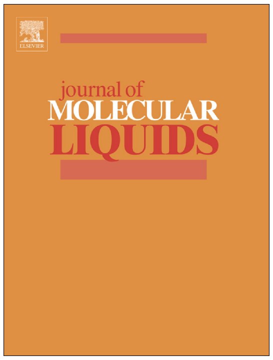

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Efficient Removal of Phenolic Compounds from Model Oil Using Benzyl Imidazolium-Based Ionic Liquids

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Abstract

Three benzyl imidazolium-based room temperature ionic liquids (RTILs) with various substituents namely allyl, benzyl, and vinyl were synthesized and used as solvents in liquid-liquid extraction for the removal of phenolic compounds from hexane as the model oil. The RTILs were characterized using ^{1}H NMR, ^{13}C NMR, FT-IR, and CHN elemental analyses. Their density and viscosity were also measured. Five main parameters were evaluated through the removal process; the effect of IL substituent, the phase volume ratio of IL and model oil, phase contact time, and temperature. IL containing allylic substituent showed outstanding performance with approximately 95% efficiency under selected optimized conditions. To ensure that the RTIL can be used as a solvent for the removal of phenol, various other types of model oil apart from hexane such as petroleum ether, heptane, and cyclohexane were also used. The RTIL exhibited good recyclability and negligible loss of mass even after six cycles. Further mechanistic interactions between RTIL and phenol were studied by ^{1}H NMR and FT-IR.

Keywords: Room temperature ionic liquid, Benzyl imidazolium, Phenol, Liquid-liquid extraction, Model oil

1. Introduction

Phenol is a major industrial chemical usually produced from a multi-step process with benzene as the feedstock [1]. Other major sources of phenolic compounds are coal liquefaction oil, coal tar, petroleum, and biomass via pyrolysis [2-4]. Phenol is separated from coal via pyrolysis of low-rank coals, carbonization, hydropyrolysis, and liquefaction. It is used industrially for the production of phenolic resins, bisphenol A, caprolactam, and other phenolic compounds. In addition, they have been widely employed in many industrial processes as synthesis intermediates or as raw materials in the manufacturing of herbicides, pesticides, insecticides, pharmaceuticals, and dyes [5].

Coal tar has a relatively high concentration of phenolic compounds. Thus, it is desirable to separate phenolic compounds from the oil mixture before further refining for economic reasons. The traditional method currently employed to separate phenols from oil mixtures is through the use of strongly alkaline and acidic chemicals. However, this method produces excessive amounts of phenol-containing wastewater [6, 7]. Therefore, an environmentally friendly and efficient method becomes necessary to exhaustively extract phenols from oil.

In recent times, a new type of green solvent has emerged as an alternative reaction media to traditional organic solvents. Ionic liquids (ILs) can be broadly defined as ionic species that melt at or below 100 °C. Their structure typically consist of organic cations and either inorganic or organic anions [8]. Room temperature ionic liquids (RTILs) are a subset of ILs and they exist as liquids at room temperature [9, 10]. ILs have caught considerable attention in the analytical chemistry field due to their unique solvent properties including negligible vapour pressures, high thermal stabilities, variable viscosities, adjustable miscibility, reusability, and non-flammability [11-13].

The choice of both cations and anions allows us to tweak the properties of the resulting ILs to obtain the desired solvent properties [14, 15]. In order to enhance the properties of ILs as extractants, their substituent alkyl group can be customized. In fact, increasing the chain length of the substituent groups on the cations modifies the viscosity, hydrophobicity, and melting point [15].

Recently, there has been a growing interest in manipulating ionic liquids and other types of salts for the removal of phenolic compounds from oil. In 2013, Yucui Hou and co-workers studied several imidazolium-based ILs with different cationic alkyl chain length to separate phenol from hexane model oil. The study proved that imidazolium IL with shorter alkyl chain length in particularly [Bmim]Cl extracted phenol with a higher efficiency compared to its longer alkyl counterparts. The anions effect was also studied and the extraction efficiency using Cl^- surpassed Br^-, BF_4^-, and PF_6^- due to the higher electronegativity of Cl^- [16]. Tiantian Jiao et. al designed imidazole and its homolog compounds as new extraction agents for the separation of phenolic compounds from coal tar. They managed to prove that imidazole could extract phenols via the formation of hydrogen bonds [7].

Thus, in order to increase their extraction capability toward phenolic compounds, it is in our interest to synthesize a series of benzyl imidazolium-based ILs with allyl, benzyl and vinyl substituents. By employing substituents with double bonds and aromatic rings, phenols can be extracted by enhancing the π-π interaction. Due to the aromatic characteristic of phenolic compounds, the designation of new ionic liquids with aromatic and double bond moieties could open up a new frontier in the separation studies of phenolic compounds. In this study, the allylic benzyl imidazolium IL was selected for the removal of phenol and the effects of experimental conditions such as phase volume ratio, phase contact time, temperature and type of model oil used were studied. The regeneration of IL and the reaction mechanism were also investigated.

2. Experimental

2.1 Reagents and Materials

1-benzylimidazole (99%), allyl chloride (98%) and 1-vinylimidazole (≥99%) were purchased from Aldrich whereas benzyl chloride was commercially available from Merck. Acetonitrile (AcN) supplied by Merck were used as solvents in the synthesis part. For the model oil, n-hexane for liquid chromatography was purchased from Merck whereas n-heptane and petroleum ether were supplied by Friedemann and Schmidt while cyclohexane was obtained from Fisher Scientific. Crystallized phenol (Ph) was supplied by Scharlau, 2-nitrophenol (2-NP) (98%), 4-nitrophenol (4-NP) (≥99%), 2-chlorophenol (2-CP) (≥99%), 2,4,6-trichlorophenol (2,4,6-TCP) (98%), 2,4-dinitrophenol (2,4-DNP) of analytical standard and 2,4-dichlorophenol (2,4-DCP) were supplied by Sigma-Aldrich. 2,4,6-trinitrophenol (2,4,6-TNP) was purchased from R&M Chemicals while 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), toluene and xylene were commercially available from Merck. Standard fluoranthene and fluorene were purchased from Sigma-Aldrich. Ethyl acetate from R&M Chemicals was used in the synthesis part. Ultrapure water was used throughout this experiment. All chemicals were used as received without further purification.

