Removal of cadmium using electrospun nanofibers

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Abstract. The present study reports on the capability of CTA/ Aliquat 336 electrospun fibers in extracting Cd(II) from aqueous phase. The CTA/Aliquat 336 electrospun fibers were produced by electrospun a polymer solution containing CTA and Aliquat 336 in DMC and methanol with a ratio of 8:2 respectively. The effect of different Aliquat 336 concentration on the performance of Cd(II) removal was examined. Extraction experiment was conducted in a batch mode using 5 ppm of Cd(II) in 1 M HCl solution. Results showed that the extraction of Cd(II) increased as Aliquat 336 concentration increased. Morphology structure of the CTA/ Aliquat 336 electrospun fibers were also carried out using scanning electron microscopy (SEM).

Keywords: electrospun fibers, metal ion extraction, electrospinning method, Aliquat 336.

1. Introduction

Heavy metals remain in environment because they are non-biodegradable. Zinc, cadmium and iron are usually used in battery manufacturing (1) and pigment use in paint (2). However, cadmium is one the most toxic heavy metal which can cause kidney damage, renal disorder and also a human carcinogen (3). Conventionally, there are many treatments used for heavy metals removal including membrane filtration (4), adsorbent (5) and solvent-solvent extraction.

Polymer inclusion membranes (PIMS) has received a lot of attention in metal ions extraction due to high stability compared to other liquid membrane processes and more environmental friendly compared to solvent extraction method (6). Basically, PIMs is made from polymer, carrier and/or plasticizer. The polymer is a base layer which provides mechanical strength to PIMs while carrier is acting like a guest specific host which control the selectivity of components that can pass through the film. On the other hand, plasticizer can improves compatibility between polymer and carrier and also enhances flexibility of the membrane. Aliquat 336 is one of the most used carriers in PIMS. Many studies have reported on the successful of metal ions removal using PIMs incorporated with Aliquat 336 (7, 8, 9). However, the amount of Aliquat 336 in PIMS need to reach certain threshold in order to extract metal ions. For example, (10) stated that extraction of metallic ions only occurred when the proportion of Aliquat 336 in PIMS is 30 wt.% or higher. The critical Aliquat 336 content in PIMS was also confirmed by other researcher (11, 12).

Electrospinning method has become popular in producing nanofibers with simple, effective and versatile. This technique is known since 1930’s for the interest in application of nanotechnology and biotechnology. In recent years, electrospun fibers have successfully developed for metal ions applications (10, 13, 14). This is due to the higher surface area and less amount of carrier used compare to PIMs. Similar to the polymer solution used in PIMs, the solution is electrospun using electrospinning equipment which consists of high voltage supplier, metal collector and syringe pump. Due to high voltage, the polymer solution was ejected from the syringe needle onto a metal collector producing fibrous mat which can be collected after few hours. (10) reported that the extraction of Cd(II) has improved from 74 % to 98 % of Cd(II) removal when used PVC/Aliquat 336 PIMs containing 40 wt.% of carrier and PVC/Aliquat 336 electrospun fibers containing 25 wt.
of carrier respectively. (15) Was also reported on the improvement of Cd(II) removal when used PVC electrosyn fibers compared to PVC PIM.

In this study, electrospun fibers made of cellulose triacetate (CTA) incorporated with Aliquat 336 as a carrier was produced. The electrospun fibers were produced at different Aliquat 336 concentration in order to investigate the extraction rate of Cd(II) ions. This study provides insight for further development in CTA/Aliquat 336 electrospun fibers in extracting metal ions.

2. Experimental

2.1 Preparation of polymer solution

For this study, CTA and Aliquat 336 solutions were prepared with different Aliquat 336 concentrations (0, 2, 4, and 6 wt%). A total mixture of CTA and Aliquat 336 of 600 mg was dissolved in methanol and dichloromethane in a ratio of 8:2 respectively. The solution was stir vigorously until homogenous. Then, the solution was transferred into media bottle and left until all bubble are removed.

