

Extraction of phenol from aqueous solution using ionic liquid-based emulsion liquid membrane

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The ionic liquid-based emulsion liquid membrane (ELM) has been developed to extract phenol from aqueous solution. The effects of ionic liquid type, internal NaOH concentration, Aliquat 336 concentration, liquid paraffin concentration, carrier type and concentration, homogenizer speed, volume ratio of emulsion to external phase, stirring speed and initial phenol concentration on extraction efficiencies of phenol have been studied. The results show that Aliquat 336 is the most preferred ionic liquid during extraction of phenol by ELM. The optimal experimental conditions during extraction of phenol are Aliquat 336 concentration of 4%, internal NaOH concentration of 378 mg·L⁻¹, liquid paraffin concentration of 3%, 1-octanol concentration of 3%, homogenizer speed of 6500 r·min⁻¹, volume ratio of emulsion to external phase of 1:1, stirring speed of 200 r·min⁻¹, and initial phenol concentration of 1019 mg·L⁻¹. The extraction efficiency of phenol by ionic liquid-based ELM could be above 94%. Orthogonal experiments show that during extraction of phenol by ELM, the order of importance of the four factors is volume ratio of emulsion to external phase > homogenizer speed > volume fraction of Aliquat 336 > internal NaOH concentration. The recycled ionic liquid-based ELM with Span-80 have been demulsified by centrifuge successfully. The demulsification efficiency of ELM reaches nearly 100% in 20 min.

Keywords: Demulsification, Emulsion liquid membrane, Extraction, Ionic liquids, Phenol

Introduction

In the last decades, water pollution has brought the very big puzzle for people's health. Phenol and its derivatives are often present in a lot of industrial wastewater and even in natural water source. Phenolic pollutants derive from many industrial processes, including coal coking, coal gasification, coal liquefaction, petroleum refining, wood processing, pharmaceuticals producing, papermaking, and plastic processing. As permanent organic pollutants, phenolic compounds are known for their high water solubility, high mobility, high toxicity, and non-biodegradability¹⁻³. Therefore, the discharge of phenolic wastewater is strictly controlled. The phenol concentration in potable water and industrial wastewater should be no more than 0.001 mg·L⁻¹ and 1 mg·L⁻¹, respectively⁴. Removal of phenols from wastewater has attracted great environmental interest over recent years. Various treatment methods have been applied for phenolic compounds removal in wastewater such as adsorption⁵⁻⁶, distillation⁷, membrane separation⁸, advanced oxidation^{1,9}, biochemical treatment¹⁰⁻¹¹, and extraction¹²⁻¹⁵.

However, most of these treatments display major disadvantages such as high operating costs, long time, low removal efficiencies, large material consumption or secondary pollutant. During removal of phenols using adsorption, a large amount of adsorbents are consumed and the operation cost is unacceptable. Then, removal of phenols using distillation is also hindered by its high energy consumption. Besides, membrane separation could reduce phenolic wastewater discharge at some extent, but phenolic compounds are still present in the concentrate. In fact, the issues have not been fundamentally solved. Furthermore, advanced oxidation seems to be a good choice for removal of phenols. However, at this stage, the immature technology, secondary pollution and high cost block its large-scale applications in treatment of phenolic wastewater. Moreover, biochemical treatment could be just applied in treatment of low concentration phenolic wastewater due to non-biodegradability and biotoxicity of phenolic compounds. Unlike the above treatment methods, extraction is regard as one economically viable and nondestructive treatment method when

phenol content in wastewater is more than $50 \text{ mg} \cdot \text{L}^{-1}$ (Ref.4).

As a novel extraction technology, extraction by emulsion liquid membrane (ELM) has a lot of incomparable advantages compared to solvent extraction, such as low solvent usage, large interfacial area, high mass transfer rate, high extraction efficiency, high selectivity, low cost, simple operation, low energy consumption, and extraction and back extraction coupled in a system¹⁶⁻¹⁷. The ELM system is classified as a water in oil in water (W/O/W) pattern and an oil in water in oil (O/W/O) pattern. When both the internal and external phase are aqueous phase it is called W/O/W pattern. On the contrary, when both the internal and external phase are organic phase, it is named O/W/O pattern. The pattern of extraction of phenolic compounds from wastewater by ELM is W/O/W. Basically, W/O/W emulsion liquid membrane system comprises of three phases that are organic phase, internal phase and external phase¹⁸. The organic phase consists of diluents, surfactants, carriers, and reinforcing/modifying agents. The internal phase is stripping solution while the external phase is phenolic wastewater. Recently, ELM technology has emerged as a highly efficient method for removing and recovering of phenolic compounds from various phenolic wastewater. The formulation of ELM always occupies the leading role in recovery of phenols. During recovery of phenols by ELM, the diluents in organic phase are hexane¹⁹⁻²⁰, isoparaffinic hydrocarbon solvent²¹, kerosene²²⁻³⁰, and mixture of kerosene and vegetable oil³¹⁻³³. The surfactants in organic phase contain polyamine ECA 4360J²¹, OP-4²⁴, Montane-80²⁵⁻²⁶, Span-80^{19-20, 22-23, 27-28, 30-31}, Fe₂O₃ nanoparticles²⁹ and mixture of Span-80 and Tween-80³². The carriers include Tributyl phosphate (TBP)^{23,28,30}, Cyanex923^{21-22, 27}, ethyl acetate³⁰, and 1-octanol³⁰. The reinforcing/modifying agents embraces isodecanol²¹, ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]⁺[PF₆]⁻)²³, Ethylene-propylene-diene terpolymer²⁵, Styrene butadiene rubber²⁶, ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([BMIM]⁺[NTf₂]⁻)^{29, 32}, and liquid paraffin³⁰. The internal solutions are NH₄OH¹⁹, Na₂CO₃²⁰ and NaOH²¹⁻³² solution.