2.2 Instrumentation

The Fourier Transform Infrared (FTIR) spectra were recorded by Perkin-Elmer Spectrum 400 FTIR spectrometer at room temperature equipped with a diamond attenuated total reflectance attachment. All spectra were recorded with characteristic peaks in the range of 450–4000 cm^{-1}. The Proton Nuclear Magnetic Resonance (^1H NMR) and ^{13}C NMR spectra were recorded by Lambda JEOL 400 MHz FT-NMR spectrometer. All the samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) with tetramethylsilane (TMS) as an internal reference for the calibration of proton chemical shift.

Elemental analyses (CHN) were performed using Pelkin-Elmer 2400 Series II Elemental Analyser. Electronic spectra were recorded by Shimadzu UV-Vis-NIR 3600 spectrometer in the range of 200-800 nm using a 1 cm quartz cell.

The densities of all products were obtained from Automatic Density Meter Rudolph Research Analytical DDM 2910 at 25 °C. The viscosities were measured using Anton Paar Physica MCR 301 rheometer at 25 °C.

A HPLC system consisting of a Shimadzu (Tokyo, Japan) LC-20AT pump, SPD-M20A diode array detector, SIL-20A HT auto sampler and CTO-10AS VP column oven was used for the separation and quantification of the analytes. The separation was conducted using a C-18 reverse phase column (250 mm x 4.6 mm; particle size 5 µm) hypersil gold, Thermo science USA. A mobile phase of methanol:water (80:20, v/v) was used at a flow rate of 1.0 mL min^{-1}. The injection volume was 10 µL. The detection for phenol was found at a retention time of 3.56 min and a wavelength of 272 nm; for 2,4-DCP it is at 4.37 min and 286 nm; for fluorene, 6.91 min and 262 nm ; for fluoranthene, 8.34 min and 286 nm; and for 2,4-DNP, the peak is found at 9.37 min and 267 nm.

2.3 Synthesis of ILs

All ILs were synthesized according to the literature with some modifications [17]. The synthesis involved a 1:2 molar ratio for the imidazole precursor to alkyl halide. Excess amount of alkyl halide was used so that imidazole can be completely reacted.

2.3.1 1-Allyl-3-benzylimidazolium chloride

Allyl chloride (0.10 mol, 7.652 g) was added dropwise over a period of 30 minutes to a round-bottomed flask containing 1-benzylimidazole (0.05 mol, 7.910 g) in 20 mL AcN under continuous stirring. The mixture was then stirred for about 1 hour and subsequently refluxed at 70 °C for 24 hours till a light brown liquid forms. Excess reactants and solvent were removed by rotary evaporation. The crude product was then diluted in an appropriate volume of water and washed three times with 15 mL ethyl acetate in a separating funnel. Finally, excess water was removed by rotary evaporation and dried under vacuum at 60 °C overnight to yield a light golden brown liquid (11.418 g, 97.29%). Density (ρ, g cm^{-3}) of the liquid is 1.1578 and the viscosity (η, Pa.s) is 3.2593.

^{1}H NMR (DMSO-d$_6$, δ, ppm): 4.869 (2H, d, NCH$_2$); 5.259-5.353 (2H, dd, C=CH); 5.476 (2H, s, NCH$_2$); 6.035 (1H, m, CH); 7.344-7.459 (5H, m, CH aromatic); 7.780 (1H, s, NC=CH); 7.897 (1H, s, NC=CH); 9.550 (1H, s, N=CH).

FT-IR (υ, cm^{-1}): 3383.02 (Quaternary N), 3127.65 (sp^2 C-H vinyl), 3054.50 (sp^2 C-H aromatic), 2977.69 (sp^2 C-H imidazolium ring), 2851.38 (sp^3 C-H), 1644.60 (C=N), 1605.74 (C=C vinyl), 1558.55, 1497.69 (C=C aromatic), 1451.94 (CH$_2$ methylene), 1153.90 (C-N).

^{13}C NMR (DMSO-d$_6$, δ, ppm): 136.870 (C4), 135.526 (C6), 132.284 (C5), 129.500 (C8), 129.252 (C10), 128.928 (C9), 123.388 (C11), 123.188 (C2), 120.881 (C1), 52.346 (C7), 51.479 (C3).

Anal. calcd. (%) for $C_{13}H_{15}N_2Cl$: C, 66.520; H, 6.440; N, 11.930. Found: C, 65.337; H, 6.867; N, 11.698.

2.3.2 1,3-Dibenzylimidazolium chloride

The same method was used to synthesize 1,3-dibenzylimidazolium chloride [DBZIM]Cl with 1-benzylimidazole (0.05 mol, 7.910 g) and benzyl chloride (0.10 mol, 12.658 g). A pale yellow viscous liquid (13.976 g, 98.15%) is obtained. Density (ρ, g cm^{-3}): 1.1871. Viscosity (η, Pa.s): 1395.3.

^{1}H NMR (DMSO-d$_6$, δ, ppm): 5.432 (4H, s, NCH$_2$); 7.321-7.420 (10H, m, CH aromatic); 7.847 (2H, s, NC=CH); 9.638 (1H, s, N=CH).

^{13}C NMR (DMSO-d$_6$, δ, ppm): 136.927 (C6), 135.440 (C7), 129.529 (C4), 129.290 (C3), 128.947 (C2), 123.388 (C1), 52.461 (C5).

FT-IR (υ, cm^{-1}): 3382.37 (Quaternary N), 3054.10 (sp^2 C-H aromatic), 2981.98 (sp^2 C-H imidazolium ring), 2847.55 (sp^3 C-H), 1626.25 (C=N), 1557.37, 1497.33 (C=C aromatic), 1454.98 (CH$_2$ methylene), 1148.99 (C-N).

Anal. calcd. (%) for $C_{17}H_{17}N_2Cl$: C, 71.70; H, 6.020; N, 9.840. Found: C, 69.933; H, 6.406; N, 9.534.

2.3.1 1-Benzyl-3-vinylimidazolium chloride

1-vinylimidazole (0.05 mol, 4.706 g) and benzyl chloride (0.10 mol, 12.658 g) were used to synthesize 1-benzyl-3-vinylimidazolium chloride [BZVIM]Cl. A dark brown viscous liquid is obtained (10.833 g, 98.17%). Density (ρ, g cm^{-3}): 1.1948. Viscosity (η, Pa.s): 39.898.

