

Improved Membranes for the Extraction of Heavy Metals

Jianying Xu, Wei Shen¹, Rohani Paimin², and Xungai Wang*

School of Engineering and Technology, Deakin University, Geelong, Victoria 3217, Australia

¹*Department of chemical Engineering, Monash University, Clayton, Victoria 3168, Australia*

²*Chemical Sciences, School of Molecular Sciences, Victoria University of Technology,*

P.O. Box 14428, MCMC, Melbourne, Victoria 8001, Australia

(Received October 8, 2003; Revised December 2, 2003; Accepted December 9, 2003)

Abstract: This work presents a series of experimental tests on new practical approaches in membrane design to improve extraction capacity and rate. We chose an extraction system involving Aliquat 336 as the extractant and Cd(II) as the metal ion to be extracted to demonstrate these new approaches. The core element in the new membrane assembly was the extractant loaded sintered glass filter. This membrane assembly provided a large interface area between the extractant and the aqueous solution containing metal ions. By recycling the aqueous solution through the membrane assembly, the extraction rate was significantly improved. The membrane assembly also offered good extraction capacity.

Keywords: Membranes, Extraction, Heavy metals, Aliquat 336

Introduction

Supported liquid membranes (SLMs) have been extensively studied and used in the extraction of metals, as they offer high transport rates and good selectivity. They are therefore regarded as a viable alternative technique in industrial applications that overcomes many of the major downsides of solvent extraction technology [1-14]. The main drawback of this system, however, is the membrane's limited lifetime (poor stability) due to the loss of extractant during use. Using 'entangled' membrane that comprises of homogeneous mixture of the extractant, plasticizer and poly(vinyl chloride) tends to reduce the loss of extractant from the membrane. Recent studies have revealed that the loss of extractant (Aliquat 336) from a PVC composite membrane to the aqueous phase was insignificant during extraction experiments [15,16]. However, a major disadvantage of polymer composite membranes in general is their extremely low extraction rate [15,16].

The mechanical strength and stability of the above 'entangled' membrane are dependent on the amount of Aliquat 336 that is homogenised into the PVC. The mechanical strength of the membrane is greatly compromised when the content of Aliquat 336 is increased to greater than 50 % [12]. As a consequence, the extraction capacity of this type of membrane is also compromised. In order to overcome the limitation on extraction capacity, larger quantity of extractant needs to be incorporated into the membrane. Work carried out recently in our group using 'encapsulated' membrane has overcome the limitation on extraction limitation and greatly increased the extraction capacity [15]. However, the encapsulated membrane did not raise the membrane extraction rate to a practically feasible level.

Further research is on the way to better understand the

extraction dynamics of a membrane system and to increase the extraction capacity. Some researchers have investigated this by increasing the contact area between the aqueous phase and the membrane by changing the configuration of the extractor [17-20]. Others have looked into the possibility of increasing the porosity of the membrane by incorporating silica micro beads into the membrane [21-23]. These studies have provided further insight into the relationship between the internal structures of the membrane and the extraction dynamics.

Obviously, the activity and the mobility of the extractant molecules on the membrane surface, and the area of phase contact govern the amount of metal being extracted. It has been pointed out by several authors [24-26] that an important characteristic of the membrane in its ability to extract metal is its porosity expressed by the pore size, the distribution of the pores and the effective number of pores in the membrane's upper layer (skin). These characteristics determine the effective contact between an aqueous solution containing the metal and the extractant in the membrane.

In this paper we investigated the factors that affect the extraction rate of metal ions by different types of membrane. We selected Cd(II) in HCl solution as the metal ion system for our study. Practical solutions to increasing the extraction rate via modifying the membrane structure have been carried out and this has been the main theme of this paper. Various attempts, including using sintered glass disc as the supporting matrix for the extractant, have been tested.

Experimental

Reagents and Chemicals

Aliquat 336 (Fluka) was obtained as a mixture of quaternary ammonium chlorides and used as received. High molecular weight (> 90000) poly(vinyl chloride) (Fluka, Selectophore)

*Corresponding author: xwang@deakin.edu.au

was used for membrane preparation. Tetrahydrofuran (THF) was HPLC grade (BDH) and was purified before use by passing through an activated alumina column to remove stabilisers and peroxides. Hydrochloric acid (HCl), cadmium (II) chloride was of analytical grade (BDH). A series of Cd(II) standard solutions was prepared in the solution of 2.0 M HCl, using a stock solution of 1000 $\mu\text{g/l}$ (BDH Spectrosol) for atomic absorption spectroscopic measurements.

Glass beads (SIGMA) used were of the sizes 200-400 mesh and 80-120 mesh, with the pore sizes of 170 Å and 700 Å respectively. These beads had been coated with 44 $\mu\text{mol/g}$ of aminopropyl group and were used as received.