2.2 Preparation of CTA/Aliquat 336 electrospun fibers

CTA/ Aliquat 336 electrospun fibers was prepared by electrospinning method. The polymer solution was placed into a 5 mL plastic syringe that attached with 23-gauge needle tip. The polymer solution was electrospun at 20 kV with 1 mL/h of flow rate for 8 hours. The distance between syringe tip and aluminium collector was 140 mm. Later, the CTA/Aliquat 336 electrospun fibers was collected from the aluminium collector and used in Cd(II) ions extraction.

2.3 Cadmium extraction protocol for CTA / Aliquat 336 electrospun fibers

The extraction study was conducted in batch mode. The CTA/ Aliquat 336 electrospun fibers weighing of 0.05 ± 0.01 g was cut into smaller pieces and placed in a beaker containing 250 mL extraction solution. The extraction solution contained a 5 ppm of Cd(II) in 1 M of hydrochloric acid (HCl). The extraction solution was stirred during the experiment and sample of aliquots was taken at 0, 5, 30, 60, 180, 300 and 1440 minutes for Cd(II) analysis using atomic absorption spectroscopy (AAS). Then, the sample was diluted according to dilution protocol prior AAS analysis. The extraction rate of Cd(II) was calculate by using below equation:

\[
\text{Extraction efficiency, (\%)} = \frac{C_i - C_o}{C_o} \times 100\%
\]  

(A.1)

\( C_i \) = initial concentration

\( C_o \) = final concentration

2.4 Morphology surface analysis

The surface morphology of electrospun fibers at different Aliquat 336 concentration was observed by using scanning electron microscopy (SEM) (JSM-IT100, Jeol USA). Square sections of samples approximately 10 mm by 10 mm were mounted on aluminium stubs. The power used is 10 kV with magnification of times 10, 50 and 100.

3. Results and discussion

3.1 Extraction of cadmium by CTA/ Aliquat 336 electrospun fibers
The removal of Cd(II) ions in 1 M HCl by CTA/ Aliquat 336 electrospun fibers at different Aliquat 336 concentration (0, 2, 4 and 6wt%) was showed in Figure 1. The extraction rate increased with increasing of Aliquat 336 content. At the highest Aliquat 336 content (6wt%) the Cd(II) removal was 84 % removed. This result showed that the CTA/Aliquat 336 electrospun fibers has a capability to remove Cd(II) ions at lower Aliquat 336 content compared to PIMs using similar carrier. However, CTA electrospun fibers without Aliquat 336 content show insignificant removal of Cd(II) ions.

The transport of Cd(II) ions is based on the ion exchange mechanism which involve the formation of carrier-complex in the aqueous solution. In a chloride solutions, different chloro complexes can be formed depending on metal and chloride concentration. According to (16), trichloro complex is a predominant species form when the chloride concentration is above 0.1 M HCl. Thus, the extraction of Cd(II) can be described as:

\[
CdCl_3^- + CH_3(CH_2)_2N^+Cl^- \leftrightarrow CH_3(CH_2)_2N^+CdCl_3^- + Cl^-
\]

Figure 1: The extraction of Cd(II) against Aliquat 336 content in CTA/Aliquat 336 electrospun fibers.

3.2 Membrane surface morphology
Figure 2, 3, and 4 show the surface morphology of CTA/Aliquat 336 electrospun fibers at Aliquat 336 content of 0, 4 and 6 wt% respectively. A fibrous web like structure could be seen in all samples showing that electrospinning method has successfully produced fibrous mats. The surface morphology of CTA electrospun fibers without Aliquat 336 content revealed a compact and uniform structure of fibers (Figure 2). As Aliquat 336 content increased to 4wt% the diameter of fibers decreased from 1.60 µm (without Aliquat 336) to 0.30 µm (Figure 3). It can be seen that as Aliquat 336 content further increased to 6wt% the fibers diameter increased to 1.06 µm (Figure 4). Besides, the number and size of beads also increased with the increasing of Aliquat 336 concentration. The formation of beads is probably due to either instability in parameter during electrospinning process or during the increasing in concentration of Aliquat 336 (17). However, the structure of nanofibers become dense as the concentration of Aliquat 336 increased.