^{1}H NMR (DMSO-d$_6$, δ, ppm): 5.384-5.362 (1H, dd, C=CH); 5.471 (2H, s, NCH$_2$); 5.965-6.004 (1H, dd, C=CH); 7.314 (1H, q, NCH) 7.345-7.469 (10H, m, CH aromatic); 7.974 (1H, s, NC=CH); 8.262 (1H, s, NC=CH); 9.921 (1H, s, N=CH).

^{13}C NMR (DMSO-d$_6$, δ, ppm): 136.165 (C3), 135.068 (C5), 129.510 (C4), 129.433 (C7), 129.357 (C8), 129.090 (C9), 123.789 (C10), 120.061 (C2), 109.315 (C1), 52.632 (C6).

FT-IR (υ, cm^{-1}): 3382.68 (Quaternary N), 3119.73 (sp^2 C-H vinyl), 3055.57 (sp^2 C-H aromatic), 2998.95 (sp^2 C-H imidazolium ring), 2861.01 (sp^3 C-H), 1650.44 (C=N), 1566.79 (C=C vinyl), 1548.26, 1497.71 (C=C aromatic), 1454.44 (CH$_2$ methylene), 1160.21 (C-N).

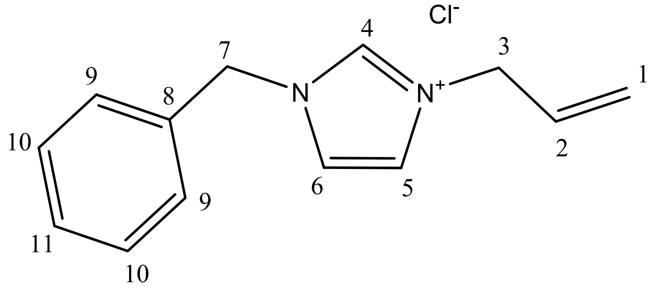
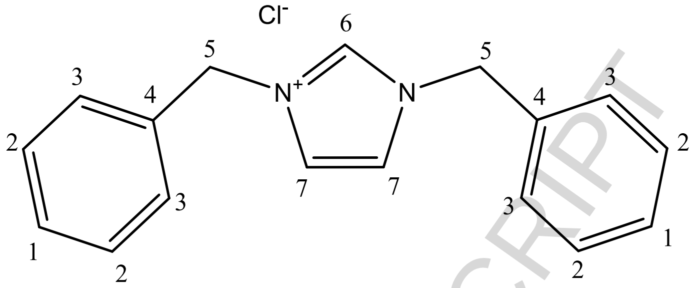
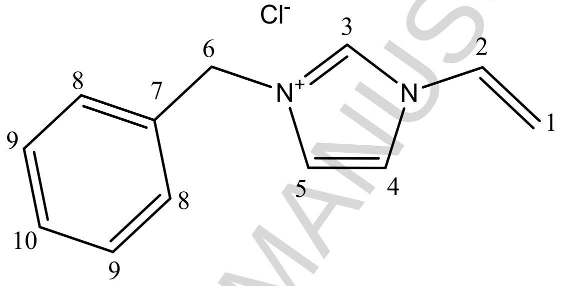
Anal. calcd. (%) for $C_{12}H_{13}N_2Cl$: C, 64.782; H, 5.448; N, 12.63. Found: C, 65.310; H, 5.940; N, 12.690.

All synthesized ILs were stored in a desiccator due to their hygroscopic property. The name and structure for all ILs are tabulated in Table 1. The three ILs are hydrophilic and thus they are used as solvents for the removal of phenol from model oil in this work.

Table 1

Name and structure of benzyl imidazolium-based ILs.

RTIL	Structure	Abbreviation

1-Allyl-3-benzylimidazolium chloride		[ABZIM]Cl
1,3-Dibenzylimidazolium chloride		[DBZIM]Cl
1-Benzyl-3-vinylimidazolium chloride		[BZVIM]Cl

2.4 Solubility Test

A preliminary study was carried out in order to investigate the solubility of IL in the model oil. A specific amount of IL was charged in a capped glass vial and then pure hexane was added to the IL. Fig. 1 shows the two immiscible phases of [ABZIM]Cl and the model oil. The IL forms the bottom layer while the model oil forms the top layer. The vial was then placed in a shaker at room temperature. The vial was shaken for 30 min and then allowed to settle. The upper hexane layer was decanted and analysed by UV-Vis spectroscopy and ^{1}H NMR spectroscopy. For UV-Vis analysis, pure IL was dissolved in water to a concentration of 0.10 g/L and its spectrum was then recorded. The spectrum of final hexane phase was also recorded. For ^{1}H NMR analysis, pure hexane and final hexane phase were dissolved in $CDCl_3$ while the ionic liquid phase after extraction was dissolved in DMSO-D_6. Their NMR spectra were recorded and analysed accordingly.

Fig. 1. Golden brown [ABZIM]Cl at the bottom while colourless model oil on the top.

For UV-Vis analysis, the absorption of the final hexane phase was compared with the absorption of pure ionic liquid. The maximum absorption of the ionic liquid appeared at 256 nm. No ionic liquid absorption was found in the final hexane phase after extraction. Thus, it can be concluded that the ionic liquid does not contaminate the model oil (refer to Supplementary Information, Fig. S1).

Moreover, the ^{1}H NMR spectrum of the final hexane phase showed no evidence of any ionic liquid contamination. The NMR spectrum of the ionic liquid was also recorded and no hexane chemical shift was observed. Thus, it can also be concluded that the ionic liquid is not soluble in the model oil (refer to Supplementary Information, Fig. S2).

2.4.1 Liquid-liquid extraction for quantitative solubility analysis

A quantitative analysis was also carried out in order to determine the solubility of [ABZIM]Cl in hexane. The procedure involved the mixing of 0.l mL [ABZIM]Cl with 4 mL hexane under the optimized conditions. A calibration curve was set up by preparing various concentrations concentration (50ppm, 200ppm, 400ppm, 600 and 800ppm) of standard solution of [ABZIM]Cl in water, Fig. S3. A standard solution of [ABZIM]Cl with a concentration of 500 ppm was also prepared as a reference.

After the LLE procedure, the hexane layer was decanted out and the [ABZIM]Cl layer was diluted with water until its concentration reaches 500 ppm. This sample was then analysed by UV-Vis spectrophotometer where the maximum absorption of [ABZIM]Cl appeared at wavelength, $\lambda = 256$ nm.

