Experimental Study on Performance of Modified Hybrid Liquid Membrane Process for Removal of Cadmium from Wastewater

Hossein Khormaei, Hamid Reza Mortaheb*, Mohammad Hasan Amini, and Babak Mokhtarani
Chemistry and Chemical Engineering Research Center of Iran, Tehran, I. R. Iran
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Abstract

Liquid membrane processes have attracted many interests in recent years for removal of heavy metals such as cadmium from industrial wastewaters. In this study, a modified hybrid liquid membrane system is introduced. The setup is worked by applying the water-insoluble dioctyl phthalate as the organic solvent. N-octanol and tetra butyl ammonium bromide are added to the organic phase to increase the system efficiency. The effects of different parameters such as pHs of the feed and stripping phases, the complexing agent concentration, the organic film thickness, initial concentration of cadmium, and the carrier concentration on the cadmium removal are studied. The results demonstrate the increase in the removal rate and capacity comparing to those of previously studied hybrid liquid membrane system. An electrical potential is then applied to the hybrid liquid membrane system. The results show higher removal rate and capacity compared to the corresponded values in the system without applying electrical potential.

Keywords: Hybrid liquid membrane, Mass transfer, Cadmium, Removal efficiency, Electro-assisted process.

1. Introduction

Cadmium is applied in many industries such as electroplating and metallurgy, and also in manufacturing pigments and ceramics [1-4]. This heavy metal is known by its toxicity and tendency to accumulate in the living organisms, which causes serious diseases and disorders [5]. Cadmium affects the action of enzymes and hinders respiration, photosynthesis, transpiration, and chlorosis [6, 7]. Production of this metal has been increased due to its growing industrial applications [8, 9]. Therefore, developing an effective, precise, and low cost process for removal of cadmium from wastewater is of high importance. In recent years, several methods for removal of cadmium have been proposed using processes such as adsorption [10-13], chemical deposition [14], polymer inclusion membrane [21-23], supported liquid membrane [15-18], emulsion liquid membrane [19, 20], and hybrid liquid membrane [26-32]. Hybrid liquid membrane (HLM) is a modified supported liquid membrane process, which can effectively remove heavy metals at low concentrations in wastewater. The conventional HLM process includes a bulk of liquid membrane containing a dissolved carrier inserted between the feed and stripping aqueous phases. The phases are separated by two supporting filters [24, 25]. The specie, which is to be removed, is transferred from the feed phase to the liquid membrane phase by making a complexation with the carrier. The complex is then broken at the liquid membrane-stripping interface and the specie is transferred into the stripping phase. The advantages of HLM compared to other liquid membrane systems are their higher removal efficiency and greater stability of the membrane phase. Several modifications have been proposed for HLM systems containing strip dispersion hybrid liquid membrane [28], aqueous hybrid liquid membrane [29-31], and emulsion hybrid liquid membrane [32]. Each of these methods has its own advantages and disadvantages.

In the present research, a conventional hybrid liquid membrane system is proposed by applying dioctyl phthalate as the organic.

* Corresponding author: Tel: +98 2144787751 Email: mortaheb@ccerci.ac.ir

Since the solubility of dioctyl phethalate in water (0.27 mg/l) is much lower compared to that of the conventional organic solvents, its application causes less pollution. Removal performance of the HLM process by applying the new organic phase is studied in the present research. The enhancement of mass transfer rate in this system by inducing an electrical current is also investigated.

