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Fabrication and characterization of electrospun PVDF-aliquat 336 fibre membrane for removal of cadmium from hydrochloric acid solutions

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Abstract The use of polyvinylidene fluoride (PVDF) electrospun fibre membrane incorporating aliquat 336 for the removal of cadmium from hydrochloric acid solutions was investigated. Scanning electron microscopy (SEM) was used to determined fibre diameter and to observe the fibre morphology. Energy dispersive spectroscopy (EDS) analysis was carried out to follow the fate of the aliquat 336 in the fibre membrane formed via electrospinning process and to detect the presence of cadmium in fibre membrane after it has acted as an ion exchange media. The amount of cadmium removed by the fibre membranes was determined by flame atomic absorption spectroscopy. The maximum capacity of the PVDF-aliquat 336 electrospun fibre membranes was determined to be 0.46 mg/g.

Introduction

Cadmium is a toxic metal. Humans are exposed to it primarily via inhalation of cadmium-containing dust and orally via food and water [1, 2]. It is a known human carcinogen. In the environment, it is a pollutant causing toxic effects in living organisms in aquatic ecosystems. It enters the water system through industrial discharge; hence, its removal from aqueous systems has attracted considerable attention [3–12].

There are several conventional methods available for the removal of cadmium from water including precipitation, flocculation, ion exchange, and liquid membrane filtration. To date, the most popular method involved liquid membrane systems [3–5, 9–11].

Aliquat 336® is a water insoluble quaternary ammonium salt composed of a large organic cation associated with a chloride as shown in Fig. 1. It is a mixture of C_8 (octyl) and C_{10} (capryl) chains with C_8 predominating. One of the main uses of aliquat 336 is as a phase transfer catalyst in the catalytic oxidation of cyclohexene to 1,6-hexanedioic acid. It is also used extensively as a metal extraction agent [5, 10, 13].

Electrospinning is a technique used to produce fibres measuring in the nano- to micro-metre diameter range. A typical electrospinning apparatus is schematically shown in Fig. 2. In the presence of a strong electric field, an electrostatic charge is introduced to the stream of polymer solution. The electrically charged jet of polymer solution accelerates and thins out in the electric field, usually evaporating any solvent before reaching the grounded collector plate [14]. In this case, the collector is a rotating drum. This results in the formation of a fine non-woven membrane consisting of an interconnected web or membrane of very fine fibres. These electrospun membranes have a large specific surface area, very small pore sizes and therefore have potential for use as a filter media.

Wang et al. [10] have reported the use of aliquat 336/PVC film cast membrane for the extraction of cadmium and copper from hydrochloric acid solutions. They proposed that the mechanism by which the aliquat 336/PVC membrane worked is that it combines metal–ion complex through forming a 1:1 complex with negatively charged trichlorocadmate ions as shown in Fig. 3.

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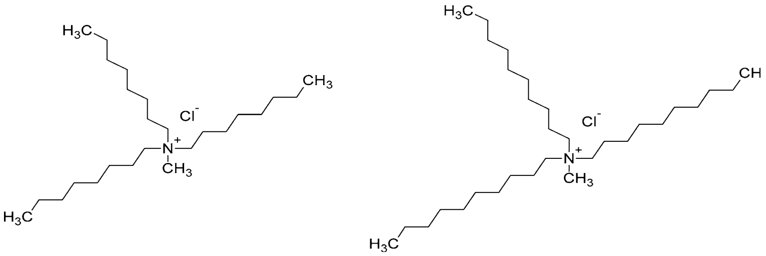


Fig. 1 Aliquat® 336 (left showing R groups as C_8 and right showing R-group as C_{10})