This experiment was done in triplicate and it was found that the solubility of [ABZIM]Cl in hexane is (0.00215±0.00007) wt%. Almost a similar result was observed when aromatic compound was used as model oil where the solubility of [ABZIM]Cl in toluene is (0.0032±0.0004) wt%. The results prove that the solubilities of the IL in hexane and toluene are very low which indicates that the IL has good properties and it is important for its application.

2.5 Preparation of model oil and synthetic oil

Each phenolic compound was dissolved in hexane to obtain a standard stock solution with a concentration of 100 ppm. All stock solutions were stored in the refrigerator. Working solutions were prepared daily by diluting the standard stock solutions with hexane.

In order to study the extractive performance of the ionic liquid in a real sample, a synthetic oil was prepared simulating those of real oil [18]. In this study, 2,4-DCP, 2,4-DNP and phenol were chosen as representatives for phenolic compounds while two types of polyaromatic hydrocarbons (PAHs), fluorene and fluoranthene were chosen to represent the aromatic compounds. 50 ppm of 2,4-DCP, 2 ppm of 2,4-DNP, 5 ppm of phenol, 0.5 ppm of fluorene and 1 ppm of fluoranthene were completely dissolved in hexane and then diluted to 25 mL in a volumetric flask.

2.6 Separation process in model oil and synthetic oil

First, a specific amount of IL was charged in a capped glass vial and a certain amount of model oil with a concentration of 5 ppm was added to the IL. The vial was then placed in a shaker at room temperature. After shaking for a known time and allowing it to settle, the upper hexane layer was decanted and the phenol content was analysed by UV-Vis spectroscopy. Concentrations of the phenol in hexane before and after the extraction were determined by UV-Vis spectrophotometer in which the maximum absorption of phenol in hexane appeared at wavelength, λ = 271 nm. In order to determine the concentration of phenol, various concentrations of standard solution of phenol were prepared and measured to obtain a calibration curve. Removal efficiency could be calculated by using Eq. 1 as shown below:

$$\%\,Removal = \frac{C_o - C_f}{C_o} \times 100\% \qquad \text{(Eq. 1)}$$

where C_o and C_f represent the phenol concentration in the original model oil and the upper layer after reaction respectively.

The separation process of phenolic compounds in synthetic oil was performed under optimized conditions. A specific amount of IL and synthetic oil was charged in a capped glass vial. After shaking for a set amount of time and allowing it to settle, the upper synthetic oil layer was decanted and filtered using a PTFE syringe filter (13 mm, 0.22 μm pore size). The filtrate was transferred into a vial and subsequently injected into the HPLC system for analysis. The % removal of phenolic compounds was determined by the difference in chromatograms peak area of the synthetic oil before and after extraction.

3. Results and discussion

3.1 Effect of structure of RTILs

The influences of various cation substituents (benzyl, vinyl and allyl groups) on the performance of the RTIL in the removal of phenol were investigated.

Fig. 2 shows the phenol removal efficiency for the three RTILs. [ABZIM]Cl managed to remove 78.33% phenol from the model oil while [DBZIM]Cl and [BZVIM]Cl were able to remove 73.17% and 63.83% phenol respectively. The substituent groups of the RTIL from the best to the worst performing follows the order of allyl > benzyl > vinyl. There are two explanations for how the substituents affect the phenol removal performance.

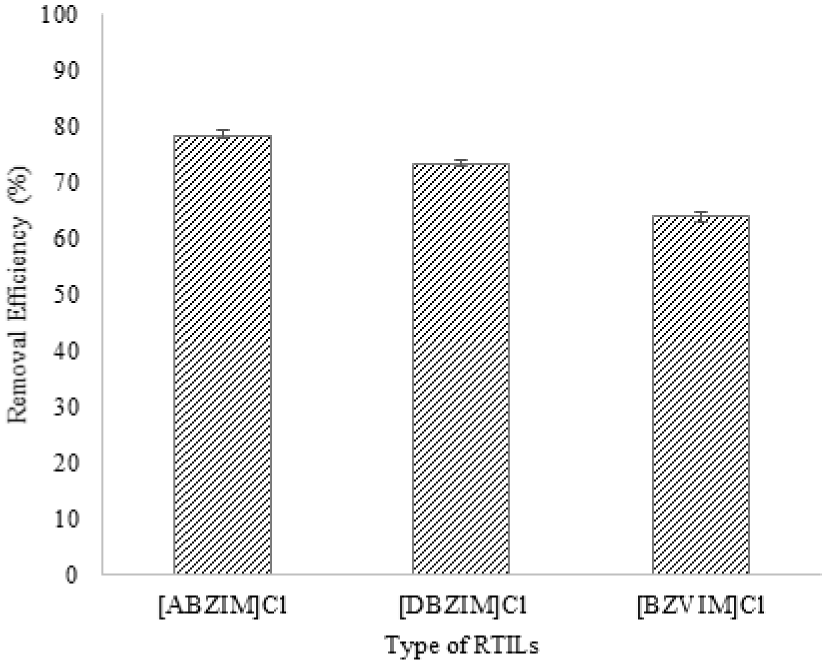


Fig. 2. Effect of RTILs structure on the phenol removal efficiency.

The first explanation is related to the ability of the RTIL to form hydrogen bonds with phenol. The main mechanism involves the chloride ion (Cl^-) of the IL which acts as the electron donor to the hydroxyl group on the phenol. The Cl^- ion has a higher probability to come in contact with the phenol, therefore causing a higher degree of hydrogen bonding to occur in the system. Thus, freely moving Cl^- anions are favourable in order to have a high removal efficiency of phenol. It is important to note that the distance of Cl^- from the imidazolium ring in IL is governed by the interionic force between the anion itself and the hydrogen on the imidazolium ring attached to the C(2) carbon [19, 20]. The numberings of the ring atoms for the imidazolium structures are depicted in Fig. 3. The strength of the C(2)-H bond can be seen from the ^1H NMR chemical shift value (δ, ppm) of the ILs. The higher the C(2)-H chemical shift, the stronger its interaction with the anion thus lowering the probability of the anion to form H-bond with phenol [21, 22]. By comparing the ^1H NMR spectra of all synthesized ILs, it can be seen that the C(2)-H of [ABZIM]Cl had the least chemical shift (δ, ppm). Thus, it can be concluded that the Cl^- of [ABZIM]Cl can move rather freely to form stronger hydrogen bonds with phenol compared to the other two ILs. The chemical shift of C(2)-H for the three RTILs are tabulated in Table 2.

