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Removal of phenolic compounds from aqueous solutions using Aliquat 336 as a carrier in emulsion liquid membrane

Arulmozhiappan Balasubramanian and Sivaramu Venkatesan†

Department of Petrochemical Technology, Anna University of Technology Tiruchirappalli,
Tiruchirappalli-620 024, Tamil Nadu, India
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Abstract−A carrier-mediated separation of phenolic compounds from the dilute aqueous solution was studied with an emulsion liquid membrane, constituted by a solution of ionic liquid (Aliquat 336) in kerosene, sodium hydroxide as a stripping agent and Sorbitan monooleate as a surfactant. The effects on various operating parameters such as surfactant concentration, carrier concentration, emulsification time, strip agent concentration, stirring speed, phase volume ratio, external phase pH and treat ratio were experimentally investigated. Additionally, a stability test was performed under a static condition using Rose Bengal dye. The results showed that the stability of emulsion and extraction was enhanced on adding Aliquat 336 in membrane phase, and it has been verified by FT-IR spectra. By selecting appropriate conditions, the stability and life span of membrane was increased by six times and the percentage of removal of phenol increases upto 99.3% at the treat ratio of 3.

Key words: Ionic Liquid, Aliquat 336, Phenolic Compounds, Surfactant, Emulsion Liquid Membrane

INTRODUCTION

Room temperature ionic liquids (RTILs) are a group of low melting point salts that consist of organic cations and organic/inorganic anions. They have negligible vapor pressure, low flammability, and can be fine-tuned according to the functional needs [1,2]. These unique properties serve them as an option to replace the volatile organic solvents for removal process of an organic pollutant like phenolic compounds [3-5]. Phenol is often present in the wastewater discharged by manufacturing processes such as in the petrochemical and agrochemical industries and in coal gasification wastewaters. Due to their potential harm to human health, most are listed as priority pollutants by the US Environmental Protection Agency [6]. There are many treatment processes used for removal of phenol like fenton, ozonation, distillation, extraction, adsorption, membrane pervaporation, membrane-based solvent extraction, electrochemical methods and some biological process [6-27]. Among the available treatment methods, emulsion liquid membrane (ELM) also attracts attention from the industry and researchers. The ELM system contains a water-oil-water system, which may be referred to as an external aqueous solution, and an internal aqueous solution is spatially separated by an immiscible liquid as membrane phase. Due to the favorable thermodynamic conditions created at the interface between the external and membrane phase, the transportation of solutes occurs from external phase to membrane phase. Simultaneously, the transported solute readily reacts with the strip agent in internal phase and gets accumulated in the internal phase itself. Due to the combination of both extraction and stripping in a single process, which shows the practical simplicity, it has less capital and operating cost compared with other processes [4-28].

The use of tricaprylmethylammonium chloride (Aliquat 336) ionic Liquid as a carrier in ELM for removal of phenolic compounds from aqueous solution is the focus of the present work. There are a number of literature studies available for removal of phenolic compounds using ELM [29-36] and by using solvent extraction using ionic liquids [37-41]. To the best of our knowledge, no work has been reported on removal of phenols using Aliquat 336 as a carrier in emulsion liquid membrane technique. The performance of Aliquat 336 as a carrier in ELM under different operating parameters, like carrier concentration, internal phase concentration, surfactant concentration, emulsification time, a phase volume ratio (I/M) (Internal to Membrane phase volume ratio), treat ratio (external to emulsion phase volume ratio), stirring speed and external phase pH, was studied. FT-IR characterization was performed for IL, IL with kerosene and membrane phase (before and after extraction). In addition, an emulsion stability test under a static condition was also carried out using Rose Bengal dye to study the effect of adding ionic liquid in emulsion.

MATERIALS AND METHODS

1. Reagents and Analysis

The phenol, p-chlorophenol, 2,4 dichlorophenol, 2,4,6 trichlorophenol and pentachlorophenol, Sodium hydroxide (NaOH) flakes, Sorbitan monooleate (Span 80), kerosene, 0.1 N Hydrochloric acid (HCl) and Ammonia solution were obtained from LOBA Chemie (India). Tri C8-C10 alkylmethylammonium chloride (Aliquat 336) was purchased from Otto Chemie (India), Sodium phenoxide trihydrate (99%) ($NaOC_6H_5 \cdot 3H_2O$) and Rose Bengal (Dye content 95%) were obtained from Sigma Aldrich (USA). Reagents used in 4 Aminoantipyrine procedure (4-AAP) spectrophotometric determination (4-aminoantipyrine, $K_3Fe(CN)_6$, K_2HPO_4, KH_2PO_4, Ammo-

