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Removal of phenolic compounds from synthesized produced water by emulsion liquid membrane stabilized by the combination of surfactant and ionic liquid

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ABSTRACT

This study was conducted to reduce the phenols concentration in produced water to meet the environmental regulatory limit. Three phenols namely phenol, 2-chlorophenol, and 4-nitrophenol were extracted individually from their aqueous solutions using emulsion liquid membranes prepared using kerosene as the membrane phase, combination of (Span 80) surfactant and a hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$, and NaOH as the stripping agent in the inner phase of the W/O emulsions. Experiments were carried out to study the influence of three emulsion composition variables, namely the ionic liquid concentration, internal aqueous stripping phase to organic phase ratio (ϕ_1), and NaOH concentration in the internal phase, as well as three process parameters, emulsion to external aqueous feed phase ratio (ϕ_2), mixing speed of feed solution, and the initial solute concentration in the feed on the rates of extraction of phenols. The emulsion stability time increases with an increase in the concentration of $[BMIM]^+[NTf2]^-$ up to 0.3% v/v in emulsion. The removal efficiency of phenol from the feed solution with 30 ppm solute was 81% after 10 min and 78% after 30 min. On the other hand, the removal efficiency of both 2-chlorophenol and 4-nitrophenol was 91% after 10 min, and 95% and 98.5%, respectively, after 30 min of permeation under the most favorable operating conditions.

Keywords: Emulsion liquid membrane; Phenolic compound; Produced water treatment; Ionic liquids

1. Introduction

Phenolic compounds are important organic intermediates. They have been largely used in plastics, pharmaceutical, paint, pulp and paper industries, and wood products. Therefore, large quantity of water contaminated with phenol is produced that needs to be treated before it is discharged. This is because to their toxicity and contribution to health problems, phenolic compounds are considered as pollutants of high-priority concerns.

Phenol is one of the most widespread organic water pollutants, because it is toxic even at low concentrations, and also its existence in natural waters causes the formation of substituted compounds throughout disinfection and oxidation processes. Phenol is fatal to fish at low concentrations (5–25 mg/L) and carries unpleasant tastes to drinking water at about 0.5 mg/L.

Hence, it is listed as a priority pollutant according to the US Environmental Protection Agency, and the total phenols in drinking water is controlled to be less than 0.5 µg/L [1]. The toxic scales typically vary between the concentrations of 10–24 mg/L for human. Fatal blood concentration of phenol is about 150 mg/100 mL [2].

Phenol and its derivatives such as 4-nitrophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol are detected in aqueous environment due to the formation of the by-products

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of various industrial processes. These compounds are created in the production of petrochemicals, dyes, plastic, pesticides, drugs, antioxidants, and paper. Most of these derivatives are very toxic and have different influences on the taste and odor of the water at low concentration [3]. Because phenol is relatively soluble and stable in water, its degradation to reach safety levels of 0.1–1 mg/L is relatively difficult [4,5].

Production of oil and gas is usually accompanied by the production and usage of huge amount of water. This produced water consists of the water that exists in subsurface formations, or flood water previously injected to the formation. As exploited reservoirs mature, the quantity of water produced increases. Produced water from oil and gas operations is currently handled as a waste product. The concentration of constituents and the volume of produced water vary significantly based on the geochemistry of the producing formation, the type of hydrocarbon produced, and the characteristics of the producing well. If produced water meets appropriate water quality criteria, it may be used beneficially for purposes such as irrigation, livestock watering, aquifer storage, and municipal and industrial uses. Treatment may be required to improve the quality of produced water so that it can be put to beneficial use. Because many produced waters released contain tens of thousands of tons of organic compounds, including hundreds of tons of phenolic compounds, untreated produced water discharges are harmful to the surrounding environment [6]. The concentration ranges of total phenols in produced water are from 0.4 to 23 mg/L [7].

Numerous treatment technologies have been suggested for treating the produced water such as biological aerated filter, hydrocyclone, dissolved air flotation, adsorption, media filtration, oxidation, settling ponds, air stripping, and ceramic and polymeric micro and ultrafiltration.

Ceramic ultrafiltration and microfiltration membranes are made from oxides, nitrides, or carbides of metals such as aluminum, titanium, or zirconium [8]. Ceramic membranes are much more resilient than polymeric membranes and are chemically and thermally stable, mechanically strong, and can achieve high flux rates. Typically, a tubular configuration is used with an inside-out flow path, where the feed water flows inside the membrane channels and permeates through the support structure to the outside of the module. These membranes typically consist of at least two layers, a porous support layer and a separating layer. Ceramic membranes are able to remove minute particles, organic matter, oil and grease, and metal oxides. Ceramic membranes alone cannot remove dissolved ions and polar organics such as phenols [9–12].

To overcome the limitations of the membrane filtration in separating dissolved ions and polar compounds, it is therefore necessary and important to develop an emulsion liquid membrane (ELM) process to efficiently separate phenolic compounds that can be integrated with the ceramic membrane filtration systems.

Liquid membrane was first suggested in 1968 by Li [13] in the Exxon laboratories, who initially used O/W emulsion to separate paraffins from aromatics, but it was quickly realized that ELMs would be a far better tool to separate solutes from aqueous streams using W/O emulsions, subsequently Li and coworkers [14–19] separated toxic substances such as phenols and heavy metals from water into ELMs.

ELMs for removal of solutes from aqueous streams are formed by preparing a W/O emulsion and then dispersing it in a continuous aqueous feed that needs to be treated. The emulsion is prepared by mixing known volume of oil phase with a suitable emulsifier having hydrophilic–lipophilic balance of value ranging between 3 and 8 to obtain the chosen emulsion. To this oil phase, known volume of aqueous phase containing the selected stripping reagent is added. The resulting oil–water mixture is then vigorously agitated using a high-speed homogenizer to produce the W/O emulsion. The resulting milky white emulsion is then dispersed in the continuous water phase with mild agitation. The emulsion breaks up into small globules of about 0.1–2 mm in diameter and within each globule there exists tiny aqueous droplets of the internal aqueous phase having size usually in the range of 1–10 μm. In this process, the pollutants transport from the aqueous feed phase to the organic phase through which they transport to the tiny aqueous globules to be reacted with the stripping reagent. The large surface area generated in this process leads to very fast rates of removal of pollutants from the feed phase. After a certain contact time between the emulsion and the feed phase, the solute is removed from the feed phase and concentrated in the emulsion phase. At the end of the contacting time, the emulsion is separated from the continuous phase by settling and the encapsulated aqueous phase can be recovered by breaking the emulsion.

It was Li [13] who visualized that the capacity of ELM for removal of solutes such as phenols in the presence of an appropriate reactive reagent could be substantially enhanced. For the case of phenol removal from bulk solutions, using an ELM would not yield any significant removal if the inner phase of the ELM consists of only water. The extraction would stop when the concentration of phenol becomes identical in the internal phase of the ELM and external aqueous phase, which would contribute to a small amount of phenol being extracted. However, if a reagent such as NaOH is present in the internal phase, then the phenol that is transferred into the internal phase reacts instantaneously as per Eq. (1) forming insoluble sodium phenolate, which is entrapped in the internal aqueous phase droplets.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \quad (1)$$

Thus, NaOH enhances the capacity of the emulsion to load the solute, maintains concentration gradient for phenol to diffuse in the emulsion resulting in enhanced transport rates, and entraps the solute in the internal aqueous phase droplets of the emulsion and does not permit the back diffusion of the species because while phenol is oil soluble, sodium phenolate is not [20]. A schematic diagram for the phenol extraction by ELM is shown in Fig. 1.