2. Transport mechanism

The transport mechanism can be explained by the following steps:

1. Tri-octyl amine (TOA, shown as Oct_3N), which is added to the organic phase, acts as a carrier. It reacts with H^+ of the feed phase at the feed-membrane interface to form $Oct_3NH^+A^-$, where A^- is a counter ion.

$$Oct_3N_{(org)} + H^+_{(feed)} + A^-_{(feed)} \rightarrow Oct_3NH^+A^-_{(org)} \quad (1)$$

2. At the feed-membrane interface, A^- in $Oct_3NH^+A^-$ is replaced by CdI_4^{2-}.

$$CdI_{4\,(feed)}^{2-} + 2\,Oct_3NH^+A^-_{(org)} \rightarrow (Oct_3NH)_2CdI_{4(org)} + 2\,A^-_{(feed)} \quad (2)$$

3. OH^- in the stripping phase reacts with the transferred $(Oct_3NH)_2CdI_4$ at the membrane-stripping interface to transfer cadmium into the stripping phase.

$$(Oct_3NH)_2CdI_{4(org)} + 2\,OH^-_{(strip)} \rightarrow 2\,Oct_3N_{(org)} + CdI_{4\,(strip)}^{2-} + 2\,H_2O_{(strip)} \quad (3)$$

3. Research method

3.1. Chemicals

The organic solvent used in the organic phase was dioctyl phthalate (DOP). N-octanol was added to the organic phase to reduce the viscosity of the organic phase and to increase the system's efficiency. Tetra butyl ammonium bromide (TBAB) was added to the organic phase to increase its polarity for better dissolving the carrier and better impregnation of the supporting membranes. All chemicals were analytical grade reagents and were used without further purification. The solutions were prepared by double distilled water. Hydrophilic PVDF membranes from Millipore with a porosity of 70% and pore size of 0.1μm were used as the supporting membranes in the setup. The contact angle of the applied membranes was measured by an optical contact angle measurement device (dataphysis-OCA20). The contact angle of the membrane was determined in the range of 83-92 degree for the front and rear sides of the membrane, which represents a weak hydrophilic inherency.

Since the membranes are applied between aqueous and organic phases, this weak hydrophilic inherency of the membranes makes them ideal for such an application.

3.2. Experimental setup and procedure

A schematic of the applied setup in the experiments is shown in Figure 1. The setup consists of a cylindrical-shape cell with two separate 75-mm compartments for feed and stripping phases. Two membranes, which are impregnated in the organic phase for 24 h before the experiment, are placed between the flanged-shape ends of each container and a spacer. The set of support membranes, the spacer, and the glass containers are fastened appropriately. By using the spacers with different thicknesses, a space with variable thickness is provided for injection of the organic phase. The setup was placed inside a water bath whose temperature is controlled by a heater magnet stirrer. A synthesized feed was used in the present study by dissolving specified amounts of cadmium chloride in deionized water. The pHs of the feed and stripping phases were adjusted by adding hydrochloric acid and sodium hydroxide solutions. The aqueous phases were stirred by two magnets in circular wells at the bottom of each container. In order to investigate about the effect of electrical current on mass transfer (as will be discussed later), two electrodes consisting a graphite mat (as the cathode) and steel (as the anode) were placed in the feed and stripping compartments, respectively. The electrical current and voltage were controlled by an electrical resource. Samples were taken from the feed phase at the specified time intervals and pHs of the aqueous phases were recorded periodically. The concentrations of cadmium in the samples were measured by atomic absorption spectroscopy (PerkinElmer 1100B).

The removal efficiency (*RE*), removal capacity (*RC*), and removal mass flux (*J*) were then calculated by using the following equations, respectively:

$$RE = ((C^0_{\mathrm{Cd}} - C_{\mathrm{Cd}}) / C^0_{\mathrm{Cd}}) \tag{4}$$

$$RC = ((C^0_{\mathrm{Cd}} V^0 - C^{\mathrm{f}}_{\mathrm{Cd}} V^{\mathrm{f}}) / C^0_{\mathrm{Cd}}) \tag{5}$$

$$J = -\frac{V}{A}\frac{\Delta C_{\mathrm{Cd}}}{\Delta t} \tag{6}$$

In which, C_{Cd} is the cadmium concentration, V is the volume of feed phase, A is the active area of supporting membrane, and superscripts 0 and f indicate the initial and final conditions, respectively. Assuming a pseudo first order kinetics for mass transfer rate, the rate constant, k, can be obtained by:

$$\ln(C^0_{\mathrm{Cd}} / C_{\mathrm{Cd}}) = k\,t \tag{7}$$

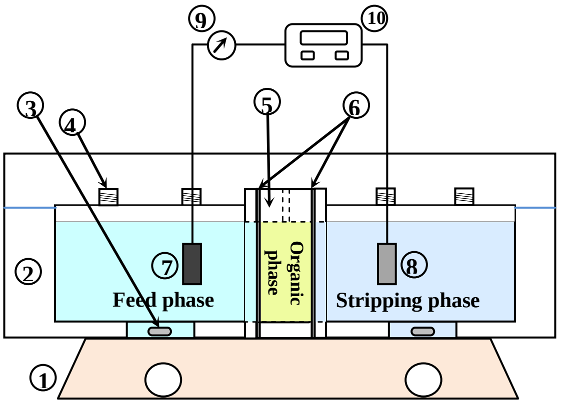

Figure 1: Schematic diagram of hybrid liquid membrane setup
(1) Magnet stirrer; (2) Water bath; (3) Magnet; (4) Sampling and measurement openings; (5) Spacer; (6) Supporting membranes; (7) Graphite fibrous mat electrode; (8) S.S electrode; (9) multi meter; (10) Electrical source.

The values of parameters used in the experiments are as listed in Table 1 unless otherwise is noted.

Table 1: Parameters applied in experiments.

Parameter	Description	Value
C^0_{Cd}	Initial cadmium conc. in feed phase	50 ppm
C_{KI}	KI conc. in feed phase	0.01 M
C_{TOA}	Carrier conc. in organic phase	0.1 M
l	Thickness of organic phase	4 mm
T	Temperature	25 °C
pH^0_f	Initial feed phase pH	1.7
pH^0_s	Initial stripping phase pH	13
N	Stirring speed of aqueous phases	500 rpm
C_{TBAB}	TBAB conc. in organic phase	0.006 M
C_{oct}	Amount of n-octanol added to organic phase	10 vol%

4. Results and analyses

4.1. Effect of adding n-octanol and tetrabutyl ammonium bromide to organic phase

Dioctyl phethalate is an oily liquid with a high viscosity (78 cP at 20ºC), which is expected to show high mass transfer resistance. Dissolving n-octanol (viscosity: 10.6 cP at 15 ºC) in the organic phase reduces its viscosity and increases its polarity. On the other hand, the supporting filters are impregnated hardly with pure dioctyl phthalate.

This may induce an excess resistance against mass transfer. Therefore, adding tetra butyl ammonium bromide, which is a strong polyelectrolyte, improves the wettability of the supporting membrane. It also causes better dissolution of the carrier-metal complex in the organic phase. The effect of adding 10 vol% of n-octanol and 0.006 M TBAB (its ultimate solubility in DOP at ambient temperature) to the organic phase is demonstrated in Figure 2.

The figure shows only trivial removal efficiencies in the absence of these substances while by adding TBAB and n-octanol, the removal efficiency is increased significantly. The same values of these additives are then used in the subsequent experiments.

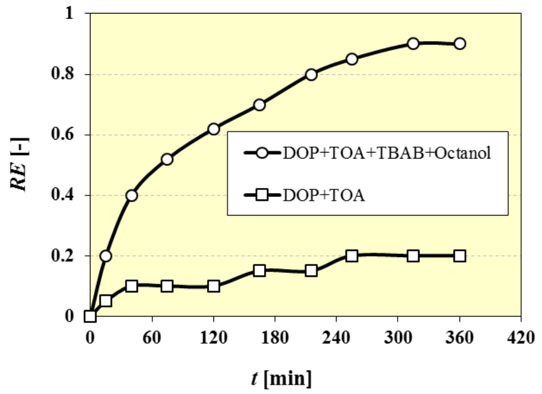

Figure2: Effect of adding n-octanol and TBAB to organic phase on removal efficiency
C_{KI}=0.01M; C_{TOA}=0.05M; C^0_{Cd}=50ppm; l=4mm; T=25°C; pH^0_f=1.7; pH^0_s=13; N =500rpm.