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†To whom correspondence should be addressed.
E-mail: venkat.set@gmail.com

nium hydroxide, and potassium ferricyanide) were of analytical grade supplied by Merck (Germany). ULTRA TURRAX IKA-T25 (Germany) was used as a high speed homogenizer for emulsion preparation. IKA RW 20 (Germany) overhead stirrer was used for the extraction studies. Sartorius Basic Meter PB-11 (Germany) was used for measuring pH. Absorbance was measured by UV-Vis spectrophotometer, Shimadzu-UV-2450 (Japan). Hybridization shaker incubator combi-SV120 (Korea) was used for phenol loading in membrane phase, and FTIR spectra were recorded on a Perkin Elmer FTIR spectrometer-spectrum RX- I (USA).

2. Stock Solution Preparation

300 ppm of Phenolic compounds (Phenol (6.5 pH), p-chlorophenol (6.5 pH), 2,4 dichlorophenol (6.3 pH), 2,4,6 trichlorophenol (6.1 pH), pentachlorophenol (6.2 pH)), 1 N NaOH, the reagents for the 4-AAP procedure and Ammonium hydroxide stock solution was prepared by dissolving them into double distilled water, respectively.

3. Experimental Procedure

Initially, an emulsion was prepared by emulsifying 0.25 N NaOH aqueous solution of strip phase with an organic phase. The organic phase (membrane phase) consisted of the appropriate volume of surfactant (Span-80), Aliquat 336 as a carrier and kerosene as a diluent. The internal strip phase was added dropwise into a beaker containing the organic phase. A phase volume ratio (I/M) of 1 (v/v) was maintained and homogenized at 8,000 rpm for 5 min to obtain a milky-white emulsion. The emulsion was dispersed in the feed phase containing phenolic compounds in a treat ratio of 3 by volume and stirred by an overhead stirrer with a speed of 200 rpm. At various time intervals, extracted samples were taken from the beaker and external phase was separated from the emulsion by laboratory centrifuge. The concentration of phenolic compounds in the aqueous external phase was determined by 4-AAP method using UV-Vis spectrophotometer at a wavelength of 510 nm [42,43]. Emulsion leakage can be justified by directly measuring the presence of sodium phenoxide, sodium 4-chlorophenoxide, sodium 2,4-dichlorophenoxide, sodium 2,4,6-trichlorophenoxide, and sodium pentachlorophenoxide concentration in the external aqueous phase after ELM extraction at a wavelength of 290 nm [6], 294, 288, 312 and 345 nm, respectively, to avoid misperception. This value was then compared with the total amount of sodium phenoxides produced by reaction of phenolic compounds with NaOH based on the amount of phenolic compounds removed using mass balance. The concentration of phenolic compounds and sodium phenoxides was found from the absorbance of phenolic compounds and sodium phenoxides calibration curves. The percentage removal and emulsion leakage of phenol and chlorophenols was determined by Eqs. (1) and (2):

$$\text{Removal of phenols (\%)} = \left[\frac{(c_0 - c_1)}{c_0}\right] \times 100 \qquad (1)$$

Where c_0 is the initial and c_1 is the final concentration of phenol in the external phase.

$$\text{Emulsion leakage (\%)} = \frac{\left\{\begin{matrix}\text{experimental leakage in sample} \\ \text{(sodium phenoxides of phenols)}\end{matrix}\right\}}{\left\{\begin{matrix}\text{theoretical full leakage} \\ \text{(sodium phenoxides of phenols)}\end{matrix}\right\}} \times 100 \qquad (2)$$