In fact, as excellent reinforcing/modifying agents for ELM system, ionic liquids could improve stability of organic liquid membrane and extraction

efficiencies of phenolic compounds. However, there are few attempts on the extraction of phenolic compounds from aqueous solution using ionic liquid-based ELM. Therefore, it is very essential to investigate the extraction of phenol from aqueous solution using ionic liquid-based ELM, systematically. In the text, the effects of ionic liquid type, internal NaOH concentration, Aliquat 336 concentration, liquid paraffin concentration, carrier type and concentration, homogenizer speed, volume ratio of emulsion to external phase, stirring speed and initial phenol concentration on extraction efficiencies of phenol have been studied. Then, the extraction processes of phenol by ELM have been optimized through orthogonal experiments. Finally, the demulsification of ELM after extraction have been also investigated.

Experimental Section

Materials and instruments

Phenol (purity>99.5%) is provided by Tianjin Hongyan Chemical Reagent Factory. 2-Octanol (purity>99%) is purchased from Shanghai Zhanyun Chemical Co., Ltd. Kerosene, 1-Octanol (purity>99.5%), Paraffin liquid (purity>99%), Tributyl phosphate (TBP, purity>99%), Sorbitan monooleate (Span-80) and Methyltrioctylammonium chloride (Aliquat 336, purity>97%) are given by Shanghai Macklin Biochemical Co., Ltd. Bis(2-ethylhexyl) phosphate (P204, purity>95%) and Mono-2-ethylhexyl (2-Ethylhexyl) phosphate (P507, purity>95%) are provided by Rhawn Reagent. 4-Aminoantipyrine (purity>98.5%), Sodium hydroxide (98%), Potassium ferricyanide (purity>99.5%), Ammonium chloride (>99.5%) and Ammonium hydroxide are purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]⁺[PF₆]⁻, purity>99%) is provided by Damas-beta. 1-Butyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ([BMIM]⁺[NTf₂]⁻, purity>98%) and 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]⁺[BF₄]⁻, purity>98%) are purchased from Anhui Cool Bioengineering Co., Ltd. The details of instruments are listed in Table 1.

Experiment setup and extraction process

As shown in Fig. 1, the entire experiment includes four steps, i.e., emulsification, extraction, phase separation and demulsification. Firstly, W/O emulsions were prepared with kerosene as diluent,

Instruments	Pattern	Producer
High Speed Homogenizer	FSH-2A	SECCO Instrument
Centrifuge	80-1	Changzhou Surui Instrument Co., Ltd.
Magnetic Stirrer	M-SCL-T	Hangzhou Qiwei Instrument Co. Ltd.
Spectrophotometer	752N	Shanghai Exact Science Instrument Co., Ltd.
Electronic analytical balance	ZA22OR4	Shanghai Zan Wei Weighing Apparatus Co., Ltd.

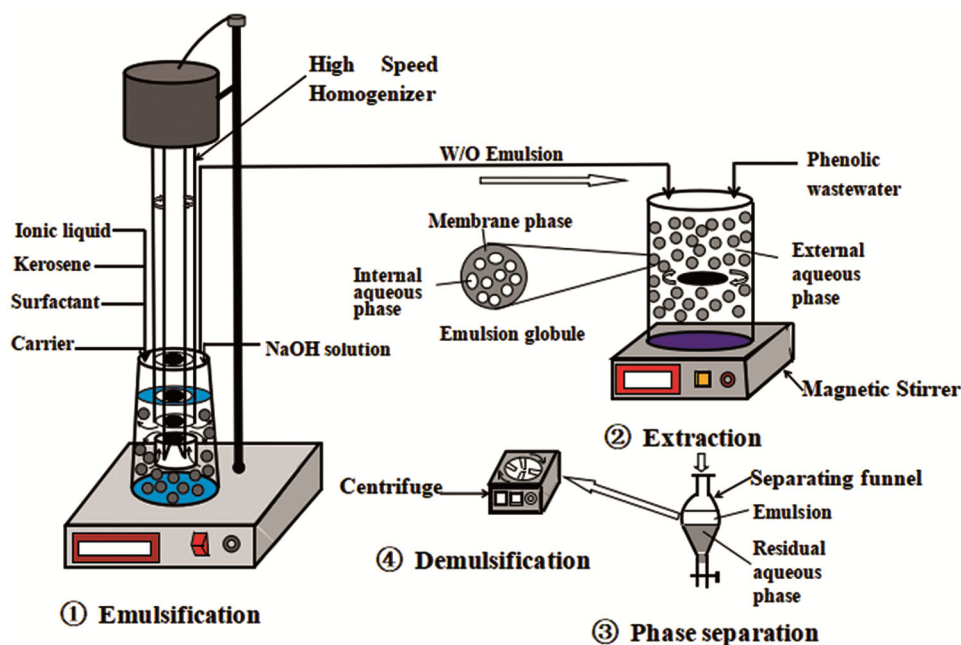


Fig. 1 — Schematic diagram of recovering phenol from wastewater by ionic liquid-based emulsion liquid membrane

Span-80 as surfactant, 1-Octanol, 2-Octanol, TBP, P204 or P507 as carriers, ionic liquids [BMIM]⁺[BF₄]⁻, [BMIM]⁺[PF₆]⁻, [BMIM]⁺[NTf₂]⁻ or Aliquat 336 as reinforcing /modifying agents, and NaOH solution as internal aqueous solution. Then, the prepared W/O emulsions were diverted into phenolic solution and stirred by magnetic stirrer for extraction of phenol.

After that, the liquid mixture was transferred to separating funnel and left for several hours in order to phase separation of emulsion and residual aqueous phase. Afterwards, the residual aqueous phase was filtered by hydrophilic PVDF membrane with pore size of 0.1 μm and phenol concentration of the residual aqueous phase could be determined by 4-aminoantipyrine (4-AAP) spectrophotometric method³⁰. Finally, the recycled emulsion was moved into centrifuge aiming at demulsification and recovery of oil membrane and sodium phenolate.

In W/O/W ELM system for extracting phenol, the transportation of phenol from external aqueous phase to internal aqueous phase depended on molecule diffusion of solutes, and complexation of solutes and carriers. Solutes could dissolve in organic liquid

membrane and complex with the carriers in organic phase, and pass through organic liquid membrane. Then, complex of phenol decomplexed at the interface of membrane and internal aqueous phase. The decomplexed carriers came back to organic liquid membrane. The phenol at the interface of membrane and internal aqueous phase reacted with NaOH in internal aqueous phase and converted into sodium phenolate. Finally, sodium phenolate was trapped by organic liquid membrane due to its insolubilization in organic liquid membrane but solubilization in aqueous phase^{30, 32}.