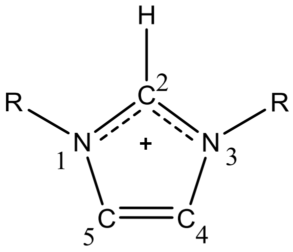


Fig. 3. The numberings of the ring atoms of imidazolium ring

Table 2

Chemical shift of carbon C(2) proton

RTILs	Chemical shift of carbon C(2) proton δ, ppm
[ABZIM]Cl	9.550
[DBZIM]Cl	9.638
[BZVIM]Cl	9.921

The second explanation of how various substituents on ILs affect its performance can be attributed to the alkyl chain length on the imidazolium ring. According to literature, the longer the N-alkyl side chains, the weaker the intramolecular hydrogen bonding between the C(2)-H and the anions [23]. As a consequence, the ability of longer alkyl chain ILs to remove phenol increases. This phenomenon can be observed in [BZVIM]Cl whose vinyl side chain is shorter than the allyl group on [ABZIM]Cl, resulting in lower interaction to form hydrogen bonds with phenol due to the close distance between the cation and Cl^- [3, 7]. The ability of [ABZIM]Cl to remove phenol from the model oil surpassed that of [DBZIM]Cl due to the larger volume occupied by the benzyl group compared to that of the allyl substituent. The large volume of the substituent also increased the molecular volume of [DBZIM]Cl, thus affecting the distance between the charge centres of the anion and the cation. As a result, the steric hindrance caused by bigger benzyl group hindered the ability of the chloride ion to form H-bond with phenol. Therefore, it should be noted that there is an optimum distance between the chloride ion and cation to form hydrogen bond with phenol [3, 7, 24].

3.2 Effect of phase volume ratio

The phase volume ratio is an important factor for the extraction process. In order to determine the effect of phase volume ratio of the model oil and IL on the phenol removal efficiency, an experiment was conducted using [ABZIM]Cl as the representative at 25 ^{0}C for 30 min. Hexane-to-[ABZIM]Cl volume ratios of 20 (4 mL/0.2 mL) to 500 (4 mL/0.008 mL) were used (Fig. 4). It can be seen that the % removal dropped significantly with increasing phase volume ratios. The decrease in removal efficiency could be due to the much greater volume of oil phase compared to IL phase used in this extraction. The performance of [ABZIM]Cl in removing phenol achieved 99.46% when a phase volume ratio of 20 is used. It is also observed that the removal efficiency remained sufficiently high at 95.24% even when a higher volume ratio of 40 (4 mL/0.1 mL) is used. Therefore, taking into account the economic efficiency, a volume ratio of 4:0.1 of model oil to IL was selected as the optimal value and used in succeeding steps in order to decrease the usage of IL in this extraction.

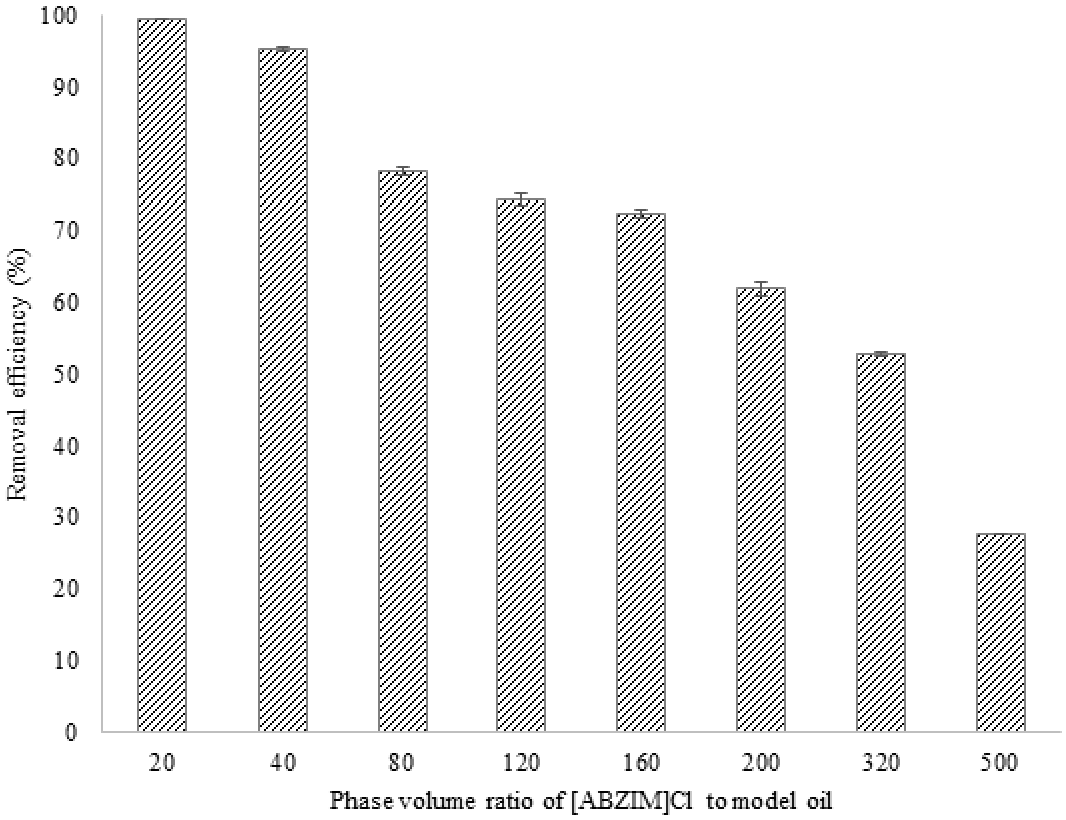


Fig. 4. Effect of phase volume ratio of [ABZIM]Cl to model oil.