The stability of the water-in-oil-in-water (W/O/W) emulsions is known as one of the most serious problems in the application of the ELM to industrial separation. The instability of the emulsion can be caused by repeated coalescence of the internal droplets on the interface, creaming due to density difference, Ostwald Ripening and flocculation. Several techniques have been proposed to improve emulsion stability, and these include the use of aliphatic solvent instead of aromatic solvent [21] aliphatic solvent with long carbon chain [22], high surfactant concentration [23], high membrane viscosity [24], the use of co-surfactants [25], adding polymer to the organic phase or non-Newtonian conversion of the membrane phase [26], the use of Janus particles as stabilizers in emulsion polymerization [27] and the use of functionalized silica particles for high internal phase emulsion [28]. Nevertheless, every remedy has its own tradeoffs.

Room temperature ionic liquids are a group of low-melting point salts that consist of organic cations and organic/inorganic anions. They have negligible vapor pressure, inflammability, thermal stability even at high temperatures, and application-based adjustable miscibility/immiscibility in chemical processes [29–34]. These unique properties serve them as an option to replace the volatile organic solvents for removal process of an organic pollutant. Ionic liquids possess a very negligible vapor pressure that has enabled them to be used as a "green solvent" in chemical synthesis [35–37], separation and purification [38–40], and in electrochemical applications [41].

Goyal et al. [42] showed that the stability of a W/O emulsion with kerosene as solvent was improved by incorporating the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$, in the membrane phase as a stabilizer. They showed that by the addition of 3 wt% $[BMIM]^+[NTf_2]^-$ the stability of the W/O emulsion could enhanced from a few minutes up to 7 h. Goyal et al. [21] used 1-butyl-3-methylimidazoli bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$, as a stabilizer in the preparation of ELM phase containing kerosene as solvent, Span 80 as surfactant, NaOH as internal phase, and TOMAC (tri-n-octylmethylammonium chloride) a second ionic liquid as carrier for the extraction of chromium. $[BMIM]^+[NTf_2]^-$ will therefore be used in this research in combination with Span 80 for the extraction of phenolic compounds, due to its low viscosity (52 mPas) compared with other ionic liquids, which facilitates the homogenous dispersion in ELM. It is also hydrophobic and has a low toxicity and a low density [42].

Therefore, in this work, the factors affecting the extraction efficiency of ELM system stabilized by a combination of (Span 80) surfactant and a hydrophobic ionic liquid $[BMIM]^+[NTf_2]^-$ for the removal of phenolic compounds (phenol, 4-nitrophenol, and 2-chlorophenol) from synthesized produced water were studied.

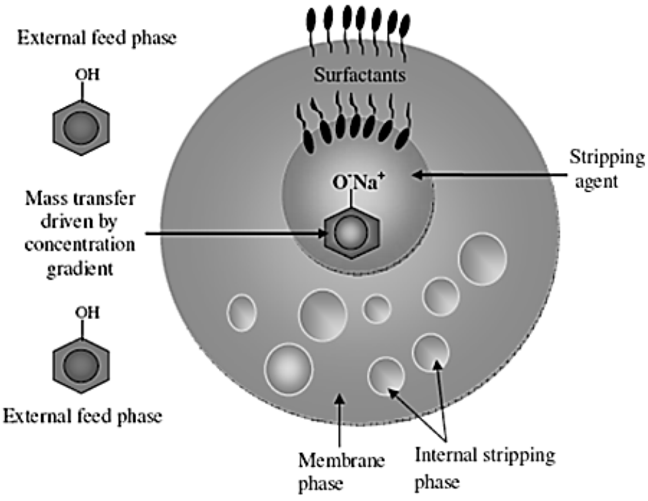


Fig. 1. Schematic of phenol extraction by ELMs.

2. Materials and methods

2.1. Chemicals

Kerosene of boiling point ranged from 175°C to 325°C, Span 80 (sorbitan monooleate), sodium hydroxide pellets, hydrochloric acid, phenol, 4-nitrophenol, 2-chlorophenol, and ionic liquid $[BMIM]^+[NTf_2]^-$ were obtained from Sigma-Aldrich (USA). The structural formula of the ionic liquid is illustrated in Fig. 2, and the physical properties are given in Table 1. The solutions of sodium hydroxide (NaOH) of desired concentration and phenolic compounds of 30 ppm (mg/L) were prepared by dissolving appropriate weight in de-ionized water.

2.2. Experimental work

Water-in-oil (W/O) type emulsion was prepared by slowly adding the internal stripping phase NaOH with concentrations, C_{io} of 0.3 and 0.5 M to the organic membrane phase which contains kerosene, 3% w/v Span 80, and ionic liquid $[BMIM]^+[NTf_2]^-$ of 0.1, 0.2,0.3, 0.4, and 0.5% v/v, with intensive mixing provided by a high-speed homogenizer Ultra Turrax IKA-T25, which is operated at a rotational speed of 7,000 rpm for 10 min so as to obtain a milky white color liquid membrane. Volume ratios of the internal stripping phase to organic phase (kerosene) (ϕ_1) were 1/1, 1/2, 1/3, and 1/7. The W/O emulsion was dispersed in the feed phase containing phenolic compounds (phenol, 4-nitrophenol, and 2-chlorophenol) with initial concentrations of 5 and 30 ppm (mg/L) in a ratio of emulsion to external aqueous feed phase ratio (ϕ_2) as 1/10, 1/12, and 1/15 by volume and stirred by IKA, model: RW20 digital overhead stirrer with an agitation speed of 200, 250, 300, and 400 rpm for 30 min. The pH of the feed phase was measured by Oakton Acorn pH meter. Fig. 3 shows the schematic diagram of the ELM process.

Samples were taken from the agitated solution at various time intervals using a micropipette. The samples were separated from the emulsion phase by filtration using a nylon syringe filter with nominal pore size of 0.2 µm (Simsii, Inc., USA).

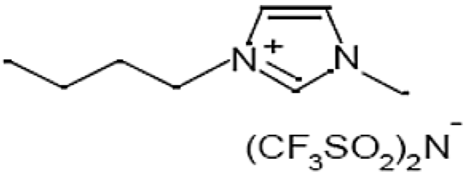


Fig. 2. Structure of $[BMIM]^+[NTf_2]^-$ ionic liquid.