Extraction efficiency

The extraction efficiency of phenol E is defines as follows³³:

$$E = \frac{C_0 - C_r}{C_0} \times 100\% \quad \dots(1)$$

Where C_0 is initial phenol concentration in aqueous phase, C_r is final phenol concentration in aqueous phase.

Demulsification efficiency

The demulsification efficiency D is defined in Eq. 2²⁴.

$$D = \frac{V_i - V_f}{V_i} \times 100\% \quad \dots(2)$$

Where V_i and V_f are initial volume of emulsion liquid membrane before demulsification and residual volume of emulsion liquid membrane after demulsification, respectively.

Results and Discussion

Effect of ionic liquid type and internal NaOH concentration

The effect of ionic liquid type and internal NaOH concentration on extraction efficiency of phenol is shown in Fig. 2. The experimental parameters observed during the process are located below Fig. 2. It is seen from Fig. 2 that extraction efficiencies of phenol with Aliquat 336 are higher than that with the three imidazolium-based ionic liquids at different internal NaOH concentration.

It may be related to the strengths of intermolecular interactions and hydrogen bonds between ionic liquids and phenol. The strong intermolecular interactions and hydrogen bonds between ionic liquids and phenol contribute to extraction of phenol^{32, 34-36}. Furthermore, extraction efficiencies of phenol with Aliquat 336 increase with internal NaOH concentration from 100 mg·L⁻¹ to 378 mg·L⁻¹ and then it remain steady. Differently, extraction efficiencies of phenol with

[Bmim]PF₆, [Bmim]NTf₂ and [Bmim]BF₄ increase with internal NaOH concentration from 100 mg·L⁻¹ to 266 mg·L⁻¹ and then decrease with internal NaOH concentration from 266 mg·L⁻¹ to 458 mg·L⁻¹. Therefore, Aliquat 336 is chosen as the optimal ionic liquid for extraction of phenol among them and internal NaOH concentration of 378 mg·L⁻¹ is recommended. The highest efficiency of phenol with Aliquat 336 could reach 94.36% at internal NaOH concentration of 378 mg·L⁻¹.

Effect of Aliquat 336 concentration

The effect of Aliquat 336 concentration on extraction efficiency of phenol is shown in Fig. 3. As seen in Fig. 3, extraction efficiency of phenol rises sharply from 69.71% to 94.36% at the beginning and then remains constant. Compared to extraction efficiency of phenol without Aliquat 336, the extraction efficiency of phenol with Aliquat 336 has obvious improvement. It is proved that Aliquat 336 becomes a reinforcing /modifying agent in extraction of phenol by ELM. The highest extraction efficiency of phenol could reach 94.36% at Aliquat 336 concentration of 4%.

Effect of liquid paraffin concentration

Liquid paraffin concentration is an important factor which affects extraction efficiency of phenol. As shown in Fig. 4, the extraction efficiency of phenol increases from 85.37% to 95.22% with the increase of liquid paraffin concentration from 1% to 4%. It is because that the addition of liquid paraffin

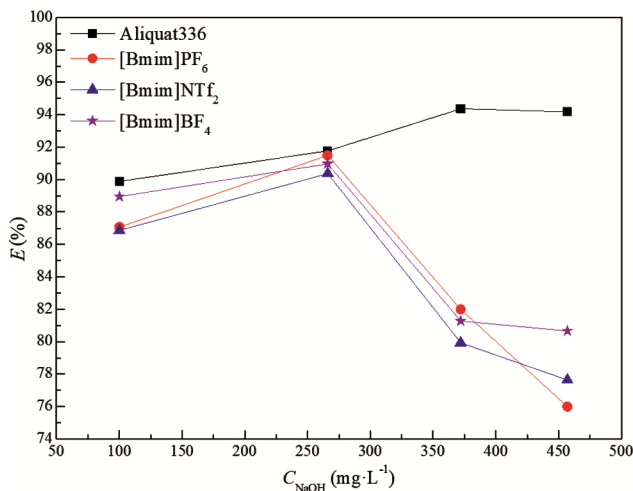


Fig. 2 — Effect of ionic liquid type and internal NaOH concentration on extraction efficiencies of phenol ($\varphi_{Span-80}=3\%$, $\varphi_{Paraffin\ liquid}=4\%$, $\varphi_{ionic\ liquid}=4\%$, $\varphi_{2-Octanol}=3\%$, $\varphi_{Kerosene}=86\%$, $C_{NaOH}=378\text{ mg}\cdot\text{L}^{-1}$, $R_{o/i}=1:1$, $R_{em/ex}=1:1$, $C_0=1018.6\text{ mg}\cdot\text{L}^{-1}$, $v_e=6500\text{ r}\cdot\text{min}^{-1}$, $\tau=1.8\text{ min}$, $v_s=200\text{ r}\cdot\text{min}^{-1}$, $t_{ex}=10\text{ min}$)

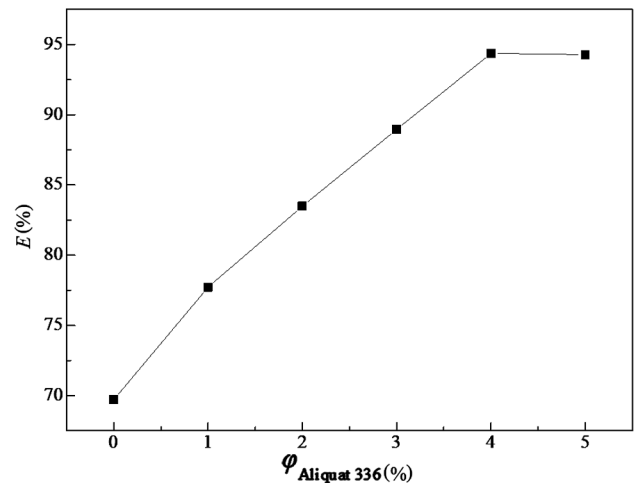


Fig. 3 — Effect of Aliquat 336 concentration on extraction efficiencies of phenol ($\varphi_{Span-80}=3\%$, $\varphi_{Paraffin\ liquid}=4\%$, $\varphi_{2-Octanol}=3\%$, $\varphi_{Kerosene}=85\%-90\%$, $C_{NaOH}=378\text{ mg}\cdot\text{L}^{-1}$, $R_{o/i}=1:1$, $R_{em/ex}=1:1$, $C_0=1018.6\text{ mg}\cdot\text{L}^{-1}$, $v_e=6500\text{ r}\cdot\text{min}^{-1}$, $\tau=1.8\text{ min}$, $v_s=200\text{ r}\cdot\text{min}^{-1}$, $t_{ex}=10\text{ min}$)