3.3 Effect of phase contact time

The phase contact time is another important parameter in the extraction process because the mass transfer of analyte between two immiscible phases requires some time to reach equilibrium [25]. The effect of contact time was investigated comprehensively from 10 min to 60 min at a volume ratio of 40 and reaction temperature at 25 ^{0}C. From Fig. 5, the removal efficiency increased sharply from 10 min to 30 min. However, the % removal reached a plateau after 30 min. Further increase of contact time from 40 min to 60 min showed a slight decrease in phenol removal efficiency which may be due to the evaporation of the hexane after long extraction times. The removal of phenol reached equilibrium after 30 min and thus, a duration of 30 min was employed as the optimum time for phenol extraction.

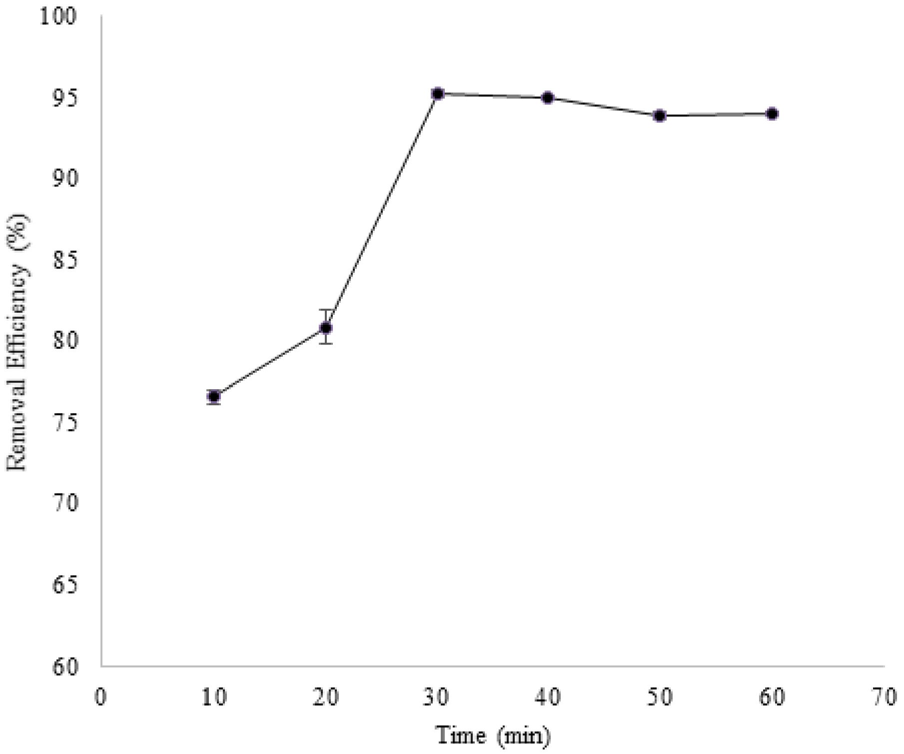


Fig. 5. The effect of time on the phenol removal efficiency.

3.4 Effect of temperature

The effect of temperature on the phenol removal efficiency was studied thoroughly at temperatures 25 ^{0}C to 60 ^{0}C at a volume ratio of 40 and contact time of 30 min. Fig. 6 shows the temperature dependence of the phenol removal efficiencies. It can be seen that increasing the reaction temperature decreased the phenol removal efficiencies. The % removal decreased gradually from 25 ^{0}C to 30 ^{0}C and then exhibited a more significant decrease at elevated temperature. Therefore, from the results obtained, the extraction procedure is best performed at room temperature.

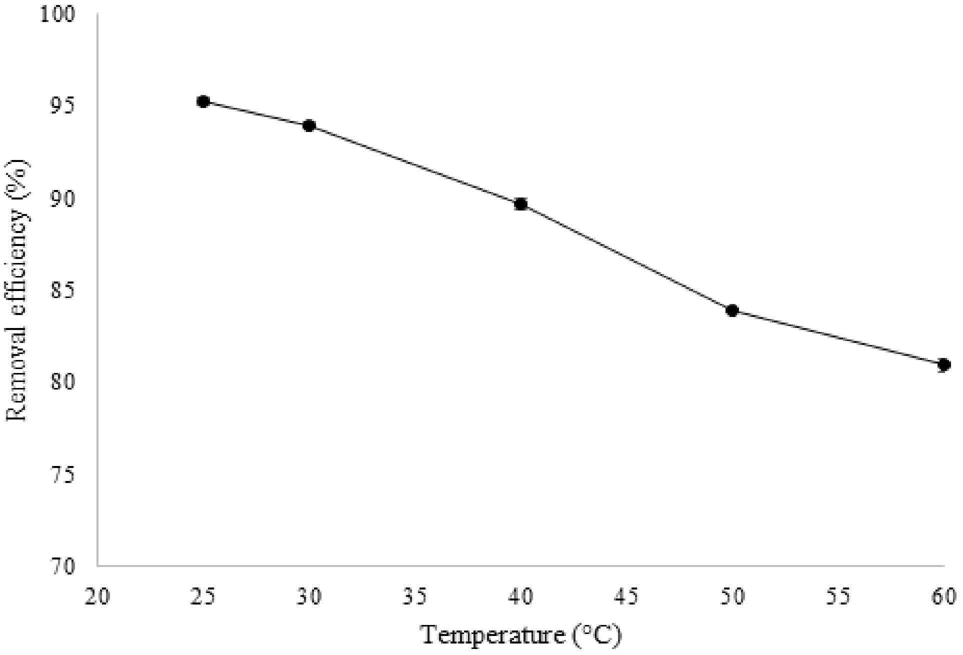


Fig. 6. Effect of temperature on phenol removal efficiency.

3.5 Types of model oil

In order to study the effectiveness of [ABZIM]Cl in removing phenols from oil, n-heptane, cyclohexane and petroleum ether were selected as the model oils as they represent non-aqueous environments. Fig. 7 shows that [ABZIM]Cl managed to remove approximately 85 % phenol from all model oils used. Thus, it can be concluded that [ABZIM]Cl is a suitable solvent to use for liquid-liquid extraction in non-aqueous media.