Table 1
Physical properties of $[BMIM]^+[NTf_2]^-$ ionic liquid

Appearance	Colorless liquid
Molecular weight (g/mol)	419.36
Density (g/cm³ at 20°C)	1.43
Refractive index	1.4282
Viscosity (cP at 25°C)	61.14
Melting point (°C)	–4
Decomposition temperature (°C)	439

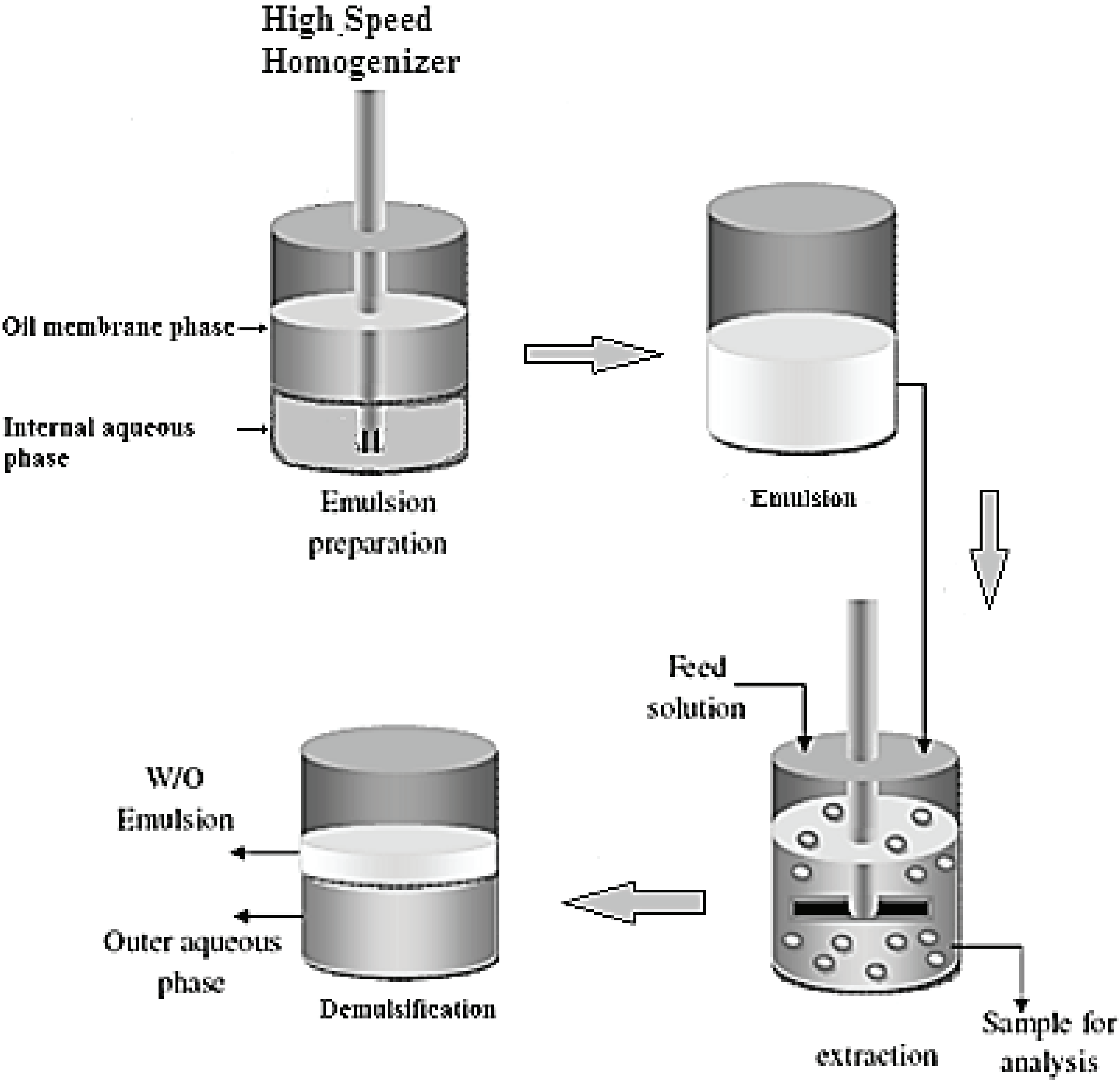


Fig. 3. Schematic representation of the removal of phenolic compounds by ELM.

Several photographs were taken for measuring the mean diameter of internal phase droplet size and emulsion globules under the operating conditions tested. The latest Hirox digital microscope model (KH-8700) was used for this purpose.

During the ELM extraction, the concentration of phenolic compounds (phenol, 4-nitrophenol, and 2-chlorophenol) in the aqueous external phase decreases with time as reflected by the decrease in light absorbance determined by Varian Cary 100 Bio Spectrophotometer. To find the phenols concentration in the external phase at any time during the process, calibration curves for absorbance vs. phenolic compounds concentration were prepared by measuring the absorbance of different known concentration samples prior to the experiments. The measurement of maximum absorbance took place at the following wavelengths: phenol, 270 nm; 4-nitrophenol, 317.6; and 2-chlophenol, 273 nm.

3. Results and discussion

In all data presented in this section, the concentration of NaOH in the internal phase was 0.3 and 0.5 M, and the external phase was water containing 5 and 30 ppm phenolic compounds (phenol, 4-nitrophenol, and 2-chlorophenol). Volume ratios of internal stripping phase to the organic phase (kerosene) (ϕ_1) were 1/1, 1/2, 1/3, and 1/7, and the emulsion to the external aqueous phase volume ratio (ϕ_2) were 1/10, 1/12, and 1/15. Surfactant (Span 80) concentrations was 3% w/v and ionic liquid $[BMIM]^+[NTf_2]^-$ 0.1, 0.2,0.3, 0.4, and 0.5% v/v. The percentage removal efficiency is defined as ($[1-C_t/C_0] \times 100$). However, presenting the results in terms of this removal efficiency does not demonstrate the effects of the studied parameters clearly. Therefore, the extraction results are presented in figures in terms of remaining fraction of the phenolic compounds (C_t/C_0) vs. contact time t which gives better illustration of the extraction results.

3.1. Stability enhancement resulting from adding $[BMIM]^+[NTf_2]^-$ in emulsion

Experiments were carried out to study the effect of ionic liquid addition on emulsion stability. The relation between emulsion stability time and the concentration of $[BMIM]^+[NTf_2]^-$ is shown in Fig. 4. The stability time increases with an increase in the concentration of $[BMIM]^+[NTf_2]^-$ up to 0.3% v/v of $[BMIM]^+[NTf_2]^-$. The stability time was found to be decreasing with higher ionic liquid concentration, which could be explained by increased emulsion sedimentation due to the high density of $[BMIM]^+[NTf_2]^-$.

The increased stability of the ELM by the addition of $[BMIM]^+[NTf_2]^-$ may be resulted from Coulombic interactions of the charges on the ions of ionic liquids $[BMIM]^+[NTf_2]^-$ and NaOH. This strong interaction helps to lower the coalescence of the internal droplets and enhance the emulsion stability [43]. There is also a possibility of hydrogen bonding present between $[BMIM]^+[NTf_2]^-$ and [OH]− group of NaOH. The hydrogen bonding may cause a strong protection surrounding the internal droplets to avoid coalescence [44].

The addition of ionic liquid can further reduce the interfacial tension, also through adsorbing in the W/O interface and thereby minimizing the repulsion of the hydrophilic head groups of the surfactants, which contributes to a more efficient packing of the surfactants at the interface and reduces the internal phase droplet size. Fig. 5 shows a schematic picture of the packed ionic liquid molecules between the Span 80 molecules.