into the organic liquid membrane may change viscosity of organic liquid membrane, leading to the increase of stability of ELM³⁰. When the liquid paraffin concentration is above 4%, the separation of emulsion liquid membrane and residual aqueous phase become very difficult after extraction. Therefore, liquid paraffin concentration of 4% is recommended.

Effect of carrier type and concentration

Carrier is another significant factor in extraction process of phenol by ELM. The effect of carrier type and concentration on extraction efficiencies of phenol is shown in Fig. 5. It could be seen that extraction efficiencies of phenol increase with the increase of carrier concentration from 1% to 4% and then it almost keep constant or slightly decreases. On one hand, the stability of ELM would be weakening by increase of carrier concentration, causing decrease of extraction efficiency of phenol. On the other hand, mass transfer of phenol between external phase and internal phase could be improved by increase of carrier concentration, leading to increase of extraction efficiency of phenol. The extraction efficiency of phenol is decided by the two factors³⁰. Therefore, the optimal carrier concentration is 3%. Besides, the extraction efficiencies of phenol with 1-octanol and 2-octanol are far higher than that with TBP, P204 and P507 under the same conditions. Hence, 1-octanol and 2-octanol are more suitable for extraction of phenol. The highest extraction efficiency of 94.67% is gained with 1-octanol at carrier concentration of 3%.

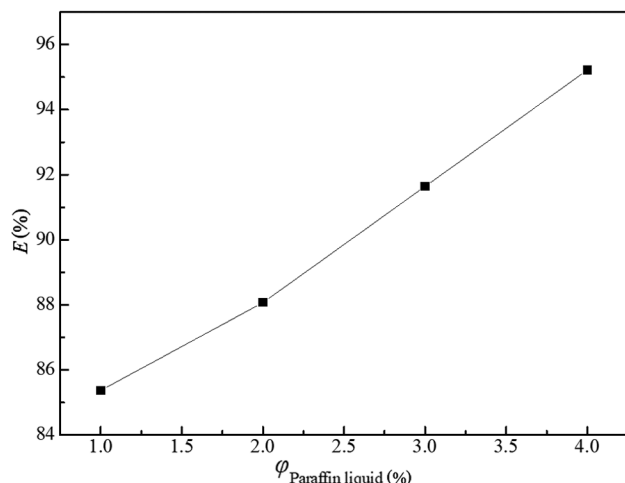


Fig. 4 — Effect of liquid paraffin concentration on extraction efficiencies of phenol
($\phi_{\text{Span-80}}=3\%$, $\phi_{\text{Aliquat336}}=4\%$, $\phi_{\text{1-Octanol}}=3\%$, $\phi_{\text{Kerosene}}=86\%-89\%$, $C_{\text{NaOH}}=378 \text{ mg}\cdot\text{L}^{-1}$, $R_{\text{o/i}}=1:1$, $R_{\text{em/ex}}=1:1$, $C_0=1018.6 \text{ mg}\cdot\text{L}^{-1}$, $v_e=6500 \text{ r}\cdot\text{min}^{-1}$, $\tau=1.8 \text{ min}$, $v_s=200 \text{ r}\cdot\text{min}^{-1}$, $t_{\text{ex}}=10 \text{ min}$)

Effect of homogenizer speed

Fig. 6 illustrates the effect of homogenizer speed on extraction efficiency of phenol. The results show that extraction efficiencies of phenol rise quickly and then reduce quickly with the increase of homogenizer speed. The highest extraction efficiency of phenol reaches 94.36% at homogenizer speed of $6500 \text{ r}\cdot\text{min}^{-1}$. The results are consistent with Rosly's work^[33]. It is because sizes of emulsion droplets are related to homogenizer speed. Low homogenizer speed means low energy which usually generates low disruptive forces to mechanically breakup the oil and water

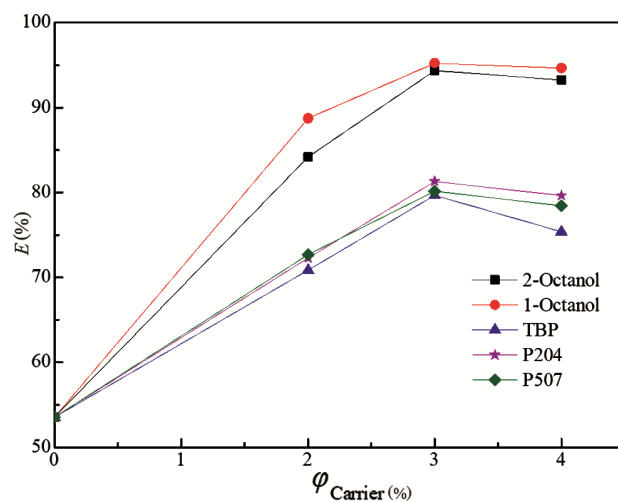


Fig. 5 — Effect of carrier type and concentration on extraction efficiencies of phenol

($\phi_{\text{Span-80}}=3\%$, $\phi_{\text{Paraffin liquid}}=4\%$, $\phi_{\text{Aliquat336}}=4\%$, $\phi_{\text{Kerosene}}=85\%-89\%$, $C_{\text{NaOH}}=378 \text{ mg}\cdot\text{L}^{-1}$, $R_{\text{o/i}}=1:1$, $R_{\text{em/ex}}=1:1$, $C_0=1018.6 \text{ mg}\cdot\text{L}^{-1}$, $v_e=6500 \text{ r}\cdot\text{min}^{-1}$, $\tau=1.8 \text{ min}$, $v_s=200 \text{ r}\cdot\text{min}^{-1}$, $t_{\text{ex}}=10 \text{ min}$)