4.2. Effect of carrier concentration

Considering the transfer mechanism, the removal efficiency is expected to be increased by increasing the carrier concentration. Figure 3 shows the effect of the carrier concentration of 0.02, 0.05, and 0.1 M on the removal efficiency. As it can be seen, the carrier concentration of 0.1 M shows the highest removal efficiency. However, increment in the removal efficiency is not proportional to the increase in the carrier concentration since excessive increasing carrier concentration may increase also the viscosity of the organic and may hinder the mass transfer.

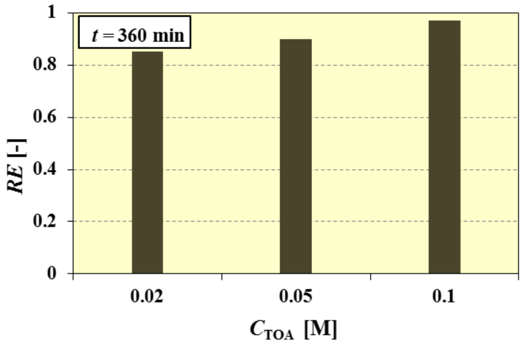

Figure3: Effect of carrier concentration on removal efficiency
C_{KI}=0.01M; C^0_{Cd}=50ppm; l=4mm; T=25°C; pH^0_f=1.7; pH^0_s=13; N =500rpm; C_{TBAB}=0.006 M; C_{oct}=10 vol%.

4.3. Effect of initial pH of feed phase

H^+ ion in the feed solution is absorbed by the carrier to produce $OctNH_3^+$. The pH of feed phase determines the availability of H^+ at the feed-organic interface and causes the cadmium ion to be transferred through the membrane. The feed solutions with pHs of 0.5, 0.7, and 3 adjusted by adding hydrochloric acid were used to study the effect of feed pH on the removal efficiency. Figure 4 shows that as pH^0_f is decreased from 3 to 1.7, the removal efficiency is increased while further decrease in pH^0_f to 0.5 results in decreasing in the removal efficiency. This phenomenon is possibly due to oxidation of I^- and its convertion to I_2, which is indicated by its yellow color in the experiments. This causes reduction of iodide concentration, which is necessary to form the complex of CdI_4^{2-}.

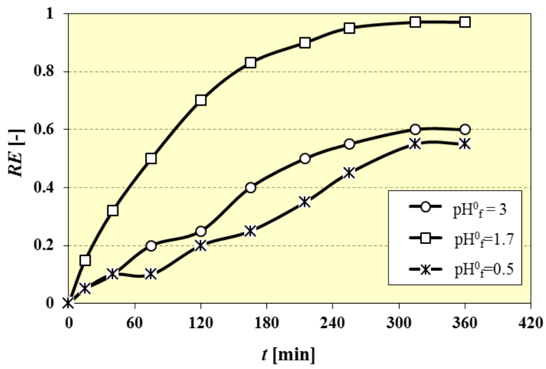

Figure 4: Effect of initial pH of feed phase on removal efficiency
C_{KI}=0.01M; C^0_{Cd}=50ppm; l=4mm; T=25°C; C_{TOA}= 0.1M; pH^0_s=13; N =500rpm; C_{TBAB}=0.006M; C_{oct}=10 vol%.

4.4. Effect of initial pH of stripping phase

Increasing pH of the stripping phase is expected to increase the removal efficiency based on the proposed mechanism. Some experiments were performed to study this effect by adjusting the initial pH of stripping phase on 9, 11, 13. Figure 5 shows that in pHs of 9 and 11, the removal efficiencies are low and close to each other. This is because the pH of stripping phase is dropped by 1-2 units during the test, which causes decrease in the driving force. However, when the initial pH of stripping phase is set to 13, a significant increase in removal efficiency is observed while the pH remained almost unchanged during the test.