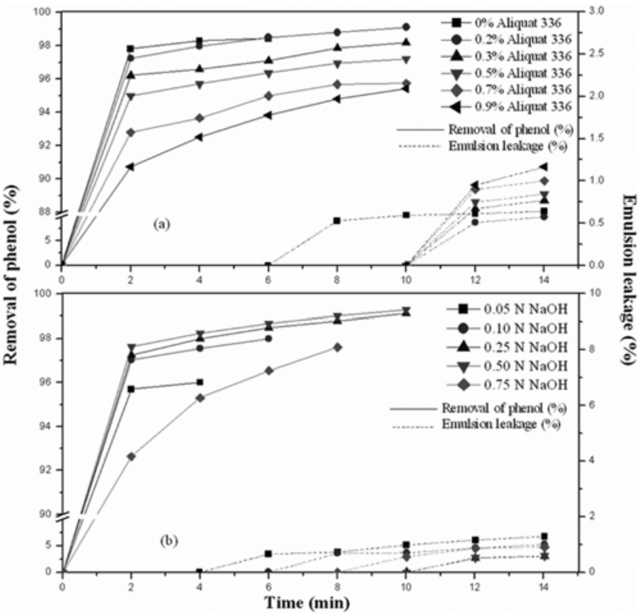

Fig. 1. (a) Effect of Aliquat 336 concentration on the emulsion leakage and removal of phenol from aqueous solutions (Concentration of Span 80 : 4% (v/v), Internal phase concentration (NaOH): 0.25 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, treat ratio: 3, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm), (b) Effect of NaOH concentration in internal phase on the emulsion leakage and removal of phenol from aqueous solutions (concentration of Span 80 : 4% (v/v); emulsification speed: 8,000 rpm; I/M ratio: 1; emulsification time: 5 min; treat ratio: 3; stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm).

RESULTS AND DISCUSSIONS

1. Effect of Carrier Concentration on Membrane Phase

The effect of Aliquat 336 carrier concentration on the removal of phenol using ELM and emulsion leakage was studied in the range of 0-0.9% (v/v), and the results are displayed in Fig. 1(a). The experimental conditions used wereas follows: surfactant concentration 4% (v/v), 0.25 N NaOH in internal phase, I/M ratio: 1 (v/v), emulsification speed and time are 8,000 rpm for 5 min and treat ratio of 3 at 200 rpm of stirring speed. From Fig. 1(a), it is observed that as the Aliqaut 336 (A-336) concentration increased from 0% to 0.2% v/v, the removal of phenol increased from 98.4% (in 6 min) to 99.12% in 10 minutes time. Beyond extraction time, sodium phenoxide started to accumulate in external phase due to membrane leakage and no phenol was detected. This is due to reaction of unextracted phenol in external phase with leaked NaOH. With further increase in carrier concentration, the percentage removal of phenol decreased. This was mainly due to increase in viscosity of the membrane phase, which minimized the diffusion of phenol [6]. Beyond 10 minutes of extraction time, for all concentrations of ionic liquids in membrane phase, membrane leakage was noted. Maximum removal of phenol with minimal leakage was obtained with Aliquat 336 concentration of 0.2% (v/v) and it was selected for further studies.

2. Effect of Stripping Agent in Strip Phase

The role of stripping agent in strip phase in phenol removal was studied in the concentration range from 0.05 to 0.75 N NaOH, and the data obtained is illustrated in Fig. 1(b). Experimental conditions are the same as mentioned previously using a carrier concentration of 0.2% (v/v). Sodium hydroxide concentration increased from 0.05 N to 0.5 N, and the percentage removal of phenol increased from 96.01% (4 min) to 99.3% (10 min). Beyond the extraction time, sodium phenoxide was measured in external phase and no phenol was detected. When the strip agent concentration was above 0.5 N NaOH, the extraction rate decreased and emulsion leakage was increased, and no phenol was observed in the external phase. This may have been due to the reaction between NaOH and Span 80 that involved a reduction in the properties of the surfactant that subsequently led to an emulsion disruption [6,7]. Hence, the optimum internal phase concentration of 0.50 N is preferred for maximum extraction of phenol with minimum leakage.

3. Effect of Surfactant Concentration

The effect of surfactant concentration on the behavior of the emulsion leakage and phenol removal efficiency was investigated in the range of 3-5% (v/v). Experiments were conducted in the same conditions as mentioned previously with an internal phase concentration of 0.50 N, and the results obtained are given in 2(a). From Fig. 2(a), percentage removal of phenol increased from 96.7% (6 min) to 99.3% (10 min) with an increase in the surfactant concentration of 3% to 4% (v/v). Beyond the maximum removal of phenol, sodium phenoxide started to accumulate in external phase due to membrane leakage and no phenol was detected. Emulsion leakage decreased with increased surfactant concentration in the membrane phase. This was mainly due to decrease in the interfacial tension between oil and water by the formation of finer droplets, which produced a stable emulsion. But, the percentage removal of phenol decreased while it exceeded surfactant concentration of 5% (v/v). It was attributed to the increase in the resistance at the interface, which does not favor the extraction kinetics and minimizes the diffusion of phenol [6,7]. Hence, the surfactant concentration of 4% (v/v) is selected in this work.