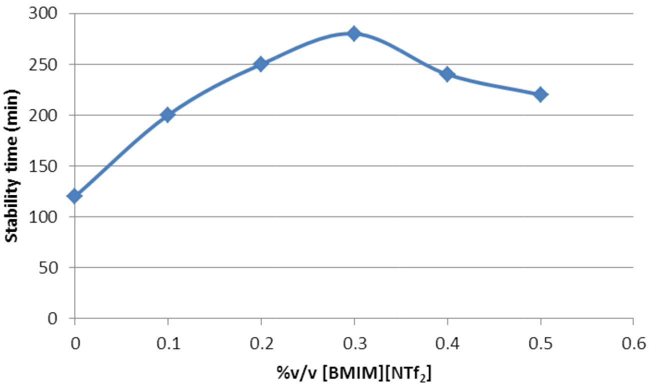


Fig. 4. The effect of $[BMIM]^+[NTf_2]^-$ concentration on the stability time of ELM. 3% w/v of Span 80, 0.3 M of NaOH, emulsification speed of 7,000 rpm, mixing speed of feed solution of 300 rpm, and $\phi_1 = 1/3$.

3.2. Effect of the internal stripping phase to organic phase ratio (ϕ_1) and NaOH concentration in the inner phase (C_{io}) on the internal drop size distribution of W/O emulsion

The size distribution of the inner phase droplets is the most important parameter in characterizing of any emulsion. Two emulsions may have the same average drop diameter and yet exhibit quite dissimilar behavior because of differences in their distribution of the diameters. Stability and resistance to creaming, rheology, chemical reactivity, and physiological efficiency are few of the phenomena influenced by both relative size and size distribution [45].

Emulsions are seldom composed of droplets of uniform sizes; if droplet size exhibits a wide statistical distribution, the emulsion is polydisperse in contrast to monodisperse systems. The ideal size depends on the methods of preparation and most emulsions are polydisperse. If droplet division takes place according to a geometrical series, a monodisperse system is approached. Polydisperse systems are due to the formation of smaller fragments.

Internal droplet sizes of emulsions prepared using kerosene as the oil phase, Span 80 and $[BMIM]^+[NTf_2]^-$ as surfactants, and NaOH as the internal phase were measured as described in the experimental work. The effect of the internal stripping phase to organic phase ratio (ϕ_1) on the internal drop size distribution of the emulsion is shown in Fig. 6.

It is seen from Fig. 6(a) that when the internal stripping phase to oil phase ratio (ϕ_1) is 1/3, almost 50% of the droplets happened to be of 1.5 μm in diameter and 35 % were of 3.2 μm in diameter, and just 15% droplets were of larger sizes. Increasing (ϕ_1) to 1/2 changes the drop sizes as well as size distribution as seen in Fig. 6(b). In this case, it was observed that 60% of droplets were having 3.5 μm diameter while 13% of size 6.7 μm and 20% of 10.2 μm in diameter. Further increasing (ϕ_1) to 1/1 changes the distribution again as seen in Fig. 6(c). One can conclude that the dominant droplet diameters in this case were 6.8 , 10.2,and 13.5 μm having frequencies of 36%, 28%, and 20%, respectively.

Fig. 7 shows optical microscopy images of internal droplets at (ϕ_1) values of 1/3, 1/2, and 1/1, respectively. One can clearly distinguish the change in the internal droplet size with increasing (ϕ_1), where larger internal droplets were obtained

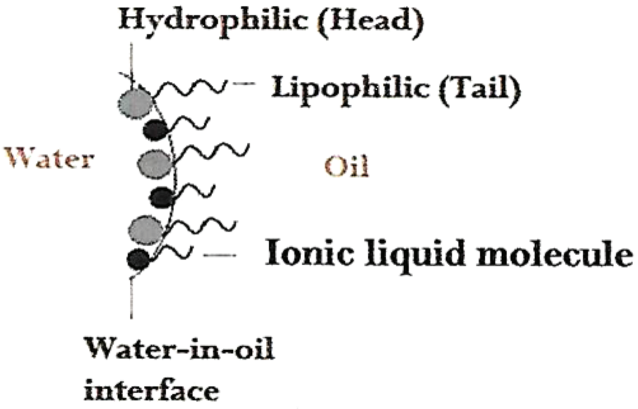
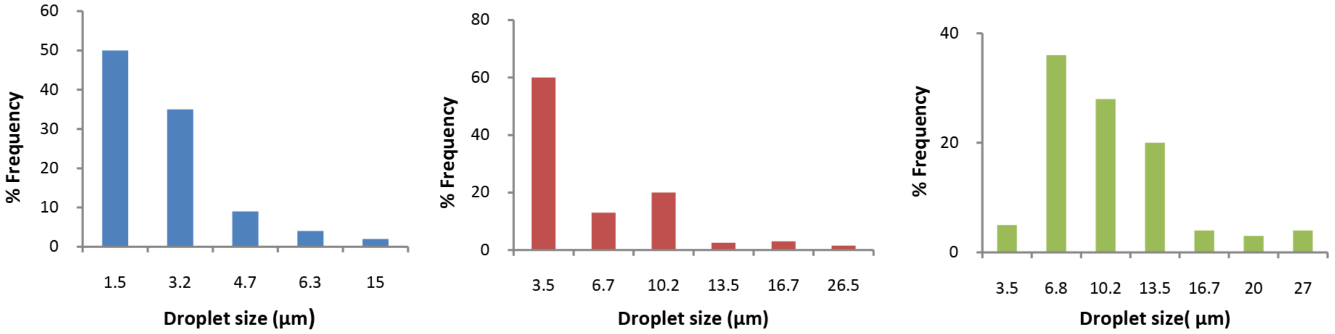
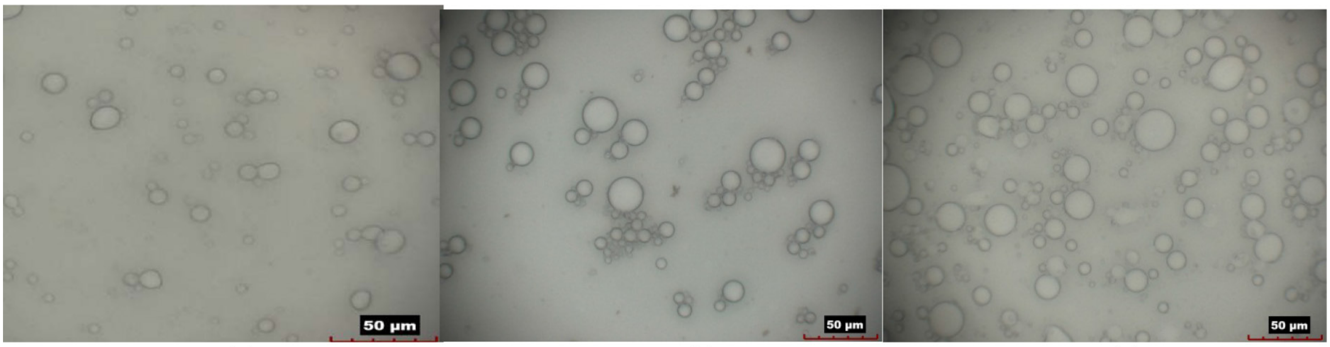


Fig. 5. Schematic picture of the ionic liquid molecules packed between the surfactant molecules consisted of hydrophilic head and lipophilic tail.