4.5. Effect of complexing agent concentration

As the cadmium ion in the feed phase is transferred in a complex form, the concentration of complexing agent in the feed phase is determined. Three concentrations of 0.01, 0.02, and 0.05 M of iodide ion in the feed phase were used. Figure 6 shows that the highest cadmium removal efficiency is obtained in the iodide concentration of 0.01 M. The decreasing of removal efficiency with increasing iodide concentration may be attributed to the presence of phase transmitting agent, tetra butyl ammonium bromide, in the organic phase, which may facilitate transferring the I^- ion from the feed-organic interface into the organic phase. This may retard formation of CdI_4^{2-} complex, and thus decrease the removal efficiency.

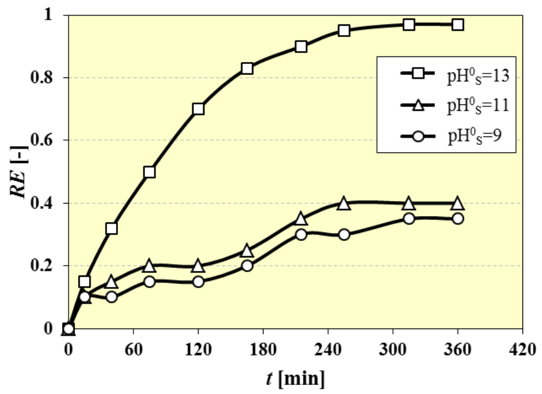

Figure5: Effect of initial pH of stripping phase on removal efficiency
C_{KI}=0.01M; C^0_{Cd}=50ppm; l=4mm; T=25°C; C_{TOA}= 0.1M; pH^0_f=1.7; N =500rpm; C_{TBAB}=0.006M; C_{oct}=10 vol%.

4.6. Effect of organic phase thickness

The effect of thickness of organic phase on mass transfer rate can be studied from two different aspects. As the thickness of organic phase increases, the amount of carrier in the organic phase is increased that may increase the initial removal flux. However, it also changes the mass transfer resistance due to increase in the diffusion path. Figure 7 demonstrates that the effect of mass transfer resistance is prominent i.e. the rate constant for the thickness of 3 mm is the highest when the thickness of organic phase is changed from 3 to 5 mm. Although, the ultimate removal efficiency for the thickness of 4 mm is the same as that for the thickness of 3 mm, its removal rate is slower. In the case of 5 mm thickness, both removal rate and removal efficiency are significantly lower compared to those for the system with the smaller thicknesses of organic phase.

4.7. Effect of initial concentration of cadmium

The increase of initial concentration of cadmium in the feed phase causes increase of the concentration gradient and thus the removal efficiency. To study the effect of initial concentration of cadmium, the results of experiments in the three feed concentrations of 50, 100, and 500 ppm are shown in Figure 8. As seen in the figure, the initial and average fluxes increase by increasing the initial cadmium concentration. However, the removal efficiency decreases due to approaching to the ultimate removal capacity of the stripping phase.

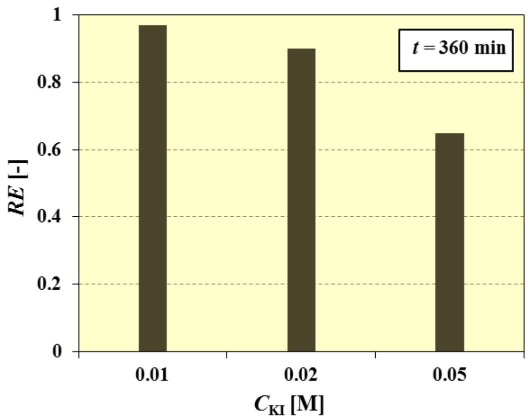

Figure6: Effect of complexing agent concentration on removal efficiency
C^0_{Cd}=50ppm; l=4mm; T=25°C; C_{TOA}= 0.1M; pH^0_f=1.7; pH^0_s=13; N =500rpm; C_{TBAB}=0.006M; C_{oct}=10 vol%.