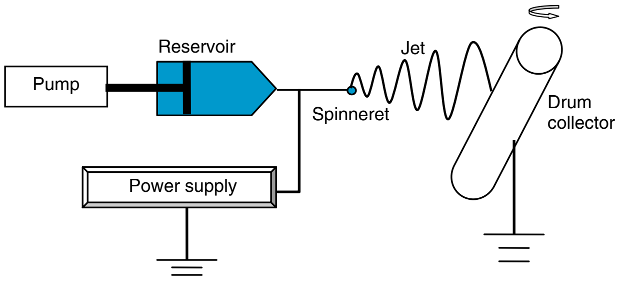


Fig. 2 Schematic representation of electrospinning process

$$\text{AliquatCl}_m + [\text{CdCl}_3]^-_a \rightleftharpoons \text{Aliquat}[\text{CdCl}_3]_m + \text{Cl}^-_a$$

Fig. 3 Reaction between Aliquat 336 ion in the membrane (m) and trichlorocadmate in acid (a) solutions

In this study, electrospun fibre membranes made from polyvinylidene fluoride (PVDF), a fluorinated thermoplastic copolymer and incorporating aliquat 336® were fabricated for cadmium extraction from 2 M HCl acid solutions. This study will report on the fabrication and characterization of PVDF and PVDF-aliquat 336 electrospun nanofibre membranes. The electrospun PVDF polymer fibre will serve as carrier for the aliquat 336 metal extraction reagent. The PVDF-aliquat 336 electrospun fibre membranes were then evaluated for their potential to remove cadmium from hydrochloric solutions.

Materials and methods

Reagent

Aliquat® 336 (Aldrich), a mixture of quaternary ammonium chlorides with trace amounts of octanol and decanol, was used as received. Polyvinylidineflouride copolymer (Arkema Group Kynar Flex® 2800-20) was used as received. The level aliquat® 336 was 30% w/w based on the weight of PVDF.

The solvent was dimethylacetamide and acetone (HPLC grade) mixed at 2:1 ratio.

Cadmium chloride AR (BDH) was dissolved in 2 M hydrochloric acid AR solution to achieve 3.0 ppm Cd solution.

A cellulosic membrane material type SM66 from Sartorius with an outer diameter of 13 mm was used as a control to the electrospun fibre membranes.

Electrospun membrane preparation

Electrospun membranes with and without aliquat® 336 were prepared by electrospinning a 20% PVDF solution. Electrospinning apparatus was constructed from a syringe pump (model NE-1000 from New Era Pump Systems, Inc.), a high voltage supply (Spellman high voltage DC power supply) and a 3 mL syringe (Terumo®) attached with 23G diameter needle. The spinneret was 20 cm from the 2.54 cm outer diameter drum collector with an applied voltage of 20 kV. A membrane was collected for 3 h at pump rate of 0.2 mL/h. The drum collector was driven by a 12 V motor controlled by a Digimess® [HY3003-3] concept series DC power supply. The drum collector speed was kept at 1.0 m/s.

Membrane characterization

The electrospun membranes were iridium coated and imaged at 2 kV. Scanning electron microscopy (SEM) analysis of electrospun membranes were carried out using a Philips XL30 Field Emission Scanning Electron Microscope (FESEM). The average fibre diameter was measured from the SEM imaging. The thickness of the membranes were measured by mounting a membrane section onto a microscope slide and using carbon tape as an adhesive on part of the membrane and placing the microscope slide under liquid nitrogen to freeze the sample before removing it and sectioning with a sharp microtome blade.

Energy dispersive spectroscopy (EDS) was performed on the membranes to confirm the presence of aliquat 336 and cadmium at 15 kV with a magnification of 5000×. EDS samples were carbon coated (approximately 24 nm) before measurement.

Membrane ion exchange capacity (IEC)

The ion exchange capacity of the electrospun membrane containing 30% aliquat 336 was determined by the same procedure described by Hwang et al. [15] but with lower acid and base concentration due to smaller sample size. Both hydrochloric acid and sodium hydroxide used was 0.005 M instead of 0.01 M. Titrations were carried out using phenolphthalein end-point.