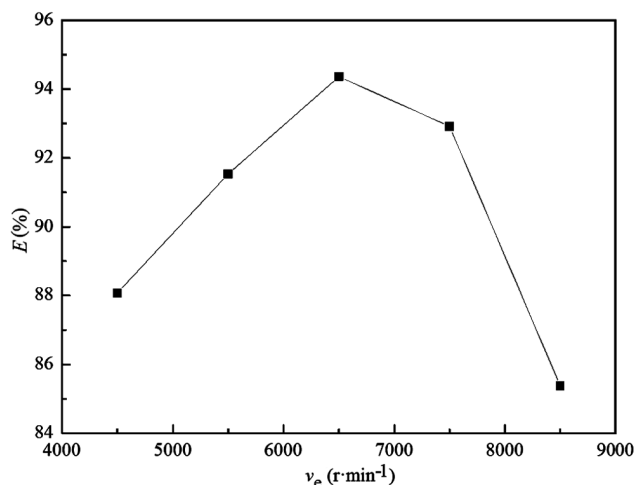


Fig. 6 — Effect of homogenizer speed on extraction efficiencies of phenol

($\phi_{\text{Span-80}}=3\%$, $\phi_{\text{Paraffin liquid}}=4\%$, $\phi_{\text{1-Octanol}}=3\%$, $\phi_{\text{Aliquat336}}=4\%$, $\phi_{\text{Kerosene}}=86\%$, $C_{\text{NaOH}}=378 \text{ mg}\cdot\text{L}^{-1}$, $R_{\text{o/i}}=1:1$, $R_{\text{em/ex}}=1:1$, $C_0=1018.6 \text{ mg}\cdot\text{L}^{-1}$, $\tau=1.8 \text{ min}$, $v_s=200 \text{ r}\cdot\text{min}^{-1}$, $t_{\text{ex}}=10 \text{ min}$)

phases into droplets and inhibited the activity of stirrer to dissipate oil droplets, leading to larger emulsion droplets³⁷. The increase of sizes of emulsion droplets could reduce stability of ELM, resulting in decrease of extraction efficiencies of phenol. Therefore, the extraction efficiencies of phenol increase with homogenizer speed from 4500 r·min⁻¹ to 6500 r·min⁻¹. However, excessive homogenizer speed causes too small emulsion droplets. The fast coalescence of the small droplets could make the liquid membrane layer to be incapable to overcome the collision force, resulting in emulsion breakage^{38,39}. Hence, excessive homogenizer speed could lead to higher emulsion breakage, resulting in decrease of extraction efficiencies of phenol.

Effect of volume ratio of emulsion to external phase

Fig. 7 shows the effect of volume ratio of emulsion to external phase on extraction efficiencies of phenol. It could be seen that the extraction efficiencies of phenol increase sharply with volume ratio of emulsion to external phase from 1:3 to 1:1 and decrease slightly with volume ratio of emulsion to external phase from 1:1 to 1:0.5. The highest extraction efficiency of 95.22% arrives at volume ratio of emulsion to external phase of 1:1. On one hand, the increase of volume ratio of emulsion to external phase means the increase of total amount of carrier, ionic liquid and sodium hydroxide within unit volume which facilitate mass transfer between internal and external phase at some extent, leading to increase of extraction efficiency of phenol. On the other hand, increase of volume ratio of emulsion to external phase could

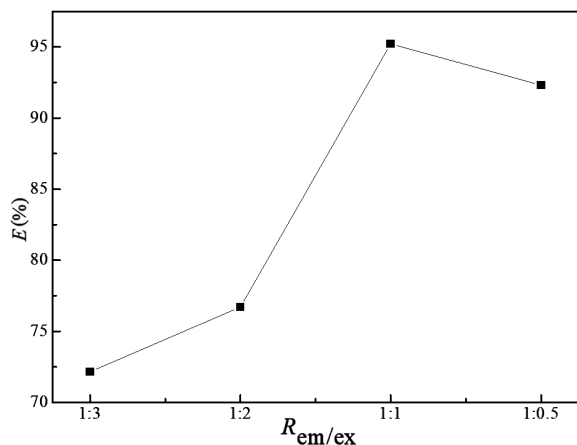


Fig. 7 — Effect of volume ratio of emulsion to external phase on extraction efficiencies of phenol
 ($\varphi_{Span-80}=3\%$, $\varphi_{Paraffin\ liquid}=4\%$, $\varphi_{1-Octanol}=3\%$, $\varphi_{Aliquat336}=4\%$, $\varphi_{Kerosene}=86\%$, $C_{NaOH}=378\text{ mg}\cdot\text{L}^{-1}$, $R_{o/i}=1:1$, $C_0=1018.6\text{ mg}\cdot\text{L}^{-1}$, $v_e=6500\text{ r}\cdot\text{min}^{-1}$, $\tau=1.8\text{ min}$, $v_s=200\text{ r}\cdot\text{min}^{-1}$, $t_{ex}=10\text{ min}$)

cause increase of viscosity and decrease of liquidity of liquid mixture, leading to decrease of extraction efficiency of phenol. The extraction efficiencies of phenol are codetermined by the two aspects. Therefore, the extraction efficiencies of phenol increase sharply at beginning and then decrease slightly with increase of volume ratio of emulsion to external phase.

Effect of stirring speed

Fig. 8 presents the effect of stirring speed on extraction efficiencies of phenol. It could be seen that the extraction efficiencies of phenol increase with stirring speed from 100 r·min⁻¹ to 200 r·min⁻¹ and then decrease with stirring speed from 200 r·min⁻¹ to 500 r·min⁻¹. The highest extraction efficiency of phenol of 94.36% is gained at 200 r·min⁻¹. It is because that at the beginning the increase of stirring speed could improve the dispersivity of emulsion droplets in external aqueous phase, leading to increase of extraction efficiencies of phenol. However, the breakage of ELM also increases with the increase of stirring speed which leads to decrease of extraction efficiencies of phenol. Therefore, during extraction process, the stirring speed is recommended as 200 r·min⁻¹.