(a) (b) (c)

Fig. 6. Internal phase droplet size distribution at (a) ϕ_1 = 1/3, (b) ϕ_1 = 1/2, (c) ϕ_1 = 1/1, 3% w/v of Span 80, emulsification speed of 7,000 rpm, C_{io} = 0.3 M, and 0.3% v/v of $[BMIM]^+[NTf_2]^-$.



(a) (b) (c)

Fig. 7. Optical microscope images of emulsions stabilized by 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, emulsification speed of 7,000 rpm, and C_{io} = 0.3 M immediately after preparation. The internal stripping phase to oil phase ratios (ϕ_1) are (a) 1/3, (b) 1/2, and (c) 1/1. The scale bars in the figure are 50 µm.

and also more agglomeration of droplet can be observed for a value of (ϕ_1) 1/1. The same observation was obtained by Morrison and Ross [46].

The change in the internal drop size distribution with increasing NaOH concentration in the inner phase (C_{io}) is shown in Fig. 8. The emulsion studied had internal stripping phase to organic phase ratio (ϕ_1) of 1/3 with C_{io} = 0.5 M. This result could be compared with Fig. 6(a) that reports the drop size distribution data for an emulsion having the same value of ϕ_1, but with C_{io} = 0.3 M. It could be clearly made out, from Fig. 8, that the internal droplet size of the emulsion showed a definite increase with increase in C_{io}. When C_{io} = 0.3 M almost 50% of the droplets happened to be of 1.5 µm in diameter and 35% were of 3.2 µm in diameter. While when C_{io} was increased to 0.5 M, 15% of droplets happened to be of 1.5 µm in diameter, 28% droplets were of 3.2 µm, 32% were of 4.7 µm, and 16% were of 6.3 µm diameter, respectively.

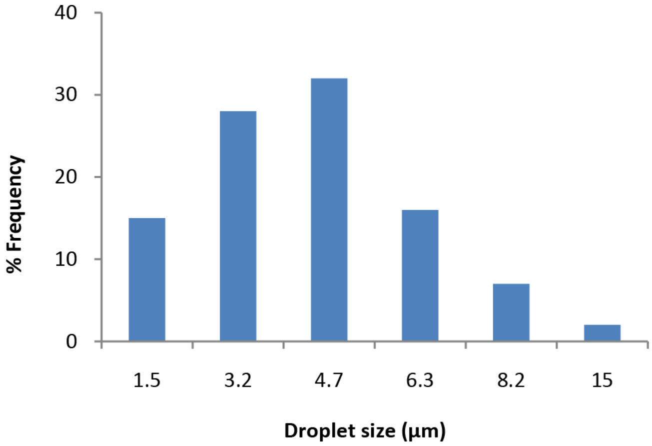


Fig. 8. Internal phase droplet size distribution at emulsification speed of 7,000 rpm, ϕ_1 = 1/3, 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, and C_{io} = 0.5 M.

3.3. Effect of stirring speed on the dispersion behavior of emulsions

The W/O emulsions containing NaOH in its internal phase when dispersed in the feed solution by agitation break down and form a large number of tiny globules with approximate size that ranges from 0.5 to 3.0 mm. Each emulsion globule contains numerous tiny encapsulated droplets of internal aqueous phase of sizes ranging from 1 to 30 µm in diameter. The effectiveness of the ELMs is never constrained by the inner surface areas. It is rather the external surface of dispersed emulsion (organic with tiny droplet of aqueous internal phase) globules that often dictates the rates of mass transfer. In order to ensure rapid mass transfer, it is necessary to disperse the emulsion appropriately in the continuous phase. The smaller the globule size, the larger the number of globules and larger the surface area are. Generally, the size of the emulsion globule depends on the viscosity of the emulsion, dispersion characteristics and concentration of the stripping reagent in the emulsion, and intensity and mode of mixing [47].

In order to assess the dispersion characteristics of ELMs in the feed solutions, a number of runs were performed at different stirring speeds (200, 250, 300, and 400 rpm). The ELMs used in these runs had internal phase fraction $\phi_1 = 1/3$, Span 80 concentration in the oil phase of 3% w/v, $[BMIM]^+[NTf_2]^-$ concentration of 0.3% v/v, internal phase NaOH concentration of 0.3 M, and the treat ratio (emulsion volume/feed volume, ϕ_2) was maintained at 1/12. It was observed that at 250 rpm, the emulsion got well dispersed in the continuous phase. It was visually observed that below 250 rpm, the emulsion was just not adequately dispersed and even at 250 rpm there was some amount of emulsion residing as a film on the surface of the aqueous phase. Increasing the stirring speed to 300 rpm resulted in a dispersion that is typical of ELMs, where globule sizes appeared to remain constant over the period of run and they were smaller in size in comparison with the globule sizes observed at 250 rpm. Increasing the mixing speed to 400 rpm leads to the formation of smaller sized globules dispersed in the external phase, thereby greater interfacial area for mass transfer. However, at the same time, the higher mixing speed affects the stability of emulsion globules which may lead to globule rupture, causing the leakage of strip agent into the external phase. Therefore, the rate of extraction level can be reduced in the long run. Consequently, a mixing speed of 300 rpm was chosen to be most appropriate for conducting the experiments.

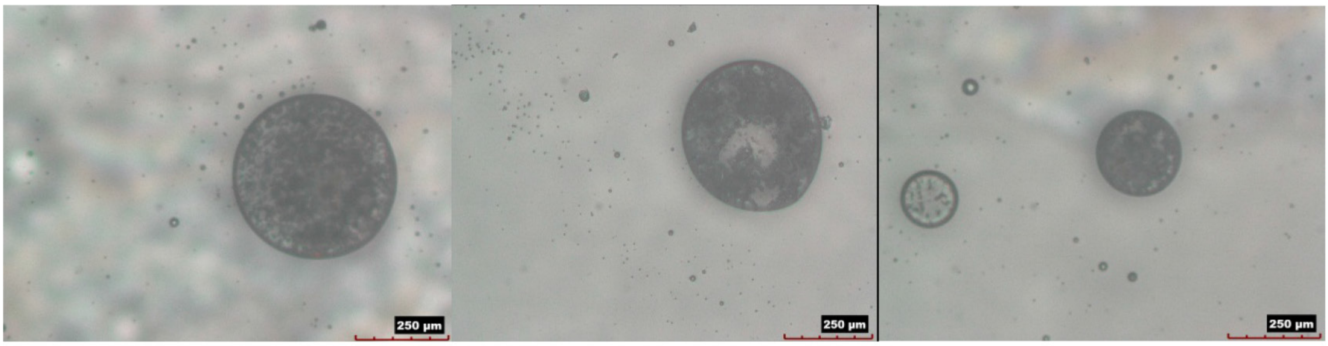
Fig. 9 shows the dispersion behavior at stirring speeds of 250, 300, and 400 rpm at time duration of 3 min. It can be seen that emulsion globules diameter is significantly reduced at higher mixing speed of feed. This was expected, as greater shear creates a higher globule surface area.