Membrane assessment

The membrane assessment was carried out on a small scale using a circular membrane with a diameter of 13 mm.

The method utilized 13 mm re-usable syringe filter holders [Sartorius] to pass 10 mL of 3.0 ppm Cd solution, a designated number of times, through the membrane before to collecting the permeate for FAA analysis. A new plastic 10 mL syringe was used for each pass.

Determination of Cd by flame atomic absorption

Analysis of permeate collected was carried out using FAA at a wavelength of 228.8 nm and a slit width of 0.5 nm. An oxidizing flame with air: acetylene was used. The Cd calibration standards used were 0.30 ppm, 0.50 ppm, 1.00 ppm, 2.00 ppm and 3.00 ppm in 2 M HCl solutions.

Results and discussion

PVDF electrospun membranes with and without 30% w/w aliquat 336 were successfully produced under the same electrospinning conditions. The level of aliquat 336 was chosen based on Wang et al. [10] study involving film cast membrane. Wang et al. [10] have also described the mechanism of Cd extraction from hydrochloric solution using aliquat 336.

SEM images of the PVDF control membranes with and without aliquat 336 are shown in Fig. 4. The average fibre diameter from 10 measurements for the PVDF fibre membrane was 554 ± 7 nm compared to 418 ± 33 nm for the PVDF-aliquat 336 fibre membrane. It can be seen that the nanofibres in the PVDF control membrane are more uniform when compared to the PVDF-aliquat 336 membranes. In the PVDF-aliquat 336 membranes there are some very fine fibres (<100 nm) that are not present in the PVDF control.

The average thickness of the electrospun membranes (collected for 3 h) was measured using an image section of the membrane as shown in Fig. 5. The average thicknesses of the PVDF control and PVDF-aliquat 336 fibre membrane from 10 measurements was found to be approximately the same at 165 ± 5 µm and 160 ± 5 µm, respectively.

EDS peak count ratios and spectra for the membranes are summarized in Table 1, Fig. 6. The spectra show the presence of carbon and fluoride in both cases as expected from the PVDF, but for the PVDF aliquat 336 membranes, there is also an additional clear peak corresponding to the chloride associated with the presence of aliquat. There is significant reduction in the peak count of the fluoride peak due to the addition of the aliquat 336; this reduction could be depend on the aliquat 336 orientates itself on the fibre surface and will be a topic of a different study.

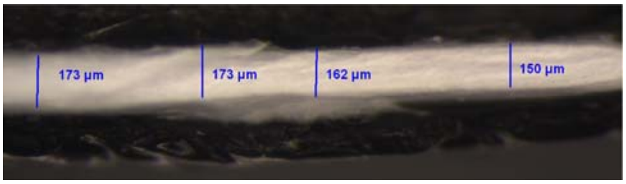


Fig. 5 Light Microscope image of cross section of membrane

Table 1 Peak count ratio of PVDF control and PVDF-aliquat 336 membrane as produced as measured by EDS

Element Label	Range (keV)	PVDF control membrane % total	PVDF-aliquat 336 membrane % total
C	0.188–0.368	100.0	93.2
Cl	2.507–2.747	0.0	6.8
Cd	3.007–3.267	0.0	0.0

