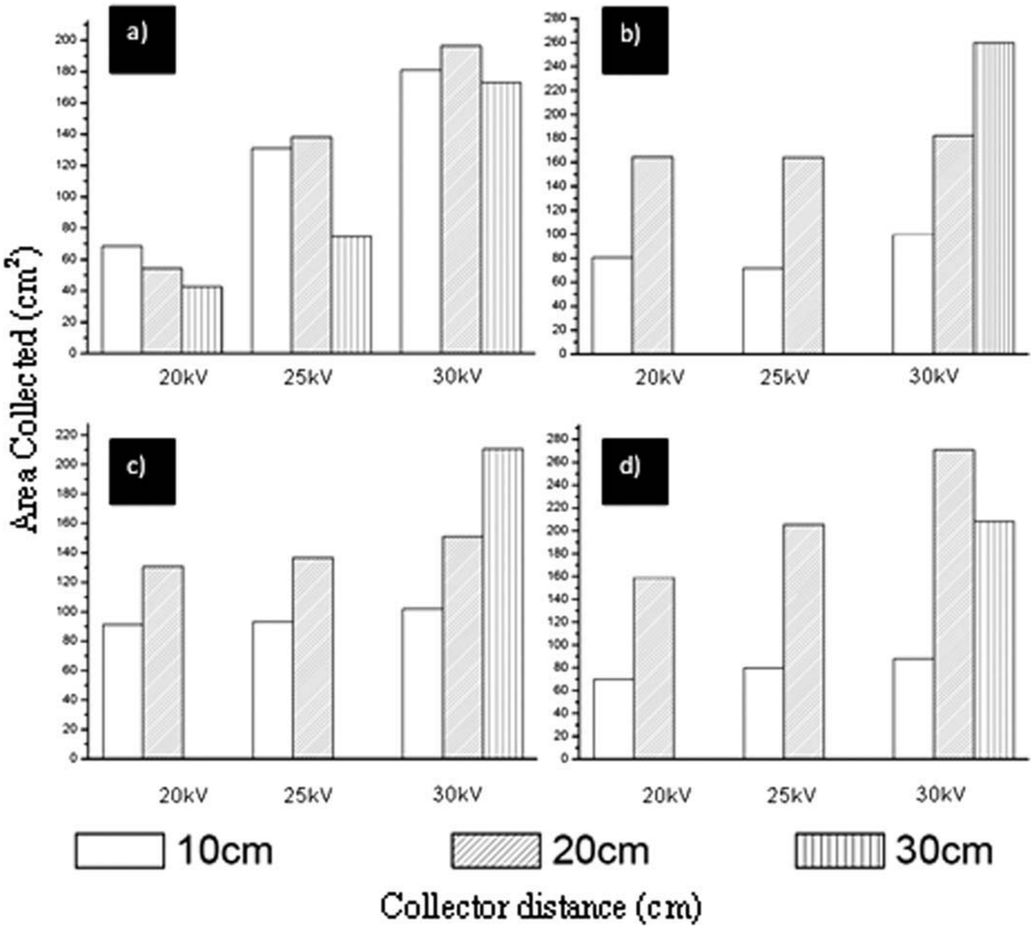

Figure 4 ImageJ-determined surface areas of (a) 0%, (b) 10%, (c) 20%, (d) 30% Aliquat at 20, 25, and 30 kV.