Effect of initial phenol concentration

Fig. 9 shows the effect of initial phenol concentration on extraction efficiencies of phenol. As can be seen from Fig. 9, the extraction efficiencies of phenol decrease from 95.22% to 87.27% with initial phenol concentration from 1019 mg·L⁻¹ to

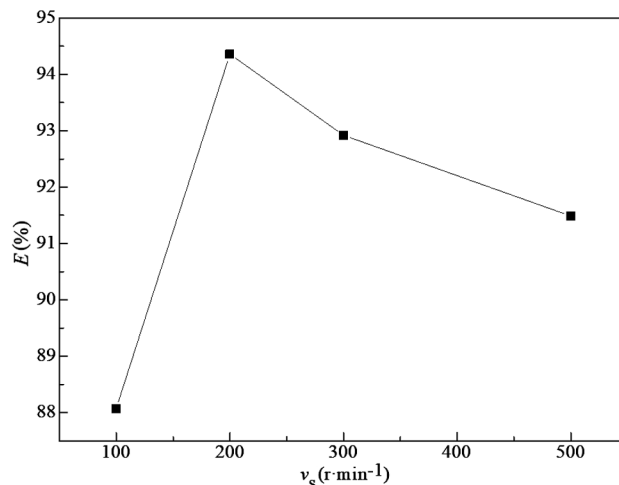


Fig. 8 — Effect of stirring speed on extraction efficiencies of phenol
 ($\varphi_{Span-80}=3\%$, $\varphi_{Paraffin\ liquid}=4\%$, $\varphi_{1-Octanol}=3\%$, $\varphi_{Aliquat336}=4\%$, $\varphi_{Kerosene}=86\%$, $C_{NaOH}=378\text{ mg}\cdot\text{L}^{-1}$, $R_{o/i}=1:1$, $R_{em/ex}=1:1$, $C_0=1018.6\text{ mg}\cdot\text{L}^{-1}$, $v_e=6500\text{ r}\cdot\text{min}^{-1}$, $\tau=1.8\text{ min}$, $t_{ex}=10\text{ min}$)

4004 mg·L⁻¹. It is because that when initial phenol concentration increase, the total amount of phenol within unit volume would increase whereas the total amount of sodium hydroxide within unit volume is fixed and limited. The increase of initial phenol concentration means relatively shortage of the total amount of sodium hydroxide, leading to decrease of extraction efficiencies of phenol.

Orthogonal experiments

Four factors such as volume fraction of Aliquat 336 (A), internal NaOH concentration (B), homogenizer speed (C) and volume ratio of emulsion to external phase (D) were considered in order to investigate the individual and interactional effects of the various factors on the extraction efficiency of phenol. The examined levels of the four factors are listed in Table 2, while the results of the orthogonal experiments are listed in Table 3, where K_i , k_i and r represent sum of every experimental data, average of every experimental data and difference between the maximum and minimum, respectively. The results show that the optimal solution is volume fraction of Aliquat 336 of 5%, internal NaOH concentration of 100 mg/L, homogenizer speed of 6500 r/min and volume ratio of emulsion to external phase of 1:1. The

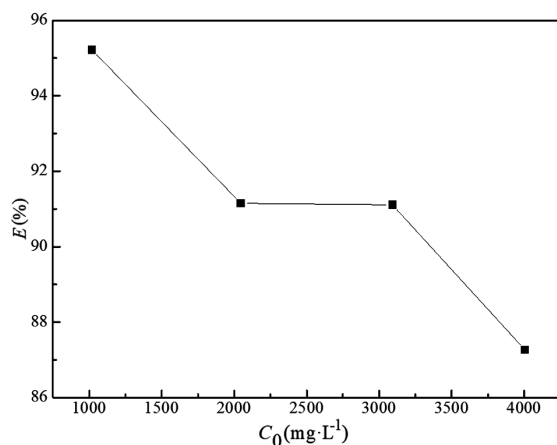


Fig. 9 — Effect of initial phenol concentration on extraction efficiencies of phenol

($\varphi_{\text{Span-80}}=3\%$, $\varphi_{\text{Paraffin liquid}}=4\%$, $\varphi_{1\text{-Octanol}}=3\%$, $\varphi_{\text{Aliquat336}}=4\%$, $\varphi_{\text{Kerosene}}=86\%$, $C_{\text{NaOH}}=378 \text{ mg}\cdot\text{L}^{-1}$, $R_{o/i}=1:1$, $R_{em/ex}=1:1$, $v_e=6500 \text{ r}\cdot\text{min}^{-1}$, $\tau=1.8 \text{ min}$, $t_{ex}=10 \text{ min}$)

Table 2 — Factors and levels of the orthogonal experiments

	Factor A	Factor B	Factor C	Factor D
Level	Volume fraction of Aliquat 336 (%)	Internal NaOH concentration (mg·L ⁻¹)	Homogenize r speed (r·min ⁻¹)	Volume ratio of emulsion to external phase
1	3	100	6500	1:1
2	4	266	7500	1:2
3	5	378	8500	1:3

validation experiments were carried out under the optimal conditions and the extraction efficiency of phenol could reach 93.47%. The order of importance of the four factors is volume ratio of emulsion to external phase > homogenizer speed > volume fraction of Aliquat 336 > internal NaOH concentration.

Centrifugal demulsification

Demulsification is a key stage to recovery of phenol and ELM. According to Qi³⁰, the recycled Span-80-based emulsion liquid membrane after extraction is more suitable for centrifugal demulsification, compared to heating demulsification. Therefore, the recycled ionic liquid-based ELM with Span-80 have been demulsified by centrifuge. The effect of centrifugal rotational speed and time on demulsification efficiencies are shown in Fig. 10. It could be seen that the demulsification

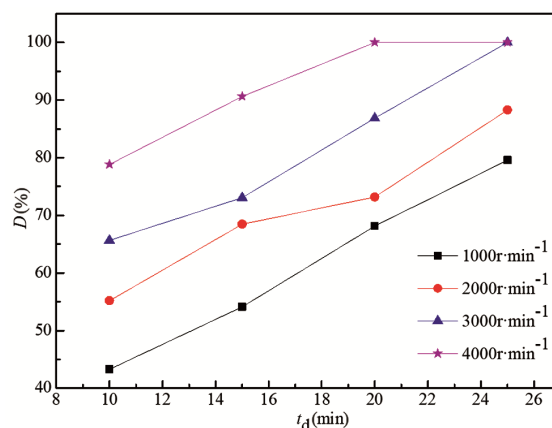


Fig. 10 — Effect of centrifugal rotational speed and time on demulsification efficiencies