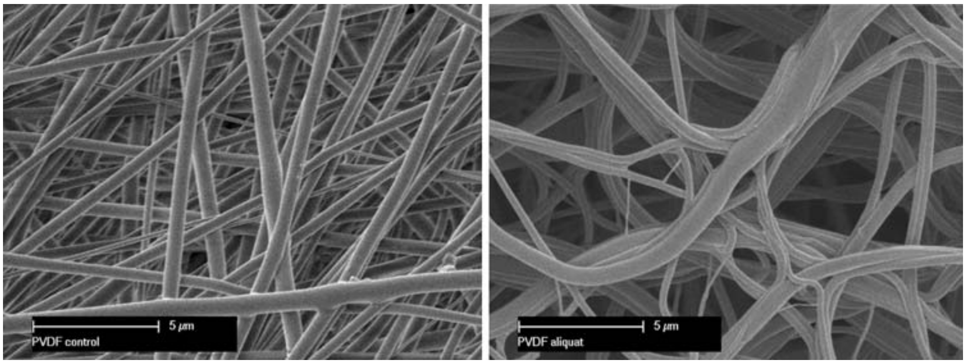
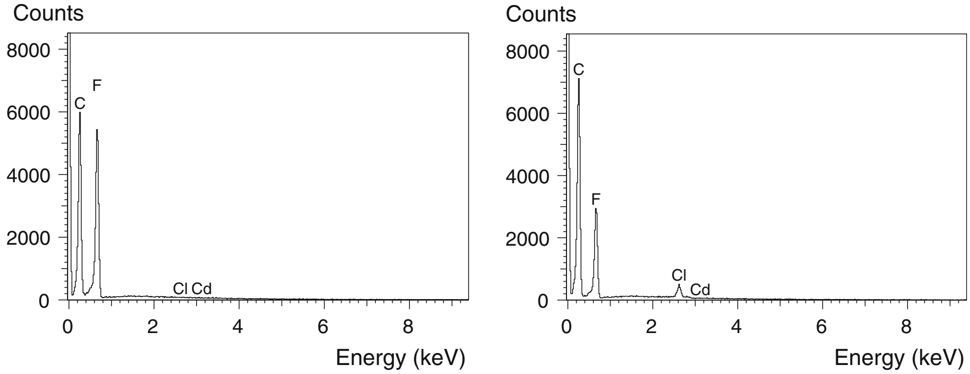


Fig. 4 SEM images of PVDF membrane without and with 30% aliquat 336

Fig. 6 EDS spectra of PVDF control (*left*) and PVDF-aliquat 336 membranes (*right*)



A feed concentration of 3.0 mg/L Cd (3.0 ppm) was chosen for this study after taking into consideration that the Australian drinking water guideline value is 0.0002 mg/L [16].

From Table 2, it can be seen that on the first pass through the membranes, there is a slight reduction in cadmium level found in permeate for all the three membranes (1a, 1b and 1c). However, when the feed was passed through between 5 and 10 times, there was a significant increase in Cd removal for PVDF-aliquat 336 fibre membrane compared with both the controls. Maximum removal was reached with 10 passes through the membrane reaching 93% removal of Cd from the solution. It can also be seen that in the absence of aliquat 336, i.e. PVDF control membrane, increasing the number of passes shows no improvement on Cd removal—removal remains at 4%.

The result in this small scale experiment gave a much higher extraction efficiency compared with those reported by Wang et al. [10] where the maximum amount of Cd extracted was under 60% for a PVC film cast loaded with 50% aliquat.

Figure 7 shows Cd sorption capacity (mg/g) against the number of passes through the membrane. The sorption capacity is calculated from the starting feed volume and initial and final Cd concentration. In this study, the maximum sorption capacity was reached at 10 passes through the syringe filter. The value obtained of 0.46 mg/g is comparable with results obtained by Hota et al. [4] who reported a value of 0.48 mg/g employing a batch method using boehmite nanoparticle-impregnated electrospun fibre membrane.