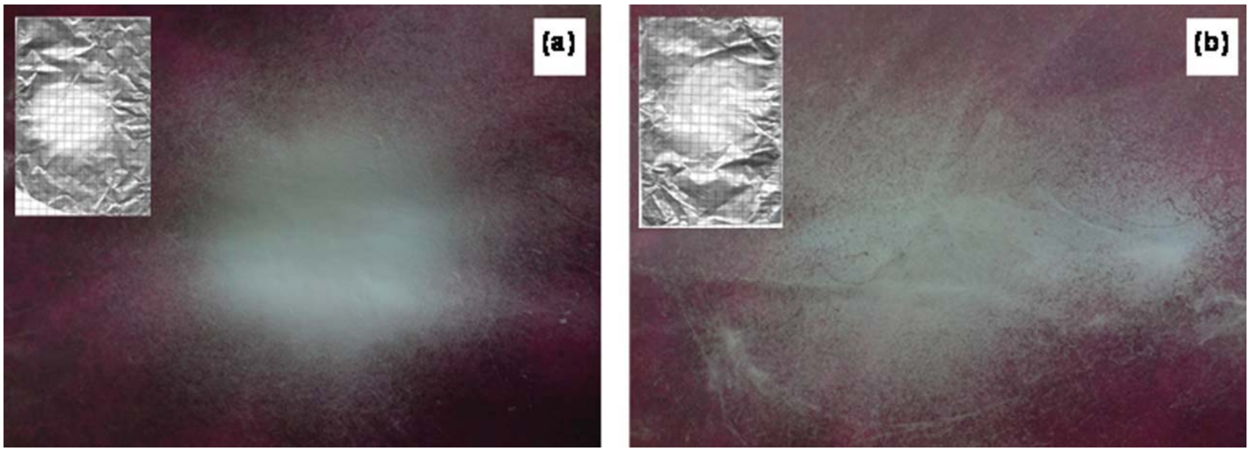

Figure 5 Surface areas of membranes electrospun with tip-to-collector distances of (a) 10 and (b) 15 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

depending on Aliquat content. In general, fiber diameters ranged from 15–245 nm at 10% Aliquat content to 9–411 nm for 30%. Also, 7–722 nm was obtained for 40% Aliquat. In contrast, 0% Aliquat yielded fiber diameters of 181–777 nm. The variation in diameter distribution of electrospun fibers could be the result of jet splitting or inhomogeneity of the solution. Fiber diameters were randomly chosen for a range of areas during SEM imaging.

SEM observations of the morphology of electrospun membranes revealed web-like structures (see Fig. 7), the occurrence of which increased with