Membrane Preparation

The 'Entangled' Membrane

The membranes used in this study were prepared by dissolving a predetermined mixture of Aliquat 336 and PVC in about 50 ml of THF. The solution obtained was homogeneous, and was then poured into a glass ring on a flat glass plate. The THF was allowed to evaporate slowly over 12 h to yield a colourless, flexible, transparent and mechanically strong membrane. All membranes made in this way contain 40 % Aliquat 336/PVC (w/w%).

The 'Glass Beads' Membrane

Membranes incorporated with glass beads were prepared by mixing Aliquat 336, PVC powder and a predetermined mass of glass beads with 50 ml of THF. This mixture was then poured into a glass ring on a flat glass plate. The THF was allowed to evaporate slowly over 12 h to yield a colourless, flexible, transparent and mechanically strong membrane. All membranes made in this way contain 30 % Aliquat 336/PVC (w/w%) and about 2 % glass beads. Membranes were then removed from the glass plate and used for the extraction study.

The 'Encapsulated' Membrane

The method of making 'encapsulated' membranes mainly involved joining together two 'entangled' membranes of the same type. Detailed preparation of this membrane has been described previously [15]. Two types of 'sandwiched' membranes were prepared. One of the membranes used two 40 % Aliquat 336/PVC (w/w%) 'Entangled' membranes, and the other used the 'Glass beads' membranes described in 2.2.1 and 2.2.2. above.

The 'Sintered Discs' Membrane

The sintered discs were obtained from a glassware supplier (PYREX[®]). The disc diameter was 50 mm and its thickness was 4.5 mm. The disc pore size ranged from 40 to 100 microns. Different amounts of Aliquat 336 were allowed to imbibe into the sintered glass discs by carefully placing the Aliquat 336 on the surface of the sintered glass discs. The

amount of Aliquat 336 adsorbed onto each sintered glass disc was accurately determined. The mass of each sintered glass disc was first measured using the electronic scale. Subsequently, the scale was zeroed, and the appropriate amount of Aliquat 336 was then carefully placed on the surface of the sintered glass disc.

The effective area for the sintered disc and encapsulated membranes is the same (9.62 cm^2).

Thickness of Polymer

A square piece of the membrane (54 mm^2) was mounted vertically on a glass slide and its thickness was measured using an optical microscope (ISSCOSZM-4).

Membrane Extraction

Membrane extraction studies were carried out in a two-compartment cell, at a room temperature of about 25 °C (Figure 1). Each compartment had a volume capacity of 220 ml. The membranes were sandwiched between the two com-

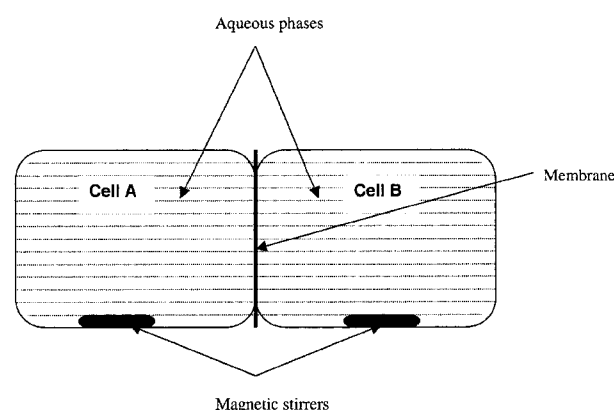


Figure 1. The membrane extraction apparatus.

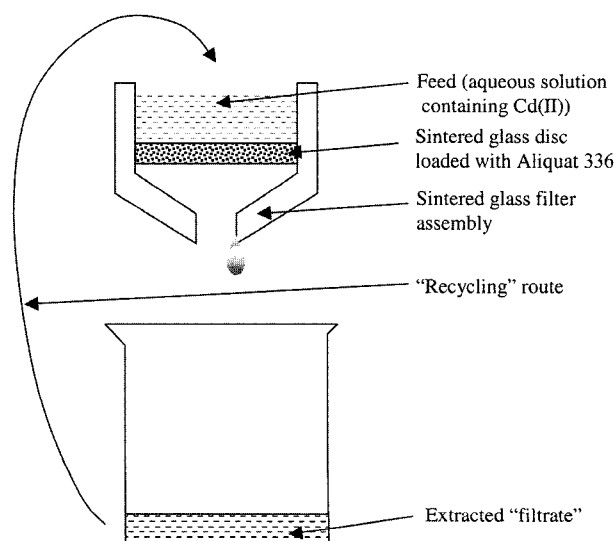


Figure 2. The set-up for the "extraction filtering system".

partments. Stirring of the aqueous solution was provided by the magnetic stirrers. An aqueous solution of Cd(II) of the same composition was placed in both compartments. After a preset extracting time, 1 ml of sample was taken from each chamber of both sides.