Table 3 — Results of the orthogonal experiments

No.	Factors and levels				Extraction efficiency of phenol (%)
	A	B	C	D	
1	1	1	1	1	89.07
2	1	2	3	2	72.16
3	1	3	2	3	69.1
4	2	1	3	3	63.87
5	2	2	2	1	85.64
6	2	3	1	2	76.72
7	3	1	2	2	81.91
8	3	2	1	3	75.54
9	3	3	3	1	85.37
K_1	230.33	234.85	241.33	260.08	
K_2	226.23	233.34	236.65	230.79	
K_3	242.82	231.19	221.4	208.51	
k_1	76.78	78.28	80.44	86.69	
k_2	75.41	77.78	78.88	76.93	
k_3	80.94	77.06	73.80	69.50	
r	5.53	1.22	6.64	17.19	
Order	D>C>A>B				
Optimal level	A ₃	B ₁	C ₁	D ₁	
Optimal solution	A ₃ B ₁ C ₁ D ₁				

efficiencies increase with centrifugal rotational speed and time. The highest demulsification efficiency reaches nearly 100% at centrifugal rotational speed of 4000 r·min⁻¹ in 20 min.

Conclusion

The ionic liquid-based emulsion liquid membrane is applied in the extraction of phenol from aqueous solution. The effects of several factors including ionic liquid type, internal NaOH concentration, Aliquat 336 concentration, liquid paraffin concentration, carrier type and concentration, homogenizer speed, volume ratio of emulsion to external phase, stirring speed and initial phenol concentration on extraction efficiency of phenol have been investigated. The results show that extraction efficiency with Aliquat 336 is the highest among the four ionic liquids. The optimal experimental conditions are Aliquat 336 concentration of 4%, internal NaOH concentration of 378 mg·L⁻¹, liquid paraffin concentration of 3%, 1-octanol concentration of 3%, homogenizer speed of 6500 r·min⁻¹, volume ratio of emulsion to external phase of 1:1, stirring speed of 200 r·min⁻¹, and initial phenol concentration of 1019 mg·L⁻¹. The extraction efficiency of phenol by ionic liquid-based ELM could be above 94%. Besides, the results of the orthogonal experiments indicate that during extraction of phenol by ELM, the order of importance of the four factors is volume ratio of emulsion to external phase > homogenizer speed > volume fraction of Aliquat 336 > internal NaOH concentration. The recycled ionic liquid-based emulsion liquid membrane with Span-80 have been demulsified by centrifuge successfully. The demulsification efficiency of ELM reaches nearly 100% in 20 min.

Conflict of interest

The authors declare no conflict of interest.

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References

- 1 Yabing Q, Oxidative degradation of phenol in aqueous solution by using heat, ZVI, AC, heat/ZVI, or heat/AC activated persulfate, *Indian J Chem Technol*, 30 (2023) 805.
- 2 Chen B, Yang S, Wu Y, Miyangzi S & Yu Q, Intensified phenols extraction and oil removal for industrial semi-coking wastewater: A novel economic pretreatment process design, *J Clean Prod*, 242 (2020) 118453.
- 3 Li H, Wan L, Chu G, Tan W, Liu B, Qin Y, Feng Y, Sun D & Fang Y, (Liquid + liquid) extraction of phenols from aqueous solutions with cineole, *J Chem Thermodyn*, 107 (2017) 95.
- 4 Asrami M R & Saïen J, Salting-out effect on extraction of phenol from aqueous solutions by [Hmim][NTf₂] ionic liquid: Experimental investigations and modeling, *Sep Purif Technol*, 204 (2018) 175.
- 5 Tanimu A, Jillani S M S, Alluhaidan A A, Ganiyu S A & Alhooshani K, 4-phenyl-1,2,3-triazole functionalized mesoporous silica SBA-15 as sorbent in an efficient stir bar-supported micro-solid-phase extraction strategy for highly to moderately polar phenols, *Talanta*, 194 (2019) 377.
- 6 Tang S, Sun J, Xia D, Zang B, Gao Y, Chen C, Shen W & Lee H K, In-syringe extraction using compressible and self-recoverable, amphiphilic graphene aerogel as sorbent for determination of phenols, *Talanta*, 195 (2019) 165.
- 7 Zhang C, Liu Y, Gao Z, Huang L & Xiong J, Process design, simulation and experimental studies of heteroazeotropic batch distillation for phenol dehydration, *Chem Eng Res Design*, 195 (2023) 682.
- 8 Alonso-Vázquez P, Valle C, Sánchez-Arévalo C, Cuartas-Urbe B E, Vincent-Vela M C, Bes-Piá A & Álvarez-nco S, Separation of phenolic compounds from canned mandarin production wastewater by ultrafiltration and nanofiltration, *J Water J Process Eng*, 59 (2024) 105041.
- 9 Arifin M N, Jusoh R, Abdullah H, Amirazali N & Setiabudi H D, Recent advances in advanced oxidation processes (AOPs) for the treatment of nitro- and alkyl-phenolic compounds, *Environ Res*, 229 (2023) 115936.
- 10 Bibi A, Bibi S, Abu-Dieyeh M & Al-Ghouthi M A, Towards sustainable physiochemical and biological techniques for the remediation of phenol from wastewater: A review on current applications and removal mechanisms, *J Clean Prod*, 417 (2023) 137810.
- 11 Li R, Xu Y, Gao J, Long-Fei R & Shao J, Novel membrane contactor-like bioreactor for selective separation and biodegradation of phenol and ammonium from coal chemical wastewater, *Sep Purif Technol*, 330 (2024) 125410.
- 12 Chen Y, Xiong K, Jiang M & Lv R, Phase equilibrium measurement, thermodynamics modeling and process simulation for extraction of phenols from coal chemical wastewater with methyl propyl ketone, *Chem Eng Res Design*, 147 (2019) 587.
- 13 Guo C, Cao Q, Chen B, Yang S & Qian Y, Development of synergistic extraction process for highly efficient removal of phenols from coal gasification wastewater, *J Clean Prod*, 211 (2019) 380.
- 14 Cesari L, Canabady-Rochelle L & Mutelet F, Extraction of phenolic compounds from aqueous solution using choline bis (trifluoromethylsulfonyl) imide, *Fluid Phase Equilib*, 446 (2017) 28.
- 15 Yang X, Wang B, Luo H, Yan S, Dai J & Bai Z, Efficient recovery of phenol from coal tar processing wastewater with tributylphosphane/diethyl carbonate/cyclohexane: Extraction cycle and mechanism study, *Chem Eng Res Design*, 157 (2020) 104.
- 16 Hussein M A, Mohammed A A & Atiya M A, Application of emulsion and Pickering emulsion liquid membrane technique for wastewater treatment: An overview, *Environ Sci Pollut Res*, 26 (2019) 36184.