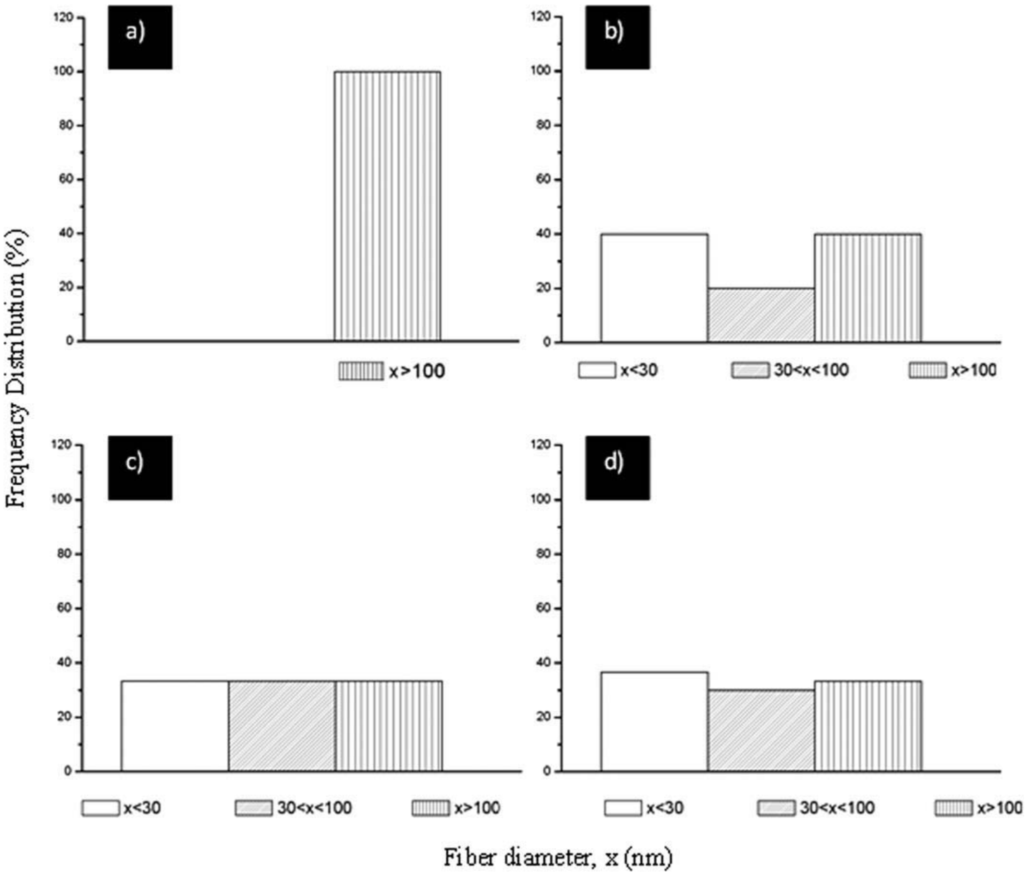

Figure 6 Average diameter of fibers incorporating (a) 0%, (b) 10%, (c) 20%, and (d) 30% Aliquat and electrospun at 10 cm and 25 kV.