The "extraction filtering system" is schematically shown by Figure 2. The Cd(II) concentration analyses were sampled either from the feed (as shown in Figure 10) or from the "extracted filtrate" (as shown in Figures 11 and 12). The concentration of Cd(II) samples taken was analysed by atomic absorption spectroscopy (AAS) (GBC 902 AA spectrophotometer). A calibration curve was established prior to each analysis using a series of Cd(II) standard solutions.

Results and Discussion

Extraction of Cd(II) Using 'Encapsulated' Membrane

Figures 3 and 4 show the extraction results using the encapsulated membranes. The configuration of this type of membrane has been reported elsewhere [15]. The thermodynamic advantage offered by the encapsulated membrane is that the activity of Aliquat 336 capsulated within the membrane is much higher and the quantity of the extractant is larger than those in a composite membrane where the Aliquat 336 molecules are entangled with polymer chains. The former factor strongly influences the rate of extraction and the latter, extraction capacity. Previous studies [27,28] have revealed that extraction capacity of a composite membrane is related to the loading level of Aliquat 336 in the membrane. The mathematical modeling results using real experimental data for Cd(II) extraction suggested that an increase in the Aliquat 336 loading level shifts the extraction equilibrium towards forming $R_3MeN^+CdCl_3^-$ complex [28]. Therefore,

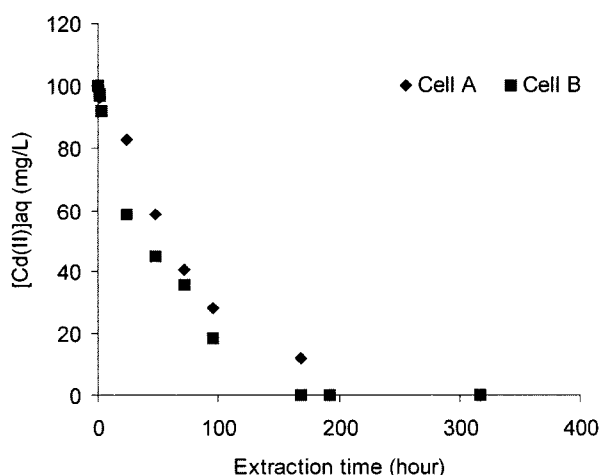


Figure 3. Aqueous Cd(II) concentration vs. extraction time of contact. Initial concentration of Cd(II) was 100 mg/l in 2.0 M HCl. 'Encapsulated' membrane containing 2 g of free Aliquat 336, placed between the two 40 % Aliquat 336/PVC (m/m%) membranes with a thickness of 0.0457 mm, was used.

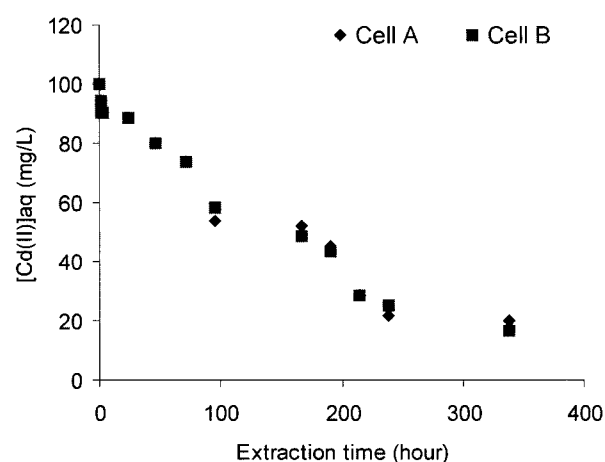


Figure 4. Aqueous Cd(II) concentration vs. time of contact. Initial concentration of Cd(II) was 100 mg/l in 2.0 M HCl. 'Encapsulated' membrane containing 3 g of free Aliquat 336, placed between the two 40% Aliquat 336/PVC (m/m%) membranes with a thickness of 0.0944 mm, was used.

from the reaction equilibrium point of view, a higher Aliquat 336 loading level in the membrane will result in a higher extraction capacity.

However, the encapsulated membrane cannot overcome the problem of low extraction rate. This is because composite polymer membranes are used to contain Aliquat 336 and in a real extraction situation the composite polymer membranes are in contact with the aqueous phase. Wang *et al.* [27] have found that the diffusion coefficient of the extracted complex, $R_3MeN^+CdCl_3^-$, in a composite membrane is smaller for membranes of low Aliquat 336 loading than that for those of higher loadings. This suggests that the transport of the extracted complex within the composite membrane is the rate-limiting step. Similar observation was reported by other workers [12].