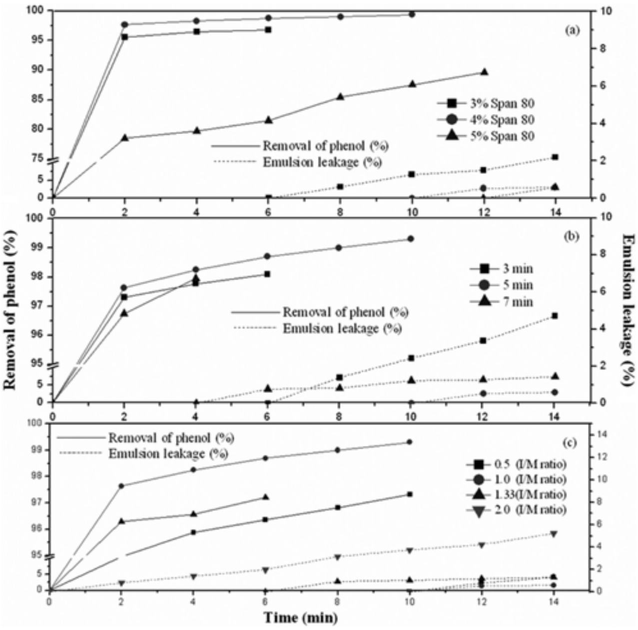

Fig. 2. (a) Effect of surfactant concentration on emulsion leakage and removal of phenol from aqueous solutions (NaOH concentration in internal phase: 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, treat ratio: 3, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm), (b) Effect of emulsification time on the emulsion leakage and removal of phenol from aqueous solutions (concentration of Span 80 : 4% (v/v), NaOH concentration in internal phase: 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, treat ratio: 3, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm), (c) Effect of internal to membrane phase ratio on the emulsion leakage and removal of phenol from aqueous solutions (concentration of Span 80 : 4% (v/v), NaOH concentration in internal phase: 0.5 N, emulsification speed: 8,000 rpm, treat ratio: 3, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm).

4. Effect of Emulsification Time

The effect of emulsification time on the removal of phenol and emulsion leakage was experimentally studied and shown in Fig. 2(b). An increase in the emulsification time from 3 min to 5 min led to an increase in the removal of phenol from 98.08% to 99.3%. Beyond the maximum extraction time, no phenol was detected in external phase due to the reaction with leaked NaOH to form sodium phenoxide. The increase in phenol removal was due to the size reduction of strip phase droplets and improved the homogeneity of the dispersed strip phase. Additionally, a lower leakage was obtained for an emulsification time of 5 min. However, prolonged emulsification time (7 min) led to a decrease in the percentage removal of phenol with an increase in leakage. This may be due to the coalescence of internal phase droplets [6,7]. Thus, an emulsification time of 5 min was chosen as an optimum value for further studies.

5. Effect of Internal to Membrane Phase Ratio (I/M)

The effect of internal to membrane phase (I/M) volume ratio on removal of phenol and emulsions leakage was experimentally studied in the range of 0.5-2. The obtained results are presented in Fig. 2(c). The percentage removal of phenol increased from 97.3% to 99.3% in 10 min with increase in I/M ratio from 0.5 to 1. This was due to the increase in interfacial area by adding more internal phase (in droplets), which enhanced the permeation rate of phenol. Beyond 10 min, no phenol was detected in external phase and sodium phenoxide was detected, which was due to emulsion leakage. However, increasing the ratio from 1.33 to 2, there was a decrease in phenol removal and significant emulsion leakage. This may be explained by the fact that at higher I/M ratio, the volume of membrane phase was not enough to confine all the internal aqueous phase, which led to unstable emulsion and leakage of internal reagent into the external phase. Hence, the optimum I/M ratio of 1 (v/v) was chosen for further study based on maximum extraction of phenol with minimum leakage.

6. Effect of Treat Ratio

The effect of external to emulsion phase volume ratio (treat ratio) in the range from 2 to 10 was studied on removal of phenol and emulsion leakage, and the results are in Fig. 3(a). With an increase in the treat ratio from 2 to 10 (v/v), decrease in removal of phenol from 99.3% to 96.08%. This was due to the area of emulsion per total external phase volume in the ELM system was being reduced and the time at which the emulsion leakage started was extended [6]. However, emulsion leakage was more prominent at a lower