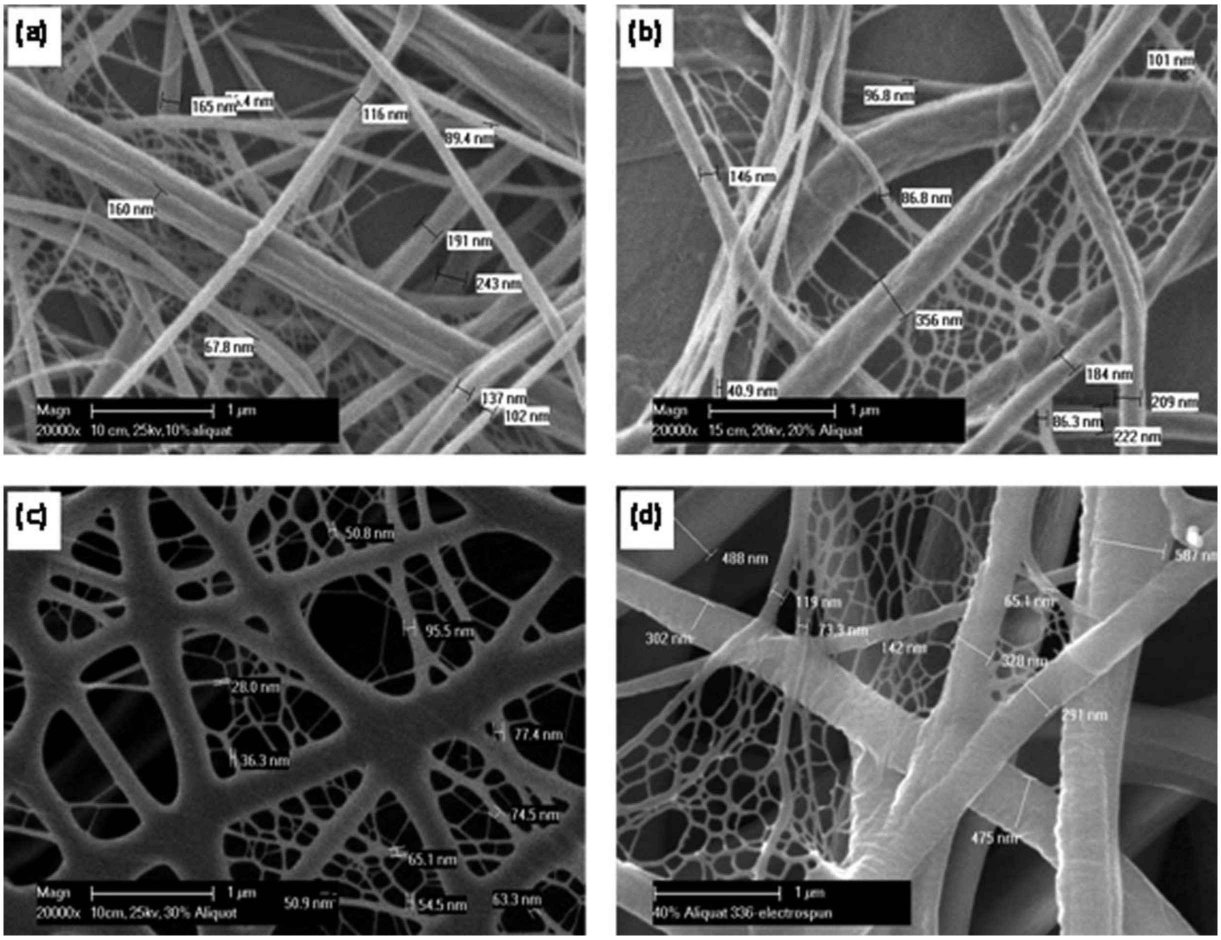

Figure 7 SEMs of membranes electrospun at 10 cm and 25 kV, and incorporating Aliquat contents of: (a) 10%, (b) 20%, (c) 30%, and (d) 40%.

increasing Aliquat content. This could explain the increased surface area of membranes containing greater amounts of Aliquat. Similar web-like structures have been observed by numerous research groups[1,6,8] studying the electrospinning of high-viscosity solutions. The BET surface area had a

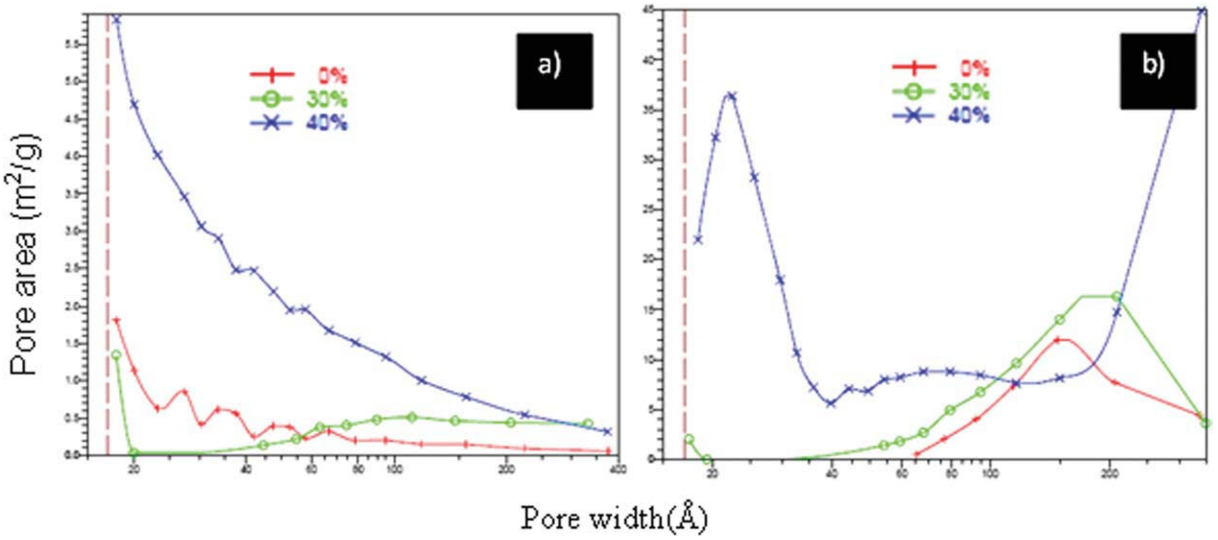

Figure 8 Pore size distribution of membranes with increasing Aliquat addition: (a) cast and (b) electropsun. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