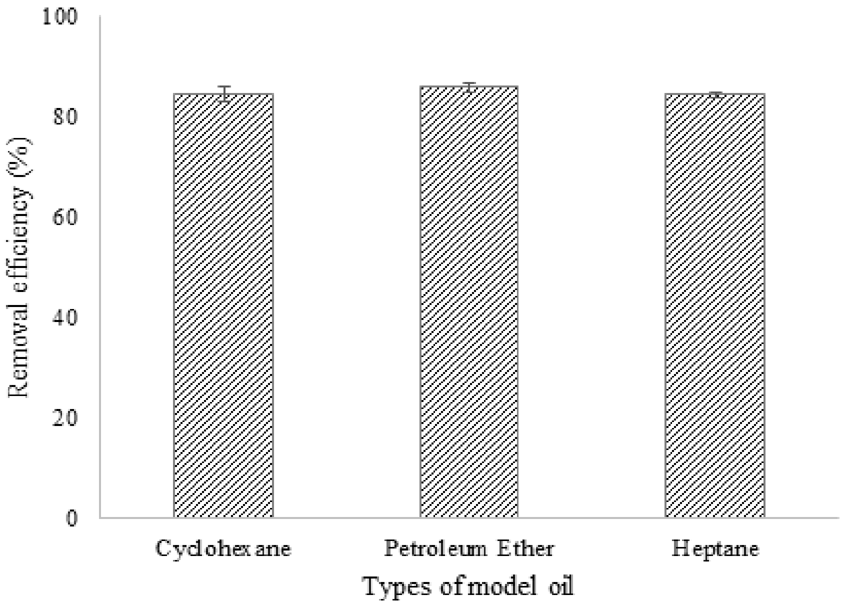


Fig. 7. Effect of types of model oil on phenol removal efficiency

3.6 Selectivity study

Nine phenolic compounds with different nitro and chlorine substituents as well as two other aromatic compounds; namely xylene and toluene were used as analytes in investigating the influence of various substituents on the removal efficiency of phenols from model oil. The % removal efficiency increased in the order of Ph > 4-CP > 3-CP > 2CP > 2,4-DCP > 2,4,6-TCP for chlorinated phenols while for nitrophenols, it increased in the order of 4-NP > 2,4-DNP > 2,4,6-TNP under the same experimental conditions. Higher removal efficiencies were observed for phenols containing lesser amounts of the hydrophobic substituents chlorine and nitro. This is because hydrophilic interaction is favourable for the reaction between IL and phenols. As an example, 2,4,6-TCP has the lowest % removal from the oil and this is attributed to the higher number of chlorine substituents [25-28].

There are usually aromatic compounds other than phenols found in oils. Thus, it is important to study the selectivity of IL towards those compounds. In our study, there was no extraction of toluene and xylene from the model oil by the IL. This is because there are no available sites where H-bond can form between IL and aromatic compounds which is vital for the extraction. The reaction mechanism is further discussed in the next section. Thus, it can be concluded that the synthesized IL is only selective towards phenolic compounds and not towards other aromatic compounds that may be present in the oil.

3.7 Reaction mechanism

The RTILs enable the separation of phenol from the model oil via dissolution of phenol from the oil phase into the ILs phase. According to literature, there are two significant interactions that govern the ability of RTILs to extract phenol. The first is the formation of hydrogen bonds in which the chloride ion acts as the electron donor to the hydroxyl group in the phenol structure. The high electronegativity of chloride ion favours hydrogen bonding and thus, plays a crucial role in the extraction process. The second driving force for the removal of phenol by imidazolium-based IL is the π-π conjugation between the imidazolium ring and the benzene ring of phenol [29]. Moreover, additional π-π interaction is contributed by the presence of benzyl and allyl substituents.

The formation of hydrogen bond between phenol and [ABZIM]Cl were analysed from the FT-IR and ^{1}H NMR spectra. FT-IR is an important tool in determining the presence of hydrogen bonding [3, 7, 24]. In order to confirm the presence of H-bonding, 1:1 mole ratio of [ABZIM]Cl and phenol were prepared and analysed. The OH vibrational frequency of pure phenol could be observed at wavenumber of 3217.16 cm^{-1} shown in Fig. 8. However, after extraction using [ABZIM]Cl, this peak shifted to a higher frequency of 3370.84 cm^{-1}. This change in the absorption peak is mainly due to the migration of the electron cloud in oxygen atom on the phenol to a higher wavenumber [30].

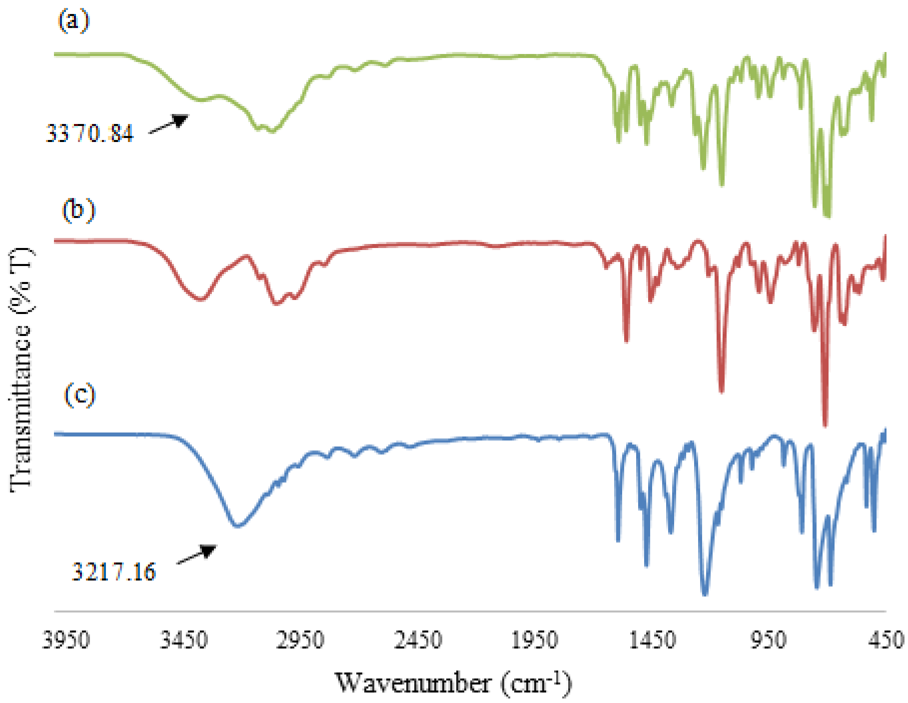


Fig. 8. FT-IR spectra of (a) [ABZIM]Cl-Phenol, (b) [ABZIM]Cl and (c) Phenol

In addition, a ^{1}H NMR analysis was also employed in order to confirm the formation of hydrogen bond between [ABZIM]Cl and phenol. From Fig. 9, it can be deduced that a hydrogen bond was formed due to the shifting of OH chemical shift on phenol from 9.2920 ppm to 9.4760 ppm after extraction with [ABZIM]Cl. Moreover, the sharp peak of OH on the pure phenol spectrum also broadened.