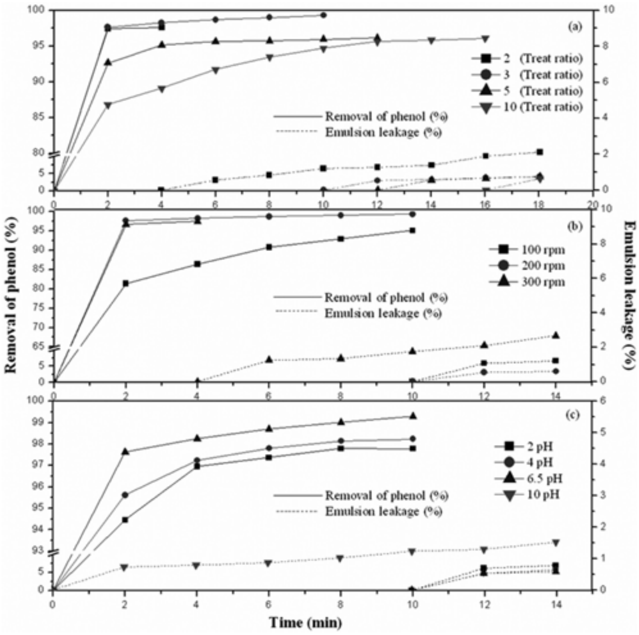

Fig. 3. (a) Effect of treat ratio on the emulsion leakage and removal of phenol from aqueous solutions (Concentration of Span 80 : 4% (v/v), Internal phase concentration (NaOH): 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm), (b) Effect of stirring speed on the emulsion leakage and removal of phenol from aqueous solutions (Concentration of Span 80 : 4% (v/v), Internal phase concentration (NaOH): 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, treat ratio: 3 and phenol concentration in external phase: 300 ppm), (c) Effect of external phase pH on the emulsion leakage and removal of phenol from aqueous solutions (Concentration of Span 80 : 4% (v/v), Internal phase concentration (NaOH): 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, treat ratio: 3, stirring speed: 200 rpm and phenol concentration in external phase: 300 ppm).

treat ratio of 2 (v/v), and this was due to coalescence of emulsion. For higher treat ratios of 3 to 10 (v/v), the emulsion leakage was insignificant and low. Thus, the treat ratio of 3 was chosen for further study.

7. Effect of Stirring Speed

To investigate the effect of stirring speed on removal of phenol and emulsion leakage, experiments were carried out in the range of 100 to 300 rpm and the results are shown in Fig. 3(b). It is evident from the Fig. 3(b) that stirring at 200 rpm provides maximum removal of phenol with lower emulsion leakage. When the stirring speed decreased (<200 rpm), the mass transfer rate of phenol was decreased due to the increase in the size of the emulsion globules. Additionally, emulsion leakage was also greater due to increase in osmotic swelling of the membrane. Above the stirring speed of 200 rpm, phenol removal was not significantly increased and it drastically affected the emulsion stability. This may be due to higher shear force from stirrer, which ruptured the membrane phase, causing the leakage of strip agent into the external phase. Therefore, optimum stirring speed for removal of phenol was chosen as 200 rpm.

8. Effect of External Phase pH

The effect of external phase pH on removal of phenol was studied in the range of 2-10, and the results are in Fig. 3(c). The unadjusted pH of the external phase was 6.5, and it was adjusted to acidic medium (2 and 4) and alkaline medium (10). From Fig. 3(c), it can be clearly observed that removal of phenol was favorable in the external phase pH 2 to 6.5. According to the literature [39], the fraction of the species in aqueous solution exists in molecular form in the range of pH≤7. Then, their anionic fraction increases with increasing in aqueous phase pH. Phenol extraction was enhanced on the hydrogen bonding between the hydroxyl H of the phenols with Cl^- anion of the ionic liquid and hydrophobic interaction between tri-n-octyl methyl ammonium cation of IL with phenol. Although the unadjusted pH of external phase gives maximum phenol removal with minimum emulsion leakage, the other acidic pH showed slight decreased phenol removal. As the external phase pH was increased to 10, no phenol removal was observed. This may be due to reverse transport of NaOH from internal to external phase, which was verified by observing the sodium phenoxide in the aqueous external phase at 290 nm. From the literature [44], the neutral form of (pH= 6.5) phenol in the external phase favors more extraction. Thus, the unadjusted external phase pH of 6.5 was chosen as the optimum value.