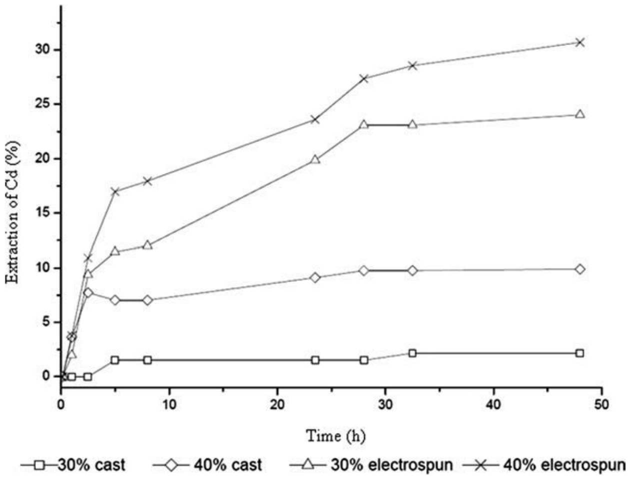

Figure 9 Comparison of Cd(II) extraction (%) of cast and electrospun membranes with 30–40% Aliquat.

tendency to increase with smaller fiber diameters, which is a valuable characteristic in the extraction process.

The 40% Aliquat in PVC membranes appeared less dense and finer fibers than the 30% membranes, possibly due to the smaller fibers obtained at the higher Aliquat content.

Figure 8 shows the pore size distribution of both cast and electrospun membranes as a function of Aliquat content. The surface of the cast membranes appears to be quite uniform compared to the electrospun membranes. The pore widths of the 40% Aliquat electrospun membranes are smaller than those of the 0 and 30% membranes, supporting the previous results for BET surface area. Pores of ~ 15–20 nm were observed in the 0–30% Aliquat electrospun membranes. As for 40%, Aliquat pore widths as low as 2–4 nm were seen. Smaller pores are desirable in obtaining membranes with higher surface areas.

Extraction studies

The effects of Aliquat concentration on Cd extraction performance were investigated. The extraction performance of membranes was determined by measuring the decrease over time in aqueous metal ion concentration in HCl solutions. Preliminary Cd extraction experiments revealed that membranes incorporating less than 20% Aliquat achieved insignificant Cd(II) extraction, even after 10 h. Subsequent extraction experiments were therefore performed using membranes incorporating 30 and 40% Aliquat (Fig. 9).

It was found that extraction performance improved in membranes with higher Aliquat content. The 30 and 40% Aliquat electrospun membranes performed significantly better in terms of both extraction rate and capacity when compared to their film-cast counterparts (Fig. 10).

The FAAS study revealed that at 40% Aliquat, cast membranes reduced the initial Cd(II) concentration of ~ 127 mg/L down to a concentration of 115 mg/L within 40 h, while 40% electrospun membranes successfully reduced the Cd(II) concentration to 88 mg/L (the best performance of all membranes). The 30% Aliquat, cast membranes extracted to a final concentration of 124 mg/L, compared to 97 mg/L for the electrospun membranes.

The maximum Cd(II) extraction was achieved within 40 h, compared to the 100 h reported by Wang et al.[7] in studies of membranes with similar thicknesses to those used here. Although Wang et al.[7] used longer extractions times, negligible extraction of Cd was observed after 40 h using membranes of 81.7 μm in thickness.

Table I summarizes the results obtained for the 30 and 40% Aliquat/PVC cast and electrospun membranes and includes data for PVC membranes as a control. The extraction capacity can be calculated