- 17 Raval A R, Kohli H P & Mahadwad O K, A comprehensive review on green emulsion liquid membrane and its applicability towards the removal of contaminants from the aquatic streams, *Water Air and Soil Pollut*, 233 (2022) 379.
- 18 Zaulkiflee N D, Ahmad A L, Lah N F C & Buddin M M H S, Removal of emerging contaminants by emulsion liquid membrane: Perspective and challenges, *Environ Sci Pollut Res*, 29 (2022) 12997.
- 19 Dâas A & Hamdaoui O, Extraction of bisphenol A from aqueous solutions by emulsion liquid membrane, *J Memb Sci*, 348 (2010) 360.
- 20 Chaouchi S & Hamdaoui O, Removal of 4-nitrophenol from water by emulsion liquid membrane, *Desal Water Treat*, 57 (2016) 5253.
- 21 Reis M T A, Freitas O M F, Agarwal S, Ferreira L M, Ismael M R C, Machado R & Carvalho J M R, Removal of phenols from aqueous solutions by emulsion liquid membranes, *J Hazard Mater*, 192 (2011) 986.
- 22 Ng Y S, Jayakumar N S & Hashim M A, Performance evaluation of organic emulsion liquid membrane on phenol removal, *J Hazard Mater*, 184 (2010) 255.
- 23 Balasubramanian A & Venkatesan S, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMIM]⁺[PF₆]⁻ in Tributyl phosphate, *Desalination*, 289 (2012) 27.
- 24 Jiao H, Peng W, Zhao J & Xu C, Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology, *Desalination*, 313 (2013) 36.
- 25 Abbassian K & Kargari A, Effect of polymer addition to membrane phase to improve the stability of emulsion liquid membrane for phenol pertraction, *Desal Water Treat*, 57 (2016) 2942.
- 26 Abbassian K & Kargari A, Modification of membrane formulation for stabilization of emulsion liquid membrane for extraction of phenol from aqueous solutions, *J Environ Chem Eng*, 4 (2016) 3926.
- 27 Messikh N, Bousba S & Bougdah N, The use of a multilayer perceptron (MLP) for modelling the phenol removal by emulsion liquid membrane, *J Environ Chem Eng*, 5 (2017) 3483.
- 28 Jusoh N, Rosly M B, Othman N, Rahman H A, Noah N F M & Sulaiman R N R, Selective extraction and recovery of polyphenols from palm oil mill sterilization condensate using emulsion liquid membrane process, *Environ Sci Pollut Res*, 27 (2020) 23246.
- 29 Al-Obaidi Q, Alabdulmuhsin M, Tolstik A, Trautman J G & Al-Dahhan M, Removal of hydrocarbons of 4-Nitrophenol by emulsion liquid membrane (ELM) using magnetic Fe₂O₃ nanoparticles and ionic liquid, *J Water Process Eng*, 39 (2021) 101729.
- 30 Qi Y & Zhang S, Efficient recovery of phenol from phenolic wastewater by emulsion liquid membrane, *Canada J Chem Eng*, 101 (2023) 1027.
- 31 Othman No, Noah N F M, Shu L Y, Yi O Z, Jusoh N, Idroas M & Goto M, Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process, *Chin J Chem Eng*, 25 (2017) 45.
- 32 Rosly M B, Jusoh N, Othman No, Rahman H A, Noah N F M & Sulaiman R N R, Effect and optimization parameters of phenol removal in emulsion liquid membrane process via fractional-factorial design, *Chem Eng Res Design*, 145 (2019) 268.
- 33 Rosly M B, Jusoh N, Othman N, Rahman H A, Sulaiman R N R & Noah N F M, Stability of emulsion liquid membrane using bifunctional diluent and blended nonionic surfactant for phenol removal, *Chem Eng Process: Process Intensif*, 148 (2020) 107790.
- 34 Khan A S, Ibrahim T H, Khamis M I, Nancarrow P & Jabbar N A, Role of cation and alkyl chain length on the extraction of phenol from aqueous solution using NTf₂-based ionic liquids: Experimental and computational analysis, *J Mol Liq*, 326 (2021) 115305.
- 35 Deng J, Luo Z, Wang C & Zhu X, Extraction of phenols from bio-oil aqueous fraction by hydrophobic ionic liquids, *J Fuel Chem Technol*, 49 (2021) 1832.
- 36 Yang Q, Xing H, Su B, Bao Z, Wang J, Yang Y & Ren Q, The essential role of hydrogen-bonding interaction in the extractive separation of phenolic compounds by ionic liquid, *AIChE J*, 59 (2013) 1657.
- 37 Håkansson A, Innings F, Trägårdh C & Bergenståhl B, High-pressure homogenization emulsification model-improved emulsifier transport and hydrodynamic coupling, *Chem Eng Sci*, 91 (2013) 44.
- 38 Silva T M, Cerize N N P & Oliveira A M, The effect of high shear homogenization on physical stability of emulsions, *Int J Chem*, 8 (2016) 52.
- 39 Sulaiman R N R, Othman No & Amin N A S, Recovery of ionized nanosilver by emulsion liquid membrane process and parameters optimization using response surface methodology, *Desal Water Treat*, 57 (2016) 3339.