9. Removal of Chlorophenols Using Ionic Liquid Based ELM

Experiments were carried out to study the removal of chlorophenols from aqueous solutions at the optimized conditions using ionic

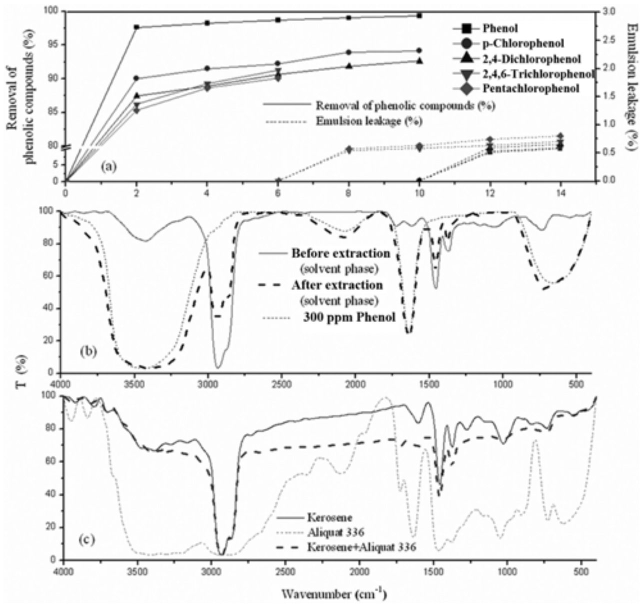

Fig. 4. (a) Removal of phenol and chlorophenols at optimized conditions of IL based ELM. (Concentration of Span 80 : 4% (v/v), Internal phase concentration (NaOH): 0.5 N, I/M ratio: 1, emulsification speed: 8,000 rpm, emulsification time: 5 min, treat ratio: 3, stirring speed: 200 rpm and phenolic compound concentration in external phase: 300 ppm), (b) FTIR spectra of Kerosene, Aliquat 336 and Kerosene+ Aliquat 336, (c) FTIR spectra of Ionic liquid based solvent extraction of phenol (Experimental conditions: aqueous phase-300 ppm of phenol, oil phase-aliquat 336/kerosene/ span 80, shaker speed and time-500 rpm for 30 min).

liquid based ELM, and the results are shown in Fig. 4(a). As can be observed from Fig. 4(a), the percentage removal of phenol, p-Chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol was 99.3, 94.14, 92.60, 91.24 and 90.06, respectively. The maximum removal of phenols with minimum emulsion leakage follows the order: phenol>p-Chlorophenol>2,4-dichlorophenol>2,4,6-trichlorophenol>pentachlorophenol. This behavior can be associated with the charged characteristics of the phenols. The acid dissociation constants (pKa) of phenol, p-chlorophenol, 2,4-dichlorophenol, 2,4, 6-trichlorophenol and pentachlorophenol in water are 9.95, 9.29, 7.85, 6.0 and 4.7, respectively [32,45]. Removal of phenol was higher while compared to all other chlorophenols, and this was due to the inverse relation between pKa and extent of dissociation. All chlorophenols were predominantly present as dissociated form in aqueous solution, which decreased their removal efficiency. All the above results were found from an average of experiments repeated three times at the same condition with a standard deviation value <5%.

10. Characterization of Aliquat 336 for Phenol Removal Using FTIR

Solvent extraction of phenol was performed using 10 mL of kerosene (95.8%), Aliquat 336 (0.2%) and Span 80 (4%) as a membrane phase with 30 mL of 300 ppm aqueous phenol concentration. The experiments were performed in a shaker incubator at 500 rpm for 30 mins and the samples were characterized by FTIR spectroscopy. Fig. 4(b) shows the IR spectrum of solvent (kerosene), Aliquat 336 and their mixture. Fig. 4(c) shows the ionic liquid dissolved solvent before and after phenol extraction. From Fig. 4(b), the peaks at the region 3,000-2,840 cm^{-1} and 1,460 cm^{-1} are attributed to C-H stretching vibration and asymmetrical bending vibration of kerosene. By comparing the IR spectra of pure kerosene with a mixture of Aliquat 336+Kerosene, the disappearance of the peak at 1,275.02 cm^{-1}, 550.22 cm^{-1} and appearance of peak at 1,717.78 cm^{-1} is due to the interaction of tri octyl methylammonium cation with kerosene. Fig. 4(c) shows the characteristic peak of extracted phenol appears at 3,396.13 cm^{-1} (-OH stretch), 1,638.34 cm^{-1} (C=0) and 727.58 cm^{-1} (out of plane C-H bend) in solvent phase after extraction as observed from the same region of aqueous phenol [46,47].