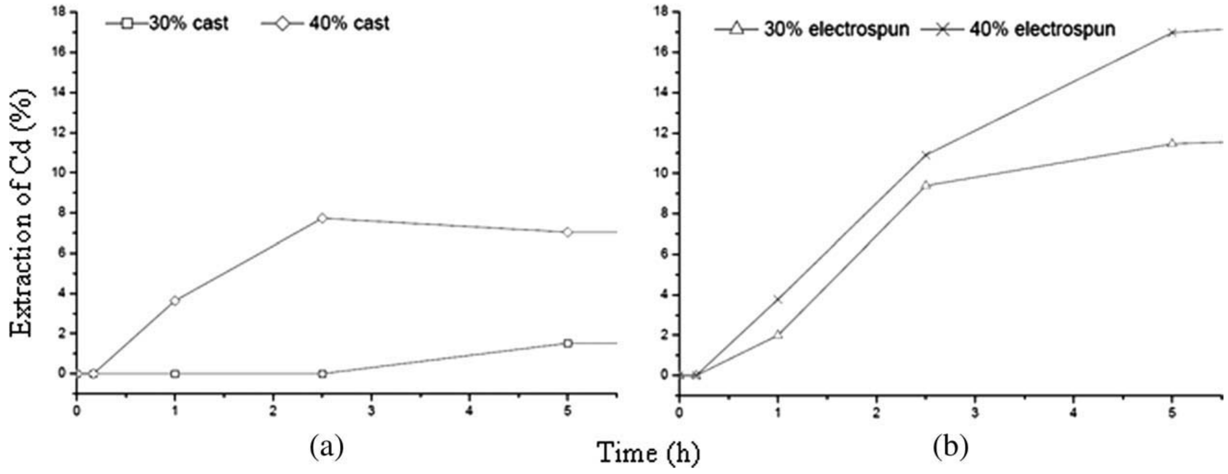

Figure 10 Extraction % rates of cast (a) and electrospun (b) membranes with 30 and 40% Aliquat.

TABLE I
Summary of Experimental Results

Membranes	Aliquat 336 content (%)	BET surface area (m^2/g)	Average membrane thickness (mm)	Mass of membrane used (g)	Total extraction of Cd after 40 h (%)	Maximum sorption capacity (mg/g)
Cast	0	1.70	0.13	0.21	1.69	0.36
	30	3.35	0.10	0.18	2.16	2.29
	40	5.44	0.06	0.16	9.89	11.9
Electrospun	0	4.67	0.29	0.16	8.55	10.1
	30	7.29	0.30	0.17	24.0	26.6
	40	11.3	0.29	0.16	30.7	35.6

from knowing the starting volume and initial and final Cd concentration and the mass of the membrane used, as shown in eq. (2):

$$\mathrm{EC} = \frac{[[V_i] - [V_f]] \times [V_s]}{M}, \tag{2}$$

where V_i is the initial Cd concentration, mg/L, V_f is the final Cd concentration, mg/L, V_s is the starting feed volume, L, M is the mass of membrane, g, and EC is the extraction capacity (mg/g).

The cast membrane at 40% Aliquat content achieved an extraction capacity of 11.9 mg/g, compared to 0.4 mg/g at 0% Aliquat. By comparison, the electrospun membranes with 40 and 0% Aliquat content achieved extraction capacities of 35.6 and 10.0 mg/g, respectively. The increased extraction capacities at higher Aliquat content may be due to the increase in surface area as a result of the production of smaller diameter fibers and increase Aliquat content.

While Ryu et al.[6] attained BET surface areas of 9–51 m^2/g for electrospun membranes made from nylon fibers, the surface areas achieved in our study were much lower than anticipated at 4.67–11.3 m^2/g for electrospun membranes and 1.70–5.44 m^2/g for film-cast membranes (Table I). These low surface areas may have been due to the use of PVC. Successive PVC additions increased viscosity of the liquid resulting to increased viscoelastic force and therefore increased fiber diameters.

Smaller surface areas may also be a result of the membrane thickness. The porosity of a membrane will decrease as membrane thickness increases due to blockage of pores. It also appears that a slight increase in surface area was achieved with higher Aliquat loadings. This is supported by the SEM observations of web-like structures in membranes incorporating Aliquat (Fig. 7).

Figure 11 shows the Cd extraction capacity versus BET surface area results for the cast and electrospun membranes. These demonstrate that the electrospun membranes performed considerably better due to their slight increase in surface area.