Figure 2: electrospun fiber of 0wt% under x200 and x1000 magnification

Figure 3: electrospun fiber of 4wt% under x200 and x1000 magnification
4. Conclusion

The CTA/ Aliquat 336 electrospun fibers have been produced in order to removed Cd(II) ions from aqueous solution. The extraction rate of Cd(II) was significantly change after the addition of Aliquat 336. From the result, the CTA/ Aliquat 336 electrospun fibers containing 6 wt% of Aliquat 336 showed the highest removal of Cd(II) ions. It is expected that the percentage removal will increase to more than 90 % if the Aliquat 336 content is further increased. Further work is underway to investigate the optimum of Aliquat 336 concentration, voltage, flow rate and distance from tip distance to metal collector on the performance of CTA/ Aliquat 336 electrospun fibers in extracting different type of metallic ions.

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5. References

1. Mohamed M, Abdul Aziz MS, Abdullah MZ, Ahmed A, Abdul Razab MKA, Khor CY. Experimental Method on Solder Joint of Ball Grid Array Using Reflow Oven. Int J Curr Sci Eng Technol. 2018;487–92.

2. Zulkefeli NSW, Ismail WMIW, Razab MKAA, Masri MN. Effect of Cathode Waste Material Concentration in Conductive Paint Coating. J Trop Resour Sustain Sci. 2016;4(December):78–81.

3. Barakat MA. New trends in removing heavy metals from industrial wastewater. Arab J Chem. 2011;4(4):361–77.
4. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. J Environ Manage. 2011;92(3):407–18.

5. Zhao X, Liu C. Efficient removal of heavy metal ions based on the optimized dissolution-diffusion-flow forward osmosis process. Chem Eng J. 2018;334(November 2017):1128–34.

6. Shahira N, Zulkefeli W, Weng SK, Syazana N, Halim A. Removal of Heavy Metals by Polymer Inclusion Membranes. 2018;

7. Wong CY, Wong WY, Loh KS, Mohamad AB. Study of the plasticising effect on polymer and its development in fuel cell application. Renew Sustain Energy Rev. 2017;79(September 2016):794–805.

8. Manzak A, Yıldız Y, Tutkun O. Characterization of polymer inclusion membrane containing Aliquat 336 as a carrier. Membr Water Treat [Internet]. 2015;6(2):95–102.

9. Vázquez MI, Romero V, Fontàs C, Anticó E, Benavente J. Polymer inclusion membranes (PIMs) with the ionic liquid (IL) Aliquat 336 as extractant: Effect of base polymer and IL concentration on their physical-chemical and elastic characteristics. J Memb Sci. 2014;

10. Abdul-Halim NS, Whitten PG, Nghiem LD. Characteristics and cadmium extraction performance of PVC/Aliquat 336 electrospun fibres in comparison with polymer inclusion membranes. Sep Sci Technol. 2016;6395(April):1–8.

11. Wang L, Paimin R, Cattrall RW, Shen W, Kolev SD. The extraction of cadmium (II) and copper (II) from hydrochloric acid solutions using an Aliquat 336/PVC membrane. 2000;176:105–11.

12. Xu J, Wang L, Shen W, Paimin R, Wang X. The Influence of the Interior Structure of Aliquat 336/PVC Membranes to their Extraction Behavior. 2010.
13. Huang Y, Miao YE, Liu T. Electrospun fibrous membranes for efficient heavy metal removal. J Appl Polym Sci. 2014;131(19):1–12.

14. Aliabadi M, Irani M, Ismaeili J, Piri H, Parnian MJ. Electrospun nanofiber membrane of PEO/Chitosan for the adsorption of nickel, cadmium, lead and copper ions from aqueous solution. Chem Eng J. 2013;220:237–43.

15. Wong L, Shen W, Truong YB. Investigation of Electrospun and Film-Cast PVC Membranes Incorporated with Aliquat 336 for Efficient Cd Extraction: A Comparative Study. 2011;336.

16. He D, Liu X, Ma M. Transfer of Cd(II) chloride species by a tri-n-octylamine-secondary octyl alcohol-kerosene multimembrane hybrid system. Solvent Extr Ion Exch. 2004;22(3):491–510.

17. Bhardwaj N, Kundu SC. Electrospinning: A fascinating fiber fabrication technique. Biotechnol Adv. 2010;28(3):325–47.