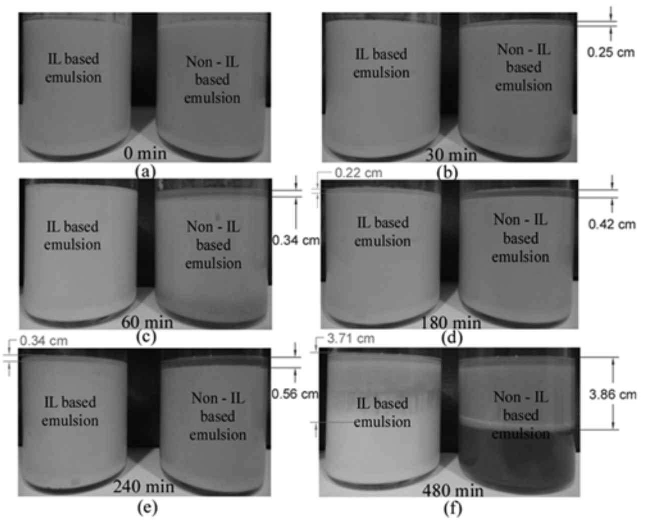

Fig. 5. Emulsion stability test for IL and non-IL based emulsion under static condition for various time intervals (Aliquat 336 concentration: 0.2% (v/v), concentration of Span 80 : 4% (v/v); Internal phase concentration (NaOH): 0.5 N; I/M ratio: 1; emulsification speed: 8,000 rpm; emulsification time: 5 min).

11. Stability Test for Aliquat 336 Based Emulsion under Static Condition

To study the stability of ionic liquid based emulsion, a set of emulsification experiments were conducted using the above optimized parameters and kept under a static condition. To facilitate the visualization of the separated membrane phase clearly with respect to time, Rose Bengal dye was dissolved in membrane phase. The emulsion images were captured at regular time interval with a digital camera (SONY Optical Steady Shot DSC-W360). The images of emulsion for IL and non-IL based emulsion are in Fig. 5. From Fig. 5(b)-(f), the non-IL based emulsion clearly becomes unstable and starts phase separation from 30 minutes itself. The IL based emulsion starts phase separation after 180 min, which shows much better stability than non-IL based emulsion. Increased stability was due to the effectual hydrogen bonding, Coulombic and Van der Waals interactions of Aliquat 336 with Kerosene, Span 80 and NaOH. These interactions avoid the coalescence of internal phase droplets and enhance the emulsion stability [48].

CONCLUSION

Removal of phenolic compounds from aqueous solutions using Aliquat 336 as a carrier in emulsion liquid membrane (ELM) was investigated. The optimum condition for maximum phenol removal was found to be as 0.2% (v/v) of Aliquat 336 in membrane phase, internal phase concentration: 0.50 N, surfactant concentration: 4% (v/v), emulsification time: 5 min, phase volume ratio (I/M): 1 (v/v), stirring speed: 200 rpm and external phase pH: 6.5. Maximum percentage removal of phenol, p-Chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol is (99.3, 94.14, 92.60, 91.24 and 90.06) obtained at the optimized conditions. The addition of Aliquat 336 in membrane phase increased the stability of the emulsion over six times than the emulsion without ionic liquid.

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REFERENCES

1. C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem*., **18**, 275 (2005).
2. S. Pandey, *Anal. Chim. Acta*, **556**, 38 (2006).
3. D. Han and K. H. Row, *Molecules*, **15**, 2405 (2010).
4. X. Han and D. W. Armstrong, *Acc. Chem. Res*., **40**, 1079 (2007).
5. H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol*., **80**, 1089 (2005).
6. Y. S. Ng, N. S. Jayakumar and M. A. Hashim, *J. Hazard. Mater*., **184**, 255 (2010).
7. A. Daas and O. Hamdaoui, *J. Membr. Sci*., **348**, 360 (2010).
8. G. Busca, S. Berardinelli, C. Resini and L. Arrighi, *J. Hazard. Mater*.,