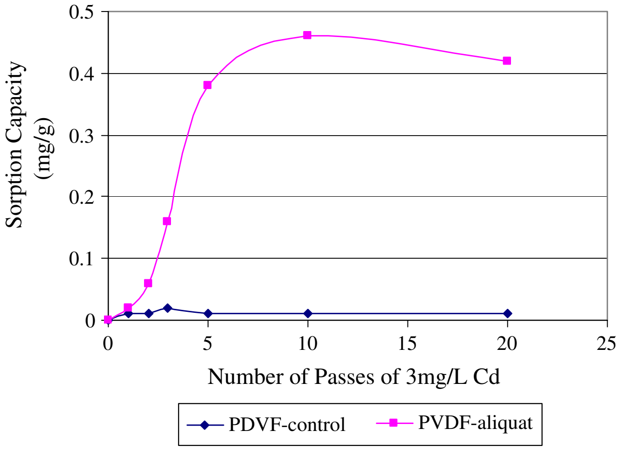


Fig. 7 Sorption of Cd (ii) from hydrochloric solution

Table 2 Evaluation of PVDF membrane as syringe filters

ID	Membrane type	Number of time the 3 ppm Cd solution was passed through the membrane	Membrane weight (circular membrane of 13 mm in diameter) (mg)	Concentration found in permeate (ppm)	% of Cd removed
1a	Sartorius (sm66) cellulose control	1	78	2.9	4
1b	PVDF control	1	79	2.9	4
1c	PVDF-aliquat	1	73	2.8	5
2a	Satorius(sm66) cellulose control	5	58	2.9	4
2b	PVDF control	5	71	2.9	4
2c	PVDF-aliquat 336	5	63	0.3	89
3a	Satorius (sm66) cellulose control	10	77	2.9	4
3b	PVDF control	10	74	2.9	4
3c	PVDF-aliquat	10	61	0.2	93

The IEC of the PVDF-aliquat 336 membrane was determined to be 0.50 ± 0.05 mmol/g. If all the sites were available, then we would have a maximum sorption of 57 mg Cd/g of membrane. However, this value is smaller than the calculated value of 83 mg Cd/g based on the mass of aliquat 336 added. Therefore, only approximately 69% of added aliquat 336 present is accessible for exchange with the hydroxide ion. We obtained a maximum value of 0.46 mg/g which is an order of magnitude lower than that determined by IEC.

EDS analysis was carried out on the used membranes to confirm that cadmium had been adsorbed onto the membrane and spectra are shown in Fig. 8.

EDS is not an analytical method and was employed in this study as a semi-quantitative assessment of the used membranes. All the PVDF control membranes show the absence of both aliquat 336 (Cl) and Cd as shown in Fig. 8 indicating that there was no physical removal of the cadmium. In the PVDF-aliquat 336 membrane spectra, there was an increasing trend in Cd peak count as the number of passes through the membrane was increased. EDS analysis of the used membranes have confirmed that the PVDF-aliquat 336 membranes have successfully captured the cadmium. Secondly, the presence of chloride in the PVDF-aliquat 336 but not in the PVDF control shows that aliquat 336 has survived the both electrospinning process and passing of Cd solution through the small-scale syringe extraction process.

According to the mechanism proposed by Wang et al. [10], assuming all 30% aliquat 336 incorporated is accessible to the trichlorocadmate ions to complex with, then the maximum sorption capacity should be 83 mg/g. However the maximum sorption capacity of the PVDF-aliquat 336 electrospun fibre membranes was determined to be