Interestingly, the role of aromatic moieties and unsaturated substituents in strengthening π-π interaction of ILs with phenyl ring of phenol can be proven from their ^{1}H NMR spectrum. This is because cationic imidazolium ring modified with unsaturated substituents such as benzyl and allyl groups could attract aromatic compounds more efficiently compared to their alkyl counterparts [31]. Table 3 shows the chemical shift changes (Δδ, ppm) for [ABZIM]Cl after extraction of phenol. The allylic protons of [ABZIM]Cl-Phenol mixture experienced a downfield shift suggesting that there was a strong interaction between the IL and phenol. Moreover, greater chemical shift changes are observed on aromatic protons of [ABZIM]Cl confirming the ability of aromatic moieties in strengthening the π-π interaction and on imidazolium protons of [ABZIM[Cl namely H10 and H11 proving that imidazolium ring could also form π-π stacking with phenol. Fig. 10 illustrates the π-π interaction of aromatic benzene ring of phenol with aromatic and allylic moieties of [ABZIM]Cl as well as H-bonding of Cl^- with hydroxyl group of phenol.

Table 3

Proton	δ, ppm			Δδ, ppm
	[ABZIM]Cl	Phenol	[ABZIM]Cl-Phenol	
H1	5.2805	-	5.2955	+ 0.0150
H2	5.3400	-	5.3630	+ 0.0230
H3	6.0430	-	6.0590	+ 0.0160
H4	4.8685	-	4.8715	+ 0.0030
H5	9.5500	-	9.4760	- 0.0740
H6	5.4760	-	5.4730	- 0.0030
H7	7.3725	-	7.3935	+ 0.0210
H8	7.4100	-	7.4230	+ 0.0130
H9	7.4945	-	7.4500	- 0.0445
H10	7.8970	-	7.7760	- 0.1210
H11	7.7800	-	7.8850	+ 0.1050
Ha	-	9.2920	9.4760	+ 0.1840
Hb	-	6.7020	6.7340	+ 0.0320
Hc	-	6.7195	6.7730	+ 0.0535
Hd	-	7.1120	7.1420	+ 0.0300

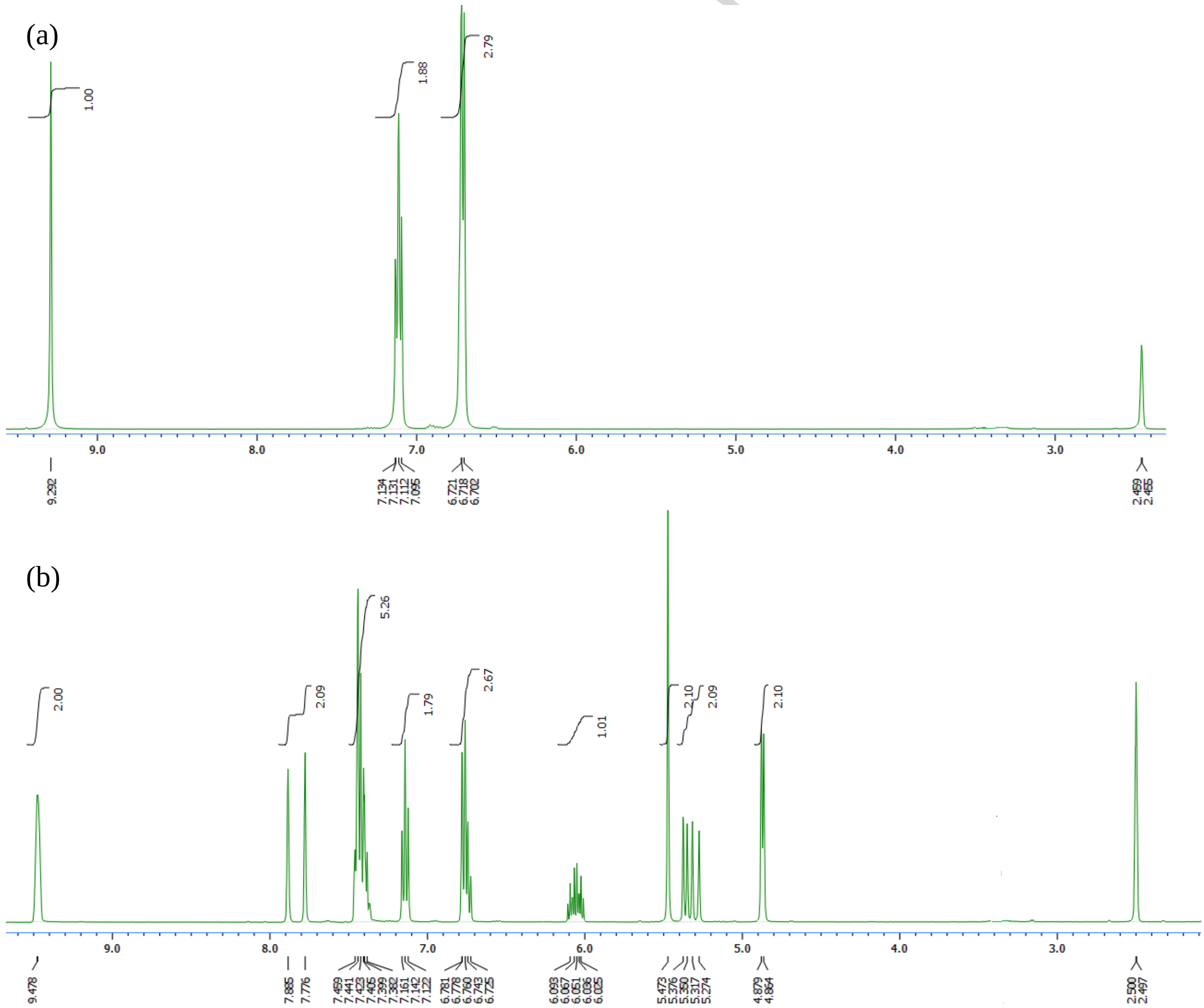


Fig. 9. ^{1}H NMR spectra of (a) pure phenol and (b) [ABZIM]Cl-Phenol.