160, 265 (2008).
9. W. Frankenfeld and N. N. Li, *Handbook of Separation Process Technology*, John Wiley & Sons, Inc., New York (1987).
10. S. H. Lin and R. S. Juang, *J. Environ. Manage*., **90**, 1336 (2009).
11. W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capala and I. Ostrowska, *Sep. Purif. Technol*., **40**, 123 (2004).
12. G. Moussavi, B. Barikbin and M. Mahmoudi, *Chem. Eng. J*., **158**, 498 (2010).
13. H. Wang and J. L. Wan, *J. Hazard. Mater*., **154**, 44 (2008).
14. P. S. Majumder and S. K. Gupt, *Bioresour. Technol*., **98**, 118 (2007).
15. V. K. Gupta, I. Ali and V. K. Saini, *Environ. Sci. Technol.*, **38**, 4012 (2004).
16. M. Kallel, C. Belaid, T. Mechichi, M. Ksibi and B. Elleuch, *Chem. Eng. J*., **150**, 391 (2009).
17. O. Chedeville, M. Debacq and C. Porte, *Desalination*, **249**, 865 (2009).
18. D. Manojlovic, D. R. Ostojic, B. M. Obradovic, M. M. Kuraica, V. D. Krsmanovic and J. Puric, *Desalination*, **213**, 116 (2007).
19. W. Kujawski, A. Warzawski, W. Ratajczak, T. Porebski, W. Capala and I. Ostrowska, *Desalination*, **163**, 287 (2004).
20. K. M. Parida and A. C. Pradhan, *J. Hazard. Mater*., **173**, 758 (2010).
21. S. Senel, A. Kara, G. Alsancak and A. Denizli, *J. Hazard. Mater*., **138**, 317 (2006).
22. O. Abdelwahab, N. K. Amin and E. S. Z. El-Ashtoukhy, *J. Hazard. Mater*., **163**, 711 (2009).
23. N. Adhoum and L. Monser, *Chem. Eng. Process*., **43**, 1281 (2004).
24. Y. Yavuz, A. S. Koparal and U. B. Ogutveren, *Desalination*, **258**, 201 (2010).
25. L. C. Branco, J. G. Crespo and C. A. M. Afonso, *Angew. Chem. Int. Ed*., **41**, 2771 (2002).
26. E. Miyako, T. Maruyama, N. Kamiya and M. Goto, *Biotechnol. Lett*., **25**, 805 (2003).
27. A. P. de los Rios, F. J. H. Fernandez, H. Presa, D. Gomez and G. Villora, *J. Membr. Sci*., **328**, 81 (2009).
28. J. Draxler and R. Marr, *Chem. Eng. Process*., **20**, 319 (1986).
29. A. Urtiaga, R. Gutierrez and I. Ortiz, *Desalination*, **245**, 444 (2009).
30. H. R. Mortaheb, M. H. Amini, F. Sadeghian, B. Mokhtarani and H. Daneshyar, *J. Hazard. Mater*., **160**, 582 (2008).
31. H. J. Park and T. S. Chung, *Korean J. Chem. Eng*., **20**, 731 (2003).
32. Y. Park, A. H. P. Skelland, L. J. Forney and J. H. Kim, *Water Res*., **40**, 1763 (2006).
33. M. T. A. Reis, O. M. F. de Freitas, M. Rosinda C. Ismael and J. M. R. Carvalho, *J. Membr. Sci*., **305**, 313 (2007).
34. F. M. M. P. Correia and M. R. J. de Carvalho, *J. Membr. Sci*., **225**, 41 (2003).
35. Y. H. Wan, X. D. Wang and X. J. Zhang, *J. Membr. Sci*., **135**, 263 (1997).
36. S. Venkatesan and K. M. Meera Sheriffa Begum, *Desalination*, **236**, 65 (2009).
37. S. T. M. Vidal, M. J. N. Correia, M. M. Marques, M. R. Ismael and M. T. A. Reis, *Sep. Sci. Technol*., **39**, 2155 (2004).
38. K. S. Khachatryan, S. V. Smirnova, I. I. Torocheshnikova, N. V. Shvedene, A. A. Formanovsky and I. V. Pletnev, *Anal. Bioanal. Chem*., **381**, 464 (2005).
39. J. Fan, Y. Fan, Y. Pei, K. Wu, J. Wang and M. Fan, *Sep. Purif. Technol*., **61**, 324 (2008).
40. C. F. Poole and S. K. Poole, *J. Chromatogr. A*., **1217**, 2268 (2010).
41. Y. C. Fan, M. L. Chen, C. Shen-Tu and Y. Zhu, *J. Anal. Chem*., **64**, 1017 (2009).
42. M. Ettinger, C. Ruchhoft and R. Lishka, *Anal. Chem*., **23**, 1783 (1951).
43. J. Lin, M. Reddy, V. Moorthi and B. E. Qoma, *Afr. J. Biotechnol*., **7**, 2232 (2008).
44. S. Nosrati, N. S. Jayakumar and M. A. Hashim, *J. Hazard. Mater*., **192**, 1283 (2011).
45. P. G. Wightman and J. B. Fein, *Appl. Geochem*., **14**, 319 (1999).
46. R. K. Mishra, P. C. Rout, K. Sarangi and K. C. Nathsarma, *Hydrometallurgy*, **108**, 93 (2011).
47. D. L. Pavia, G. M. Lampman, G. S. Kriz and J. R. Vyvyan, *Introduction to Spectroscopy* (Fourth Ed.), Brooks/Cole, Cengage Learning, Bellingham, USA (2009).
48. R. K. Goyal, N. S. Jayakumar and M. A. Hashim, *J. Hazard. Mater*., **195**, 55 (2011).