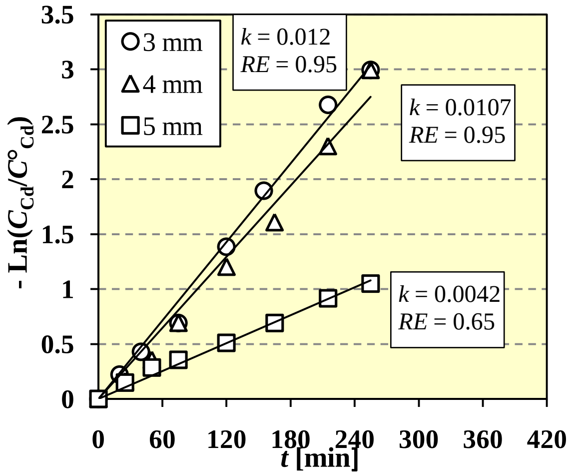

Figure 7: Effect of organic phase thickness on rate constant and removal efficiency
C^0_{Cd}=50ppm; C_{KI}=0.01M; T=25°C; C_{TOA}= 0.1M; pH^0_f=1.7; pH^0_s=13; N =500rpm; C_{TBAB}=0.006M; C_{oct}=10 vol%.

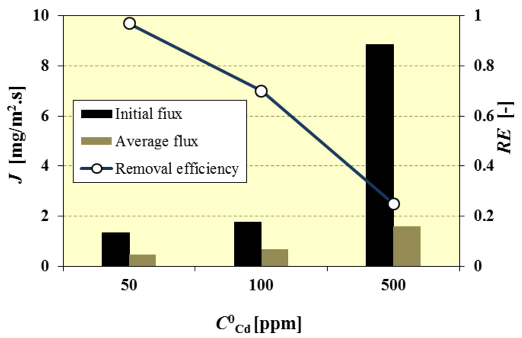

Figure8: Effect of initial concentration of cadmium on initial flux and average fluxes and removal efficiency
C_{KI}=0.01M; l=4mm; T=25°C; C_{TOA}= 0.1M; pH^0_f=1.7; pH^0_s=13; N =500rpm; C_{TBAB}=0.006M; C_{oct}=10 vol%.

4.8. Comparison of two hybrid liquid membrane systems

The performances of hybrid liquid membrane system with the organic phase applied in the present research (dioctyl phthalate, tetra butyl ammonium bromide, and n-octanol) and that in a previous research (a kerosene cut solvent) [27] are compared. Figure 9(a) shows that with the feed concentrations of 50 ppm, there is no difference between the removal efficiencies for these systems (both are about 0.95). However, when the feed concentration is increased to 100 ppm, the removal efficiency of the present system is more than that with the kerosene cut solvent (0.7 compared to 0.45). A similar result is obtained for the removal capacities of the systems as shown in Figure 9(b) i.e. the removal capacity of the present system for the feed concentration of 100 ppm is 70 mg/l while the corresponded value for the previous system is 45 mg/l. Nevertheless, the main advantage of applying present organic phase is that it causes less pollution because of its low solubility.