Taking the diffusion of the extracted complex into account, it is expected that, whereas the extraction rate of the encapsulated membrane may be relatively independent of the quantity of Aliquat 336 in the membrane (provided that this quantity is reasonably large), it is strongly affected by the thickness of the composite PVC membrane. Such an effect is clearly demonstrated in Figure 5. Thus, encapsulated membrane does not provide significant advantage in improving extraction rate.

The Effect of Glass Beads in PVC-based Composite Membrane on Extraction Rate

It has been reported [27,28] that, due to its surface active nature, Aliquat 336 tends to adsorb on the interfaces between the PVC-based membrane and air and membrane and glass. An excess interfacial concentration of Aliquat 336 due to the surface adsorption was experimentally verified using XPS by Wang [28].

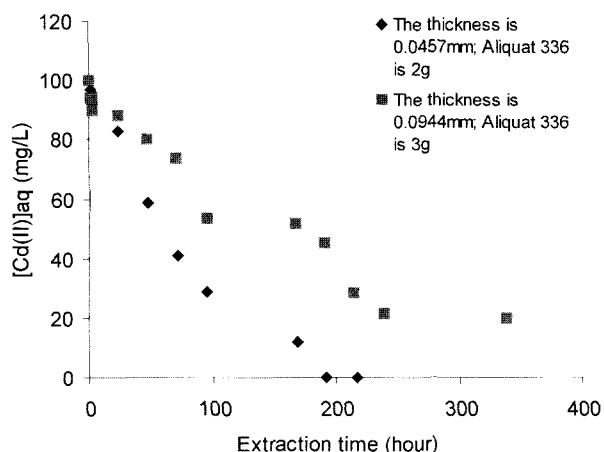


Figure 5. Aqueous Cd(II) concentration vs. time of contact. Initial concentration of Cd(II) was 100 mg/l in 2.0 M HCl. To study the effect of membrane thickness on the extraction capacity, 40 % Aliquat 336/PVC (m/m%) membranes with thicknesses of 0.0457 mm (containing 2 g Aliquat 336) and 0.0944 mm (containing 3 g Aliquat 336) were used. The extraction results from the two sets of ‘encapsulated’ membranes are presented for comparison.

The motivation for investigating the effect of glass beads in the composite membrane was as follows. When a large quantity of fine glass beads was incorporated into a composite membrane, a large polymer-glass interface area is generated. If glass beads were packed closely in the membrane, the interface between polymer and glass could well become partially continuous. This could potentially generate continuous “Aliquat 336-rich” channels extending from on surface of the composite film to the other. In this case, the extraction

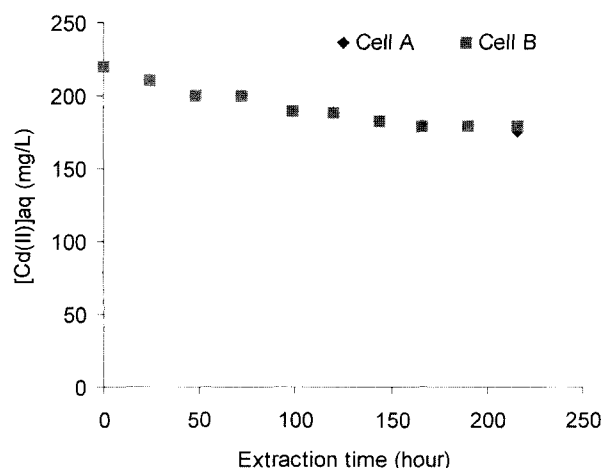


Figure 6. Aqueous Cd(II) concentration vs. time of contact, to study the extraction of Cd(II) using the ‘encapsulated’ membrane system. Initial concentration of Cd(II) was 220 mg/l in 2.0 M HCl. ‘Encapsulated’ membrane containing 2 g of free Aliquat 336, placed between the two 30 % Aliquat 336/PVC (m/m%) + 2 % glass beads of sizes 200-400 mesh and coated by aminopropyl.