3.4. Distribution coefficients of phenols between kerosene and water

The distribution coefficients for phenol, 2-chlorophenol, and 4-nitrophenol were experimentally determined by equilibrating equal volumes of aqueous solute phase with kerosene phase. Data were obtained for initial aqueous concentrations ranging from 10 to 30 ppm of these compounds. The distribution coefficient, m, is defined as the ratio of the solute concentration in the organic phase (kerosene) to the solute concentration in the aqueous phase. The distribution coefficient plots are reported for the three solutes in Fig. 10.

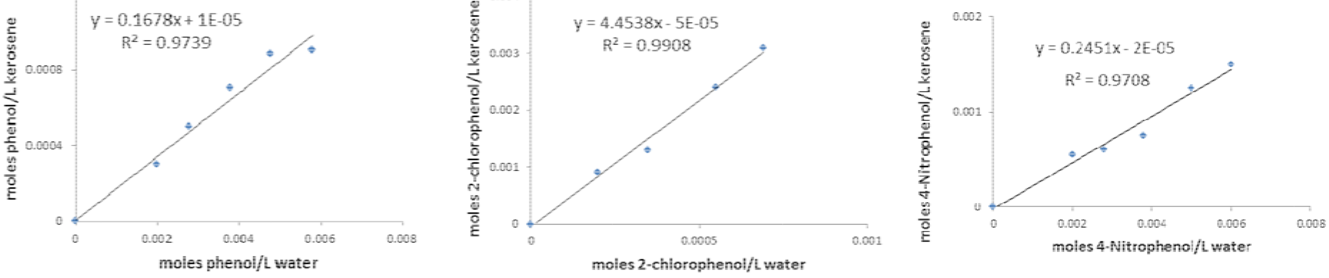
Table 2 below reports the distribution coefficients (m) for the system kerosene/water and the correlation coefficients of the fitted equation to the experimentally obtained data points for the three solutes.

One aspect that is unique with the extraction of 2-chlorophenol is that the amount extracted is much larger in



(a) (b) (c)

Fig. 9. Optical micrograph of emulsion globules with 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, $C_{io} = 0.3$ M, emulsification speed of 7,000 rpm, $\phi_1 = 1/3$, $\phi_2 = 1/12$, 30 ppm of phenol, pH of feed solution 6.8, mixing speed of feed solution (a) 250 rpm, (b) 300 rpm, and (c) 400 rpm. The scale bars in the figure are 250 μm.



(a) (b) (c)

Fig. 10. Distribution coefficients of (a) phenol, (b) 2-chlorophenol, and (c) 4-nitrophenol.

comparison with phenol and 4-nitophenol under identical conditions. This behavior stems out from the fact that 2-chlorophenol has a very favorable distribution coefficient towards kerosene over water.

3.5. Prediction of the effective diffusivities of phenolic compounds in the W/O emulsion

In order to predict the effective diffusivities (D_{eff}) of the individual solutes (phenol, 2-chlorophenol, and 4-nitrophenol) within the emulsion globules; (i.e., inside the organic phase toward the tiny internal aqueous droplets) it is necessary to first estimate the diffusion coefficients of these solutes in both water and kerosene phase. The Wilke–Chang Eq. (2) was used to evaluate the diffusion coefficients (D_{AB}) of the various solutes in both water and kerosene.

$$D_{AB} = 1.17\times10^{-16}\,\frac{T\left(\Psi M\right)^{0.5}}{\mu V_A^{0.6}} \tag{2}$$

where, ψ is the solvent association factor, for the aqueous and oil phases, which are 2.6 and 1.0, respectively; V_A is the solute molar volume (m^3/kg mol); μ is the viscosity of solvent (kg/m s), and M is the molecular weight of solvent (kg/kg mol) [48,49].

Then the effective diffusion coefficients were estimated using the Jefferson–Witzell–Sibbett equation (Eq. (3)) [50,51], following the lead of Ho et al. [52] who were the first investigators to conveniently use this equation that had been originally proposed for conductive heat transfer in dispersed systems for estimation of D_{eff} in ELMs.

$$D_{eff} = \frac{A_A}{A_S}\left[\frac{\left(0.5+n\right)D_A D_W}{0.5D_w + nD_A}\right] + D_W\frac{A_B}{A_S} \tag{3}$$

where

$$D_A = 2mD_M D_W\left[\frac{mD_M}{\left(D_W - mD_M\right)^2}\log\left(\frac{mD_M}{D_W}\right) - \frac{1}{\left(mD_M - D_W\right)}\right] \tag{4}$$

$$A_S = \left(1+2n\right)^2 \quad A_B = \left(1+2n\right)^2 - \frac{\pi}{4} \quad A_A = \pi/4 \tag{5}$$

$$\mathrm{n} = 0.403\phi_1^{-1/3} - 0.5 \tag{6}$$

m is the solute distribution coefficient between membrane phase and aquoeus phase, ϕ_1 is the internal to organic phase volume fraction (microdrop holdup), D_W is the diffusion coefficient of the solute in water, and D_M is the diffusion coefficient of solute in membrane calculated from Eq. (2). The calculated values of the diffusion coefficients for various phenolic compounds are given in Table 3.

Table 2
Distribution coefficients of phenols between water and kerosene

Solute	m	R^2
Phenol	0.168	0.974
2-Chlorophenol	4.454	0.991
4-Nitophenol	0.245	0.971

The Jefferson–Witzell–Sibbett equation was used to estimate the effective diffusivity of phenols in the emulsion mixture based on concentration driving force defined in terms of membrane phase concentration. The only emulsion parameter that influences the effective diffusivities is ϕ_1. The calculated values of the effective diffusivities for various solutes used in this investigation are presented in Table 4.

The effective diffusivity represents the diffusivity of phenols in the membrane phase (diffusion of solutes moving inside the organic phase toward the tiny aqueous internal phase droplets). It is larger than the diffusivity in the organic phase, D_M. The effective diffusivity also increases when the internal stripping phase to organic phase ratio (ϕ_1) decreases. The effective diffusivities indicate that the mobility of these compounds in the membrane phase obeys the following order: phenol > 4-nitrophenol > 2-chlorophenol.

3.6. Comparative extraction of phenols

The extraction of phenols from aqueous solution was found to be easily achieved using emulsion liquid system with membrane containing only an aliphatic solvent (kerosene) and a combination of an emulsifying agent (Span 80) and ionic liquid ($[\mathrm{BMIM}]^+[\mathrm{NTf}_2]^-$). The results obtained are presented in Fig. 11 in terms of the fraction of the phenolic compounds remaining in the aqueous feed (net extracted), C_t/C_0. This is as mentioned earlier provides clearer effects as opposed to the fraction extracted or remained ($1–C_t/C_0$). Hence, reduction in the remaining compounds means improved efficiency of extraction. Therefore, here all the data are presented in terms of C_t/C_0. As can be observed, 4-nitrophenol and 2-chlorophenol showed a different behavior from the one exhibited by phenol and that of 4-nitrophenol where the trend crosses the trend for 2-chlorophenol after 10 min of extraction time.