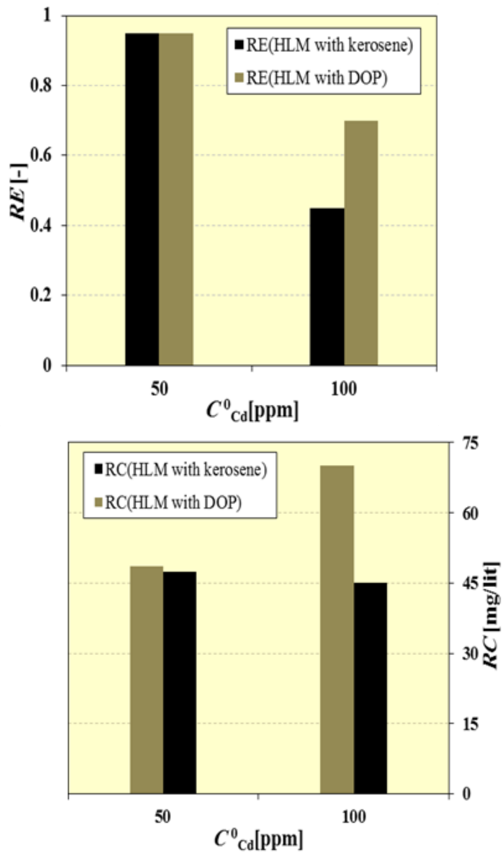

Figure9: Comparison of (a) removal efficiencies and (b) capacities of two hybrid liquid membrane systems
l=4mm; C_{KI}= 0.01M; T=25°C; C_{TOA}= 0.1M; pH^0_f =1.7; pH^0_s =13; N =500 rpm.

4.9. Electro-assisted hybrid liquid membrane

It is assumed that the mobility of the transferring ions in the hybrid liquid membrane system and thus the removal performance of the system can be promoted by applying an induced electrical potential. However, dioctyl phthalate has low conductivity and therefore induces a large electrical resistance. In order to increase the conductivity of the organic phase, tetra butyl ammonium bromide, which is a strong polyelectrolyte, was dissolved in the organic phase.ppA series of experiments were carried out using the experimental setup by applying electrical voltage on the electrodes insides the feed and stripping compartments (Figure 1) to investigate the effects of different parameters on this electro-assisted hybrid liquid membrane system. Figure 10 show that when an electrical potential of 20 V (corresponding to the current of 0.9 mA) is applied, the removal efficiency gets higher to an extent (about 5%) compared to when the electrical potential is absent. It is interesting to note that in Figure 10 that when the organic phase contains only DOP and the carrier, even applying electricity (30 V, 0.07 A) cannot significantly enhance the removal efficiency of the system.

Except for the thickness of organic film, similar results were obtained by altering the parameters of the system as those in the system without applying electricity. Figure 11 shows that when the electrical voltage is applied, unlike the experiments in the absence of electrical voltage (Figure 7), the reduction of organic phase thickness reduces the removal rate. This indicates that in the presence of electrical current, increase in the thickness of the organic phase i.e. increase in the amount of carrier and polyelectrolyte has a more controlling role in the mass transfer rate and removal efficiency than effect of the resistance caused by the membrane phase thickness.

4.9.1. Effects of electrical voltage on initial flux and removal efficiency

As the electrical voltage and consequently electrical current is increased, the ion transfer through the system may increase. Figure 12 shows the initial fluxes and removal efficiencies for the tests, in which three voltages of 10, 20, and 30 V were applied. The corresponded current in these experiments were 0.44, 0.9, and 1.47 mA, respectively. The figure shows that comparing to the case in the absence of electrical current, no significant change in initial flux is observed in the voltage of 10 V. However, the initial flux and the removal efficiency are increased when the voltage is increased to 20 V. In the voltage of 30 V, the initial flux is still increased but the removal efficiency is decreased to some extent. The reason may be related to accumulation of the organic-cadmium complex on the feed-organic interface, which may cause some resistance against mass transfer.