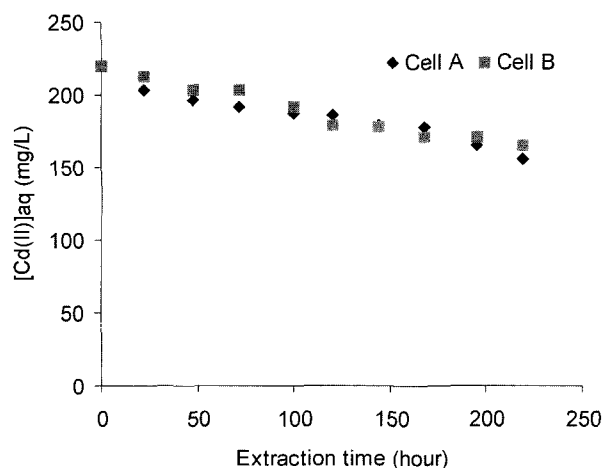


Figure 7. Aqueous Cd(II) concentration vs. time of contact, to study the extraction of Cd(II) using the ‘encapsulated’ membrane system. Initial concentration of Cd(II) was 220 mg/l in 2.0 M HCl. ‘Encapsulated’ membrane containing 2 g of free Aliquat 336, placed between the two 30 % Aliquat 336/PVC (m/m%) + 2 % glass beads of sizes 80-120 mesh and coated by aminopropyl.

rate could be improved. However, if glass beads could not pack so closely to form a continuous channel, the membrane would have a deteriorated extraction rate.

Figures 6 and 7 show that membranes incorporated with 2 % (m/m) glass beads demonstrated a substantially reduced extraction rate. The sizes of the glass beads used in Figures 6 and 7 were 200-400 mesh of pore size of 170 Å and 80-120 mesh of pore size of 700 Å respectively. These results suggest that continuous glass beads/composite polymer interface did not form. It is possible that glass beads were separated by polymer. Due to the adsorption of Aliquat 336 on to the interface, the concentration in the bulk of the composite membrane is reduced. Such a concentration reduction in the bulk is likely to be quite severe, since the specific surface area of glass beads was high.

The observations in Figures 6 and 7 further confirm that the transport of the extracted complex in the composite membrane is the rate limiting step. Any reduction of freely transportable Aliquat 336 and extracted complex molecules in the composite membrane severely reduce the extraction rate.

Extraction of Cd(II) Using ‘Sintered Glass Discs’ as the ‘Supported Liquid Membranes’

A sintered glass filter is highly porous, and some of the porous channels inside the filter are continuous, connecting one surface of the filter to the other. If Aliquat 336 was allowed to imbibe into the filter, these channels would be filled with the extractant. Also, the mobility of extracted complex in the liquid Aliquat 336 phase is expected to be higher than that in a composite membrane. However, the extraction rate would still be much lower than that in the

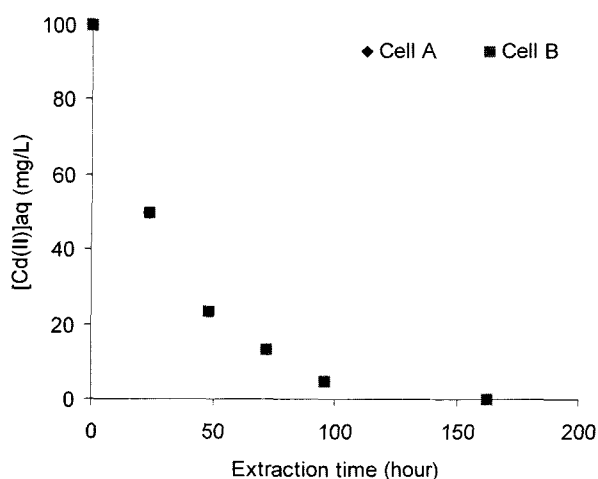


Figure 8. Aqueous Cd(II) concentration vs. time of contact, to study the extraction of Cd(II) using the 'sintered glass disc' membrane system. One piece of the 'sintered glass disc' membrane of thickness of 4.5 mm containing 2.0 g Aliquat 336 was used. Initial concentration of Cd(II) was 100 mg/l in 2.0 M HCl.

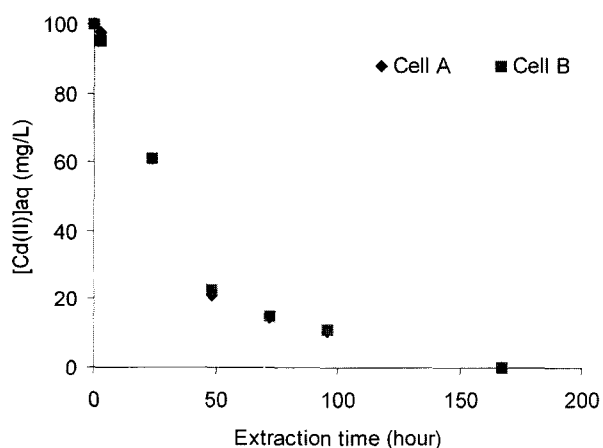


Figure 9. Aqueous Cd(II) concentration vs. time of contact, to study the extraction of Cd(II) using the 'sintered glass disc' membrane system. Three pieces of the 'sintered glass disc' membrane of thickness of 4.5 mm containing 2.0 g Aliquat 336 were used (the three pieces of the 'sintered glass disc' had a total thickness of 13.5 mm, containing 6.0 g Aliquat 336). Initial concentration of Cd(II) was 100 mg/l in 2.0 M HCl.

solvent extraction situation. This is because that undiluted Aliquat 336 is very viscous.