CONCLUSIONS

Both cast and electrospun membranes composed of 18% PVC in 40 : 60 DMF/THF and incorporating 0–40% Aliquat 336 was studied. Optimized conditions for the preparation of the electrospun membranes were found to be at an applied voltage of

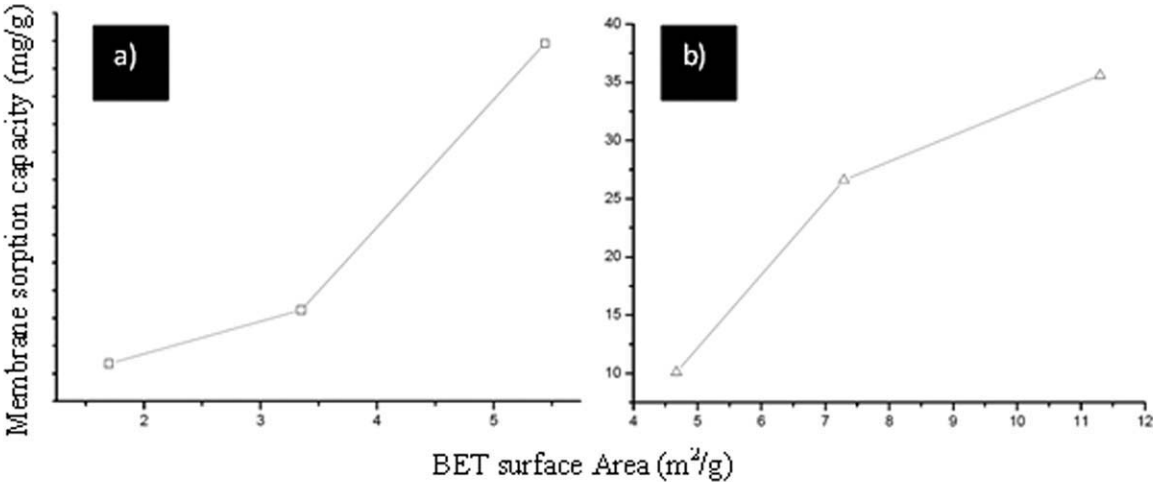

Figure 11 Cd extraction capacity versus BET surface area of cast (a) and electrospun (b) membranes.

25 kV at a rate of 200 μL/h for 8 h and at a syringe tip-to-collector working distance of 10 cm.

SEM (Fig. 7) observations of changes to the interior structure of electrospun membranes revealed that those with an Aliquat content of 10% or more contained web-like structures composed of nanofibers with diameters of less than 30 nm. The occurrence of these web-like structures increased with increasing Aliquat content. This could explain the higher BET surface areas of the electrospun membranes incorporating 40% Aliquat, which also achieved a maximum extraction capacity of 35.6 mg Cd/g, compared to 11.9 mg Cd/g for film-cast membranes with the same Aliquat content.

This study has demonstrated that electrospun PVC membranes incorporating Aliquat 336 exhibit significant improvements in both Cd(II) extraction rate and capacity compared to conventional film-cast membranes. They represent an attractive alternative for use in the extraction of trace metals in wastewaters.

Further work is underway to investigate the stability and robustness of these membranes and the possibilities of utilizing them for different (environmental/wastewater) samples. It is also intended that further study will be done to understand the reversibility of the process to recover fibers for reuse.

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References

1. Xu, J.; Shen, W.; Paimin, R.; Wang, X. Fibers Polym 2004, 5, 68.
2. Scott, K.; Hughes, R.; Eds. Industrial Membrane Separation Technology; Blackie Academic & Professional: London, 1996.
3. Jonsson, J. A.; Mathiasson, L. Trends Anal Chem 1992, 11, 106.
4. Ritcey, G. M.; Ashbrook, A. W. In Solvent Extraction; Sekine, T.; Kusakabe, S.; Eds.; Elsevier Science, Amsterdam, 1990; Vol. 1, p 37.
5. Nisbet, D. R.; Rodda, A. E.; Finkelstein, D. I.; Horne, M. K.; Forsythe, J. S.; Shen, W. Colloids Surf B Biointerfaces 2009, 71, 1.
6. Ryu, Y. J.; Kim, H. K.; Lee, K. H.; Park, H. C.; Lee, D. R. Eur Polym J 2003, 39, 1883.
7. Wang, L.; Paimin, R.; Cattrall, R. W; Shen, W.; Kolev, S. D. J Memb Sci 2000, 176, 105.
8. Heikkila, P.; Harlin, A. Eur Polym J 2008, 44, 3067.