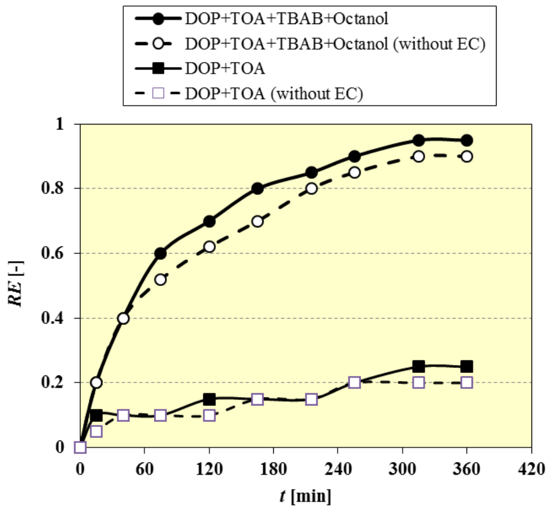

Figure 10: Effect of applying electricity on removal efficiency in the presence of n-octanol and tetrabutyl ammonium bromide in organic phase
C_{KI}=0.01M; C_{TOA}=0.05M; C^0_{Cd}=50ppm; l=4mm; T=25°C; pH^0_f=1.7; pH^0_s=13; N =500 rpm.

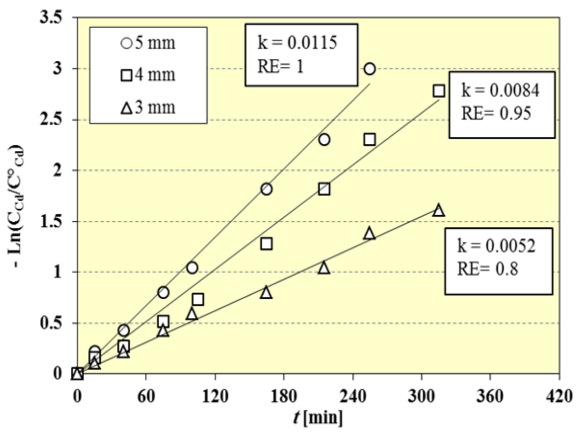

Figure 11: Effect of organic phase thickness on rate constant and removal efficiency in the presence of electrical current
C_{KI}= 0.01M; C^0_{Cd}= 50ppm; pH^0_s =13; T=25°C; C_{TOA}= 0.1M; pH^0_f =1.7; N =500rpm; C_{TBAB}= 0.006M; C_{oct}=10 vol%; V= 20 V; I= 0.9 mA.

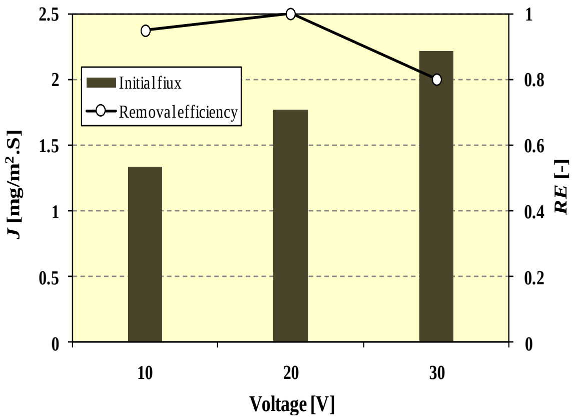

Figure 12: Effect of voltage on initial flux and removal efficiency
C^0_{Cd}= 50ppm; C_{KI}= 0.01M; l= 5mm; T=25°C; C_{TOA}= 0.1M; pH^0_f =1.7; pH^0_s =13; N =500rpm; C_{TBAB}= 0.006M; t = 360 min; C_{oct}=10 vol%.

5. Conclusion

A modified hybrid liquid membrane system was used for removal of cadmium from wastewater. Dioctyl phthalate was applied as the organic solvent to decrease the environmental pollution. N-octanol and tetra-butyl ammonium bromide were added to the organic phase to increase the system's efficiency. Effects of different parameters on the performance of the modified HLM system were studied and the optimum conditions were determined. When electrical current is applied to the hybrid liquid membrane system, higher removal efficiencies and removal rates could be obtained. The effects of various parameters are similar to those in the absence of the electrical current. However, it was found that in the electro-assisted system unlike the former one, as the thickness of the organic phase is increased, the removal rate is increased that indicates a more controlling role of the amount of polyelectrolyte and the carrier. The initial flux and removal rate are increased by increasing the voltage to a certain limit but the removal efficiency is decreased afterward possibly due to a hindrance effect by accumulation of ions near the interface of supporting membrane.

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