A predetermined quantity of Aliquat 336 was allowed to imbibe into the sintered glass discs, which were then sandwiched in between the two compartment cells. Figures 8 and 9 are extraction results obtained using sintered glass discs as the membrane support. These results are only slightly different from each other. However, the membrane used for obtaining data in Figure 9 was three times thicker than that in Figure 8; the amount of undiluted Aliquat 336

imbibed in the membrane for Figure 9 was also three times that in the Figure 8. It is clear that the quantity of the extractant in the membrane did not contribute significantly to the extraction rate.

Comparing extraction rates of the sintered glass membrane and the encapsulated membrane assembled using composite polymer membranes, the sintered glass membranes demonstrated good improvement to the extraction rate. However, this extraction rate is still considered to be slow for any practical application. This suggests that the mobility of the extracted complex within the imbibed Aliquat 336 phase is relatively slow, too. This is understandable, since the imbibed Aliquat 336 in the porous structure of sintered glass discs would be expected to have a very low convection. The transport of extracted complex would heavily rely on diffusion. The high viscosity of Aliquat 336 would make such diffusion rather slow.

Extraction of Cd(II) Using 'Sintered Glass Discs' Membranes in an 'Extraction Filtering System'

One practical approach to further improve the extraction rate (measured as $V[dC/dt]$) is to increase the membrane/ aqueous solution interface area. It is feasible that the increase of the interface area may be achieved using the sintered glass filter. If a smaller quantity of Aliquat 336 imbibes into the sintered glass filter, forming a thin layer which covers the surface of the pores, but does not block the pores, it is then possible for the aqueous phase to penetrate through the pores. In the course of penetration, extraction will occur. Due to the porous nature of the sintered glass filter, the interface area between Aliquat 336 and the aqueous phase may be greatly increased. Because of the surface active nature of Aliquat 336, it will not stop the penetration of aqueous solution into the sintered glass filter after Aliquat 336 imbibition. An "extraction filtering system" was made by allowing imbibition of a certain quantity of Aliquat 336 into the sintered glass disc of a sintered glass filter. The filter was clamped on a laboratory stand so that the aqueous solution containing Cd(II) fed into the filter was allowed to pass the sintered glass disc under gravity.

Figure 10 shows the extraction rate (Cd(II) concentration change as a function of time) of the feed solution (i.e. before the solution passed the sintered glass disc). It took 60 minutes for the feed solution containing Cd(II) ions to pass through the sintered glass disc loaded with 3.1 grams of Aliquat 336. The square point at 60 minutes (Figure 10) represents the concentration of Cd(II) ions in the extracted filtrate, i.e. the solution which has passed through the sintered glass disc. A sample of the feed solution was taken near the surface of the sintered glass disc at different times to produce the diamond data points, and the concentration of each sample was determined using AAS. These diamond data points represent the changes in the concentration of Cd(II) ions in the solution fed into the extraction filtration

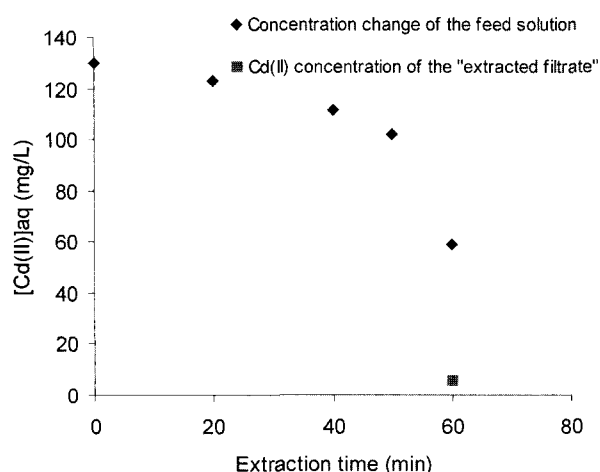


Figure 10. Aqueous Cd(II) concentration vs. time of contact, to study the extraction of Cd(II) using the 'sintered glass disc' membrane in an 'Extraction Filtration System'. One piece of the 'sintered glass disc' membrane of thickness of 4.5 mm containing 3.1 g Aliquat 336 was used. Initial concentration of Cd(II) was 130 mg/l in 2.0 M HCl.

assembly. It can be seen that the extraction rate of Cd(II) concentration in the feed solution has increased quite significantly compared with the results in Figures 8 and 9, where the sintered glass discs were used as the 'supported liquid membranes'. More remarkably, however, was the extraction effect on the "filtrate". This clearly indicates that the effect of interface area came into play.