Comparison of the extraction rates of 2-chlorophenol and 4-nitrophenol indicates that 2-chlorophenol is extracted more

Table 3
Diffusion coefficients of phenolic compounds in aqueous and membrane phases

Solute	Phenol	2-Chlorophenol	4-Nitrophenol
D_W (m^2/s)	1.0163×10^{-9}	0.9385×10^{-9}	0.9836×10^{-9}
D_M (m^2/s)	1.1417×10^{-9}	1.0543×10^{-9}	1.1049×10^{-9}

Table 4
Effective diffusivities of phenolic compound in ELM

Solute	Phenol	2-Chlorophenol	4-Nitrophenol
ϕ_1	D_{eff} (m^2/s)	D_{eff} (m^2/s)	D_{eff} (m^2/s)
1/7	7.4406×10^{-6}	1.0055×10^{-8}	1.1477×10^{-7}
1/3	6.7955×10^{-6}	1.1446×10^{-8}	1.0971×10^{-7}
1/2	6.4940×10^{-6}	1.1897×10^{-8}	1.0712×10^{-7}

rapidly than that of 4-nitrophenol in the early stages of the experiment or shorter residence contact time because the distribution coefficient (m) of 2-chlorophenol shown in Table 2 is much larger than that of 4-nitrophenol. However, at later stages longer residence contact time, the degree of extraction of 4-nitrophenol is higher because of its larger acid dissociation constant (K_a) as shown in Table 5. On the same lines, it is observed that for phenol the distribution coefficient (m) is smallest among all the solutes studied and the acid dissociation constant (K_a) is also the smallest. This explains why phenol extraction trend displays the smallest rate of extraction and also the smallest extent of extraction.

The removal of phenol from the feed solution with 30 ppm solute was 81% after 10 min and 78% after 30 min. On the other hand, the removal of both 2-chlorophenol and 4-nitrophenol was 91% after 10 min and 95% and 98.5%, respectively, after 30 min of permeation.

The removal of the studied phenolic compounds was under different sets of conditions such as the variation in ϕ_1, ϕ_2, and C_o. The results are presented and discussed in the following sections:

3.6.1. Effect of (ϕ_1) on the extraction of phenols

The phase fraction of aqueous internal phase to organic phase (ϕ_1) has a significant effect on extraction using ELMs. Change in the internal phase fraction not only leads to a change in the emulsion properties as shown in section 3.2, but also results in an increase in the capacity of the emulsion to extract the solute. The effect of the phase fraction (ϕ_1) on extraction of phenols is shown in Fig. 12 in terms of C_t/C_0 as mentioned earlier. From this figure, it was observed that for ratios (ϕ_1) of 1/1, 1/2, 1/3, and 1/7, the percentage removal of phenols increases (for which the remaining fraction of phenols C_t/C_0 decreases) with the decrease of ϕ_1. This may be due to that sufficient organic phase will be available for enclosing all the internal phase and the dispersion of the W/O emulsion was easier [53,54]. However, it was also found that decreasing the internal organic phase ratio beyond 1/3 did not enhance phenols removal. This phenomenon could be due to the builtup resistance around the membrane at the low ratio of internal aqueous stripping phase to organic phase (ϕ_1). The increase in thickness of the organic membrane phase offered resistance that slowed down the phenols permeation rate. Additionally, for larger volume ratios, the volume of membrane solution is not enough for enclosing all the stripping solution [55].

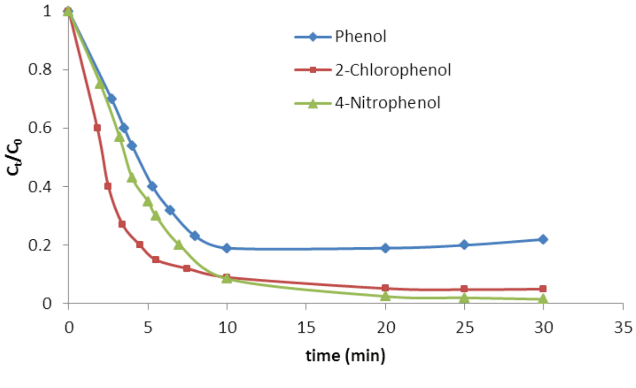


Fig. 11. Extraction trends of phenols (ϕ_1 = 1/3, 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, C_{io} = 0.3 M, 300 rpm, ϕ_2 = 1/12, and C_0 = 30 ppm).

Table 5
Acid dissociation constant for phenols at 25°C

Solute	K_a at 25°C
Phenol	1.1×10^{-10}
2-Chlorophenol	77×10^{-10}
4-Nitrophenol	708×10^{-10}

Thus, in order to obtain a uniform and homogeneous distribution of the stripping aqueous phase droplets in the organic membrane solution, the volume ratio of aqueous internal phase to organic phase (ϕ_1) of 1/3 was selected as the best volume ratio for the studied conditions.

3.6.2. Effect of Treatment ratio (ϕ_2) on the extraction of phenols

The treatment ratio ϕ_2, defined as the volume ratio of emulsion phase (organic phase plus the internal aqueous stripping phase) to the external aqueous feed phase, has an important role in determining the effectiveness of ELMs. It is known that the rate of mass transfer in ELM systems is directly related to the specific mass transfer area (m^2/m^3). The emulsion to feed ratio is identical with the solvent to feed ratio in the conventional liquid–solvent extraction. It is a measure of the emulsion holdup in the system. An increase in the emulsion to the feed ratio results in an increase of the emulsion phase holdup leading to an increase in the extraction capacity of the emulsion. It also results in an increase in overall surface area for mass transfer in the system and hence the extraction efficiency. Experiments were performed using ϕ_2 values of (1/10, 1/12, and 1/15) to study the influence of treatment ratio on the extraction of phenols. It can be seen from Fig. 13 in terms of the remaining fraction of the pollutants (C_t/C_0) that at a treatment ratio of 1/12, the extraction of the phenols from external feed phase was high and that the increase in extraction efficiency when increasing the treatment ratio was not achieved. In general, with the increase

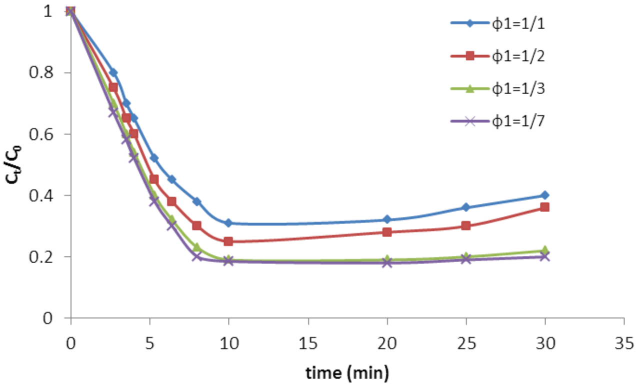


Fig. 12. Effect of phase fraction of aqueous internal phase to organic phase (ϕ_1) on the extraction of phenol, 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, C_{io} = 0.3 M, 300 rpm, ϕ_2 = 1/12, and C_0 = 30 ppm.

in treatment ratio an increase in the rate of mass transfer is verified, because the capacity of the internal phase to act as solute sink increases, but requires higher emulsion volume. It was noticed that the influence of ϕ_2 ratio on the emulsion stability was insignificant, because the breakage increases very slightly with an increase of ϕ_2 ratio [54,56].