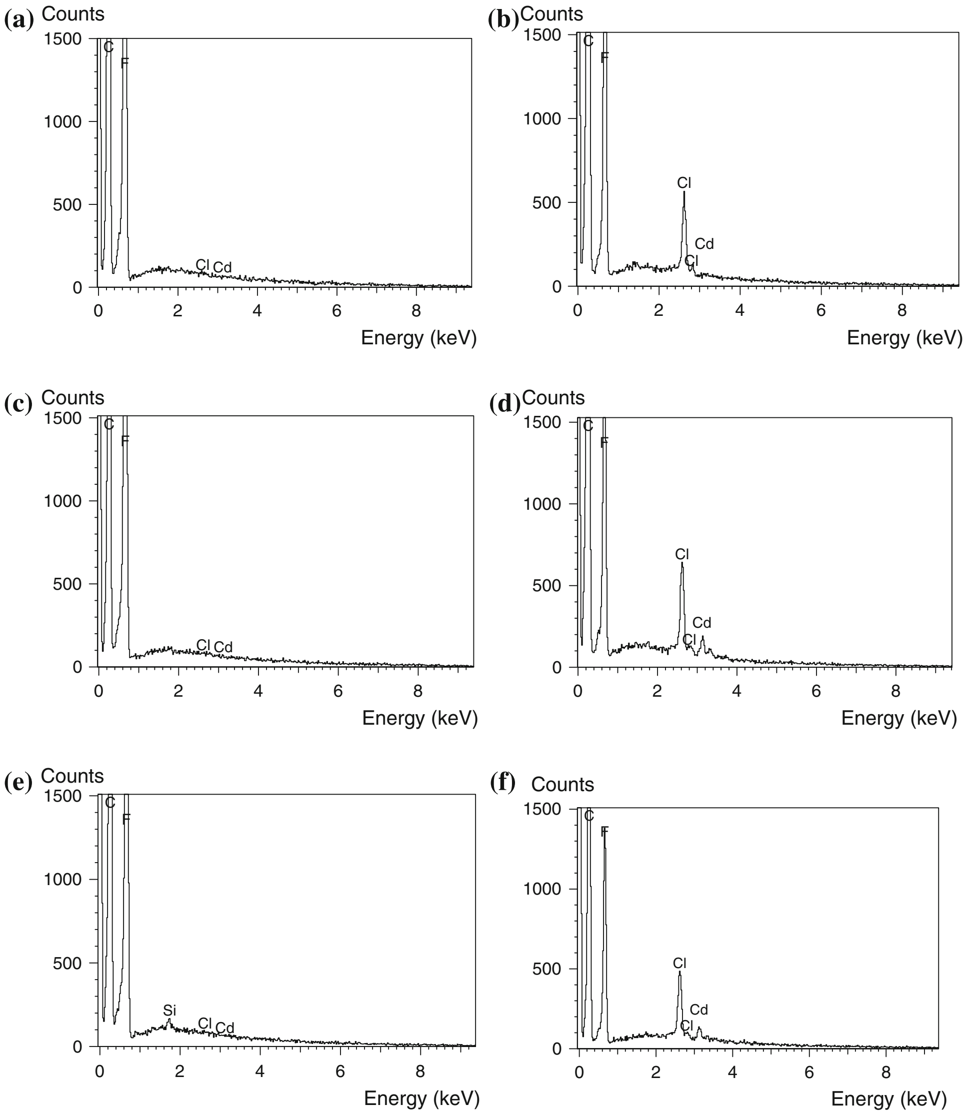


Fig. 8 EDS spectra of membranes after one, five and ten passes of 3 ppm Cd. **a** One pass PVDF control, **b** One PVDF-aliquat, **c** Five passes PVDF control, **d** Five passes PVDF-aliquat, **e** Ten passes PVDF control, **f** Ten passes PVDF-aliquat

0.46 mg/g. There are several possible reasons for this discrepancy between the determined and the calculated sorption value. A possibility could be that all aliquat 336 incorporated into the PVDF electrospun membrane was not on the surface but were buried beneath the nanofibres and cannot participate in the complex forming reaction. Other possible reasons could be attributed to the kinetics of the reaction and also that aliquat 336 may be less reactive with the polymer compared to when it is in a solvent environment. Further study is being carried out to gain a better understanding on how these electrospun PVDF-aliquat 336 fibre membranes works, including selectivity and ease of implementing them into a continuous process, such as electrodeionization [17].

Conclusions

This preliminary study shows that the commercial extraction reagent aliquat 336 (30% w/w) has been successfully added to PVDF in solvent to produce PVDF-aliquat 336 electrospun fibre membranes. Initial study has shown that these fibre membranes can be used for the removal of cadmium from hydrochloric acid. Further study is underway to investigate the robustness of these membranes and the possibilities of utilizing them for different (environmental/wastewater) samples.

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