The problem with the "extraction filtering system" is that the quantity of the extractant in the disc must be carefully controlled. The desirable extractant loading level would be one such that the extractant forms a continuous layer, covering the surface of the pore. Any excess amount will tend to block the pores. It was noticed that the quantity of Aliquat 336 loaded on the disc, 3.1 grams, was too high. As a result, the "filtering" rate was very low. Further tests showed that flow resistance is greatly reduced when the loading of Aliquat 336 was reduced from 3.1 g to 2.0 g or lower. Sintered glass discs with low loading levels allowed 100 ml of aqueous solutions to pass in less than 10 minutes. Therefore, Cd(II) in an aqueous solution can be extracted simply by recycling the solution through the membrane several times.

Figures 11 and 12 show the extraction yield as a function of the number of passes through the "extraction filtering system". Surprisingly, after 6 cycles, the Cd(II) in the aqueous phase was completely extracted out. The residual Cd(II) in the aqueous phase after such extraction was below the detecting limit of the AAS method. The time required for conducting such 6 cycles of extraction was less than 60 minutes. The system with the least Aliquat 336 (1 g) loading was more effective. These results show that the "extraction filtering

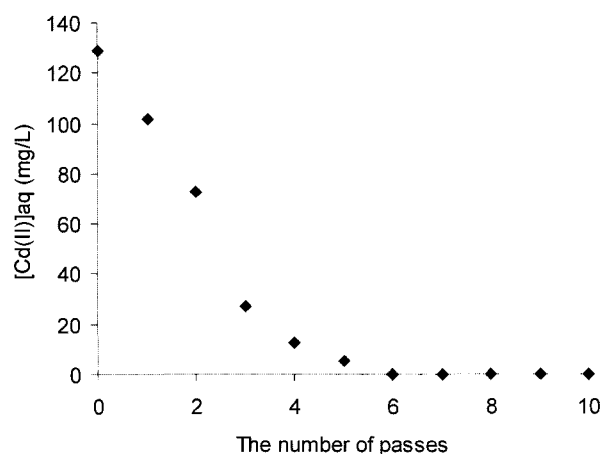


Figure 11. Aqueous Cd(II) concentration vs. the number of passes, to study the extraction of Cd(II) using the 'sintered glass disc' membrane in an 'Extraction Filtration System'. One piece of the 'sintered glass disc' membrane of thickness of 4.5 mm containing 2.0 g Aliquat 336 was used. Initial concentration of Cd(II) was 130 mg/l in 2.0 M HCl.

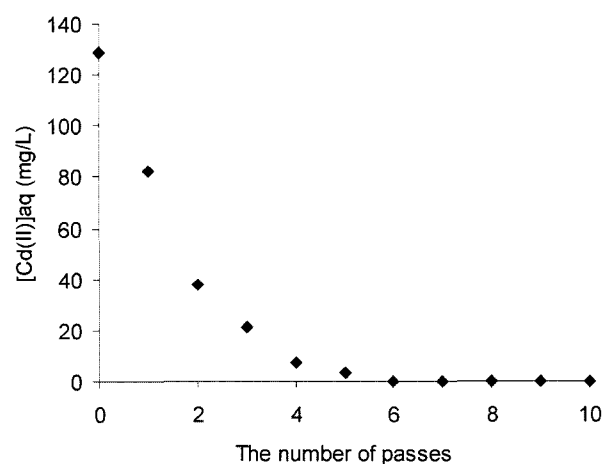


Figure 12. Aqueous Cd(II) concentration vs. the number of passes, to study the extraction of Cd(II) using the 'sintered glass disc' membrane in an 'Extraction Filtration System'. One piece of the 'sintered glass disc' membrane of thickness of 4.5 mm containing 1.0 g Aliquat 336 was used. Initial concentration of Cd(II) was 130 mg/l in 2.0 M HCl.

system" has a unique potential to rapidly and thoroughly extract heavy metal ions from an aqueous phase.

It should be mentioned that one of the typical problems associated with the liquid supported membrane is the loss of extractant. With the "extraction filtering system" in which high Aliquat 336 loading was used, the loss of extractant was also visually observable. However, no loss of extractant was visually detectable with discs of low extractant loading. Of course, extractant loss through solubility is unavoidable. This problem requires further study.

Conclusion

The present work focuses on testing new ideas and methods to improve membrane extraction rate and capacity. The major findings are:

(1) Encapsulated membrane greatly increases the extraction capacity of the membrane, but does not significantly improve the extraction rate. This is because that the encapsulated membrane requires the use of polymer composite films.

(2) The transport rate of the extracted complex and the fresh Aliquat 336 molecules in the polymer composite membranes is the rate limiting step.

(3) It is an effective way to increase the extraction rate of the membrane by increasing the interface area between the aqueous phase and the membrane. A simple approach to increase the interface area is to use the liquid supporting membrane using sintered glass discs. This membrane significantly increases the extraction rates. Since the sintered glass disc membrane does not require the use of polymer composite film, a significant rate limiting factor is removed.

(4) The "extraction filtering system" using an Aliquat 336 loaded sintered glass filter was tested. This new approach has a very good potential to increase the extraction rate. It also once again proved that increasing interface area is an effective way to increase the extraction rate.

References

1. J. de Gyves and E. Rodriguez de San Miguel, *Ind. Eng. Chem. Res.*, **38**, 2182 (1999).
2. J. Gega, W. Walkowiak, and B. Gajda, *Sep. and Pur. Tech.*, **22-23**, 551 (2001).
3. X. J. Yang and A. G. Fane, *J. Membr. Sci.*, **156**, 251 (1999).
4. A. M. Sastre, A. Madi, and F. J. Alguacil, *J. Membr. Sci.*, **166**, 213 (2000).
5. H. Boerrigter, T. Tomasberger, A. S. Booiij, W. Verboom, D. N. Reinhoudt, and F. de Jong, *J. Membr. Sci.*, **165**, 273 (2000).
6. D. He, M. Ma, and Z. Zhao, *J. Membr. Sci.*, **169**, 53 (2000).
7. L. Zhang, J. Zhou, D. Zhou, and Y. Tang, *J. Membr. Sci.*, **162**, 103 (1999).
8. R. Y. M. Huang, R. Ral, and G. Y. Moon, *J. Membr. Sci.*, **167**, 275 (2000).
9. F. J. Alguacil, M. Alonso, and A. M. Sastre, *J. Membr. Sci.*, **184**, 117 (2001).
10. W. Xu and W. Yang, *J. Membr. Sci.*, **190**, 159 (2001).
11. X. J. Yang, A. G. Fane, J. Bi, and H. J. Griesser, *J. Membr. Sci.*, **168**, 29 (2000).
12. G. Argiropoulos, R. W. Cattrall, I. C. Hamilton, S. D. Kolev, and R. Paimin, *J. Membr. Sci.*, **138**, 279 (1998).
13. S. D. Kolev, Y. Sakai, R. W. Cattrall, R. Paimin, and I. D. Potter, *Analytica Acta*, **413**, 241 (2000).
14. S. D. Kolev, G. Argiropoulos, R. W. Cattrall, I. C. Hamilton, and R. Paimin, *J. Membr. Sci.*, **137**, 261 (1997).
15. J. Xu, R. Paimin, W. Shen, and X. Wang, *Fiber Polym.*, **3**, 68 (2002).
16. J. Xu, R. Paimin, W. Shen, and X. Wang, *Fiber Polym.*, **4**, 27 (2003).
17. H. M. Yeh and C. M. Huang, *J. Membr. Sci.*, **103**, 135 (1995).
18. A. T. Shawaqfeh and R. E. Baltus, *J. Membr. Sci.*, **157**, 147 (1999).
19. H. M. Yeh, C. L. Chen, Y. Y. Peng, and C. H. Chen, *J. Membr. Sci.*, **183**, 109 (2001).
20. C. Yang and E. L. Cussler, *J. Membr. Sci.*, **166**, 229 (2000).
21. M. Tather, S. B. Tantekin-Ersolmaz, C. Atalay-Oral, and A. Erdem-Senatarlar, *J. Membr. Sci.*, **182**, 183 (2001).
22. A. Bottino, G. Capannelli, V. D'asti, and P. Piaggio, *Sep. and Pur. Tech.*, **22-23**, 269 (2001).
23. V. Parvulescu, L. Buhoci, G. Roman, B. Albu, and G. Popescu, *Sep. and Pur. Tech.*, **25**, 25 (2001).
24. K. Košutić, L. Kaštelan-Kunst, and B. Kunst, *J. Membr. Sci.*, **168**, 101 (2000).
25. P. Scovazzo, A. Hoehn, and P. Todd, *J. Membr. Sci.*, **167**, 217 (2000).
26. P. Meares, "The physical chemistry of transport and separation by membranes, in: Membrane separation processes", Chap. 1, Elsevier, Amsterdam, 1976.
27. L. Wang, R. Paimin, R. W. Cattrall, W. Shen, and S. D. Kolev, *J. Membr. Sci.*, **176**, 105 (2000).
28. L. Wang, MSc. Thesis, Victoria University of Technology, Victoria, 1999.