The small volume of the emulsion is always desirable to make ELM less expensive compared with liquid–solvent extraction, as long as there is sufficient stripping agent to extract all of the phenols from the external feed phase, therefore the ϕ_2 ratio of 1/12 was selected as the best ϕ_2 for the studied conditions.

3.6.3. Effect of C_0 on the extraction of phenols

In order to investigate the influence of the solute concentration in the feed phase, phenols concentrations were varied from 5 to 30 ppm. Because the mass transfer in ELM process is closely related to the concentration gradient between internal and external phases, it is expected that changing the concentration of solute in the external phase may affect the removal efficiency. Fig. 14 compares the removal efficiencies in the systems in terms of C_t/C_0 as mentioned earlier with two different solute concentrations of 5 and 30 ppm. As seen in the figure, at the beginning the removal efficiency in the system with lower solute concentration is slightly higher than that in the system with higher solute concentration because most of the solute diffusing within the emulsion globule is stripped by the internal aqueous phase droplets, which are situated in the peripheral regions of the emulsion globule. However, as the experiment proceeds and the solute concentration in the external phase decreases, the efficiency declines below that of the system with higher solute concentration. When initial concentration is higher, the internal droplets in the peripheral region of the globule are more rapidly saturated, and further extraction is possible when the phenolic compound permeates deeper within the globule. Therefore, an increase in initial concentration also corresponds to an increase in diffusional path lengths which resulted in an increase in the time necessary for extraction. These results are in agreement with that obtained by Lee et al. [57].

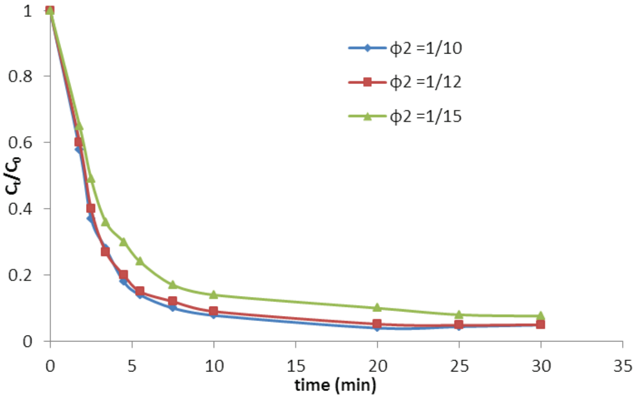


Fig. 13. Effect of treatment ratio (ϕ_2) on the extraction of 2-chlorophenol, $\phi_1 = 1/3$, 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, $C_{io} = 0.5$ M, 300 rpm, and $C_0 = 30$ ppm.

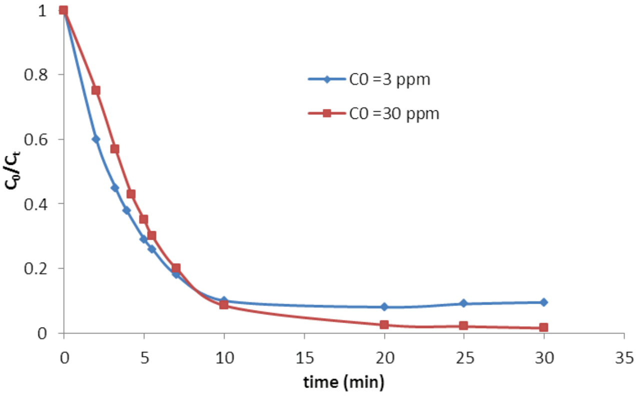


Fig. 14. Effect of 4-nitrophenol concentration on removal efficiency, $\phi_1 = 1/3$, 3% w/v of Span 80, 0.3% v/v of $[BMIM]^+[NTf_2]^-$, $\phi_2 = 1/12$, $C_{io} = 0.5$ M, and 300 rpm.

4. Conclusions

Removal of phenolic compounds from synthesized produced water by ELM was studied. Span 80 and the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$, were used for stabilizing the emulsion. The following results were obtained:

- The emulsion stability time increases with an increase in the concentration of $[BMIM]^+[NTf_2]^-$ up to 0.3% v/v of $[BMIM]^+[NTf_2]^-$. The stability time was found to be decreasing with higher ionic liquid concentration, which could be explained by the increased emulsion sedimentation due to the high density of $[BMIM]^+[NTf_2]^-$.
- The internal drop size distribution of the emulsion changes with a change in internal stripping phase to organic phase ratio (ϕ_1). Almost 50% of the droplets happen to be of 1.5 μm in diameter at small ϕ_1 values. Increasing ϕ_1 changes the drop sizes as well as size distribution and larger droplet sizes were obtained.
- The internal droplet size of the emulsion showed a definite increase with increase in NaOH concentration in the inner phase (C_{io}).
- The size of the emulsion globule in the external aqueous feed phase depends on the intensity and mode of mixing. Emulsion globule sizes progressively decreased with the increase in the stirring speeds.
- The removal efficiency of phenol from the feed solution with 30 ppm solute was 81% after 10 min and 78% after 30 min. On the other hand, the removal efficiency of both 2-chlorophenol and 4-nitrophenol was 91% after 10 min, and 95% and 98.5%, respectively, after 30 min of permeation under the most favorable operating conditions.
- The percentage removal of phenols increases with the decrease of ϕ_1 due to that sufficient availability of the organic phase for enclosing all the internal aqueous stripping phase and hence, the dispersion of the W/O emulsion was easier.
- The increase in emulsion to aqueous feed ratio ϕ_2 results in an increase of the emulsion phase holdup leading to an increase in the extraction capacity of the emulsion.
- At the beginning of ELM extraction, the removal efficiency in the system with lower solute concentration is

slightly higher than that in the system with higher solute concentration. As the experiment proceeds and solute concentration in the external phase decreases and hence, the efficiency declines below that of the system with higher solute concentration.

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Symbols

C_{io} — NaOH concentration in the inner phase (M)
C_0 — Initial concentration of phenols (ppm)
C_t — Concentration of phenols at the time of measurement (ppm)
D_{AB} — Diffusion coefficient (cm^2/s)
D_{eff} — Effective diffusion coefficient (cm^2/s)
D_M — Diffusion coefficient of solute in the organic phase (cm^2/s)
D_W — Diffusion coefficient of solute in water phase (cm^2/s)
K_a — Acid dissociation constant
m — Solute distribution coefficient between membrane phase and aqueous phase (–)
M — Molecular weight of solvent (kg/kg mol)
t — Time (min)
T — Temperature (k)
V_A — Solute molar volume (m^3/kg mol)
ϕ_1 — Volume of internal phase to volume of organic phase ratio (–)
ϕ_2 — Treat ratio (volume of emulsion to volume of feed ratio [–])
μ — Viscosity of solvent (kg/m s)
Ψ — Solvent association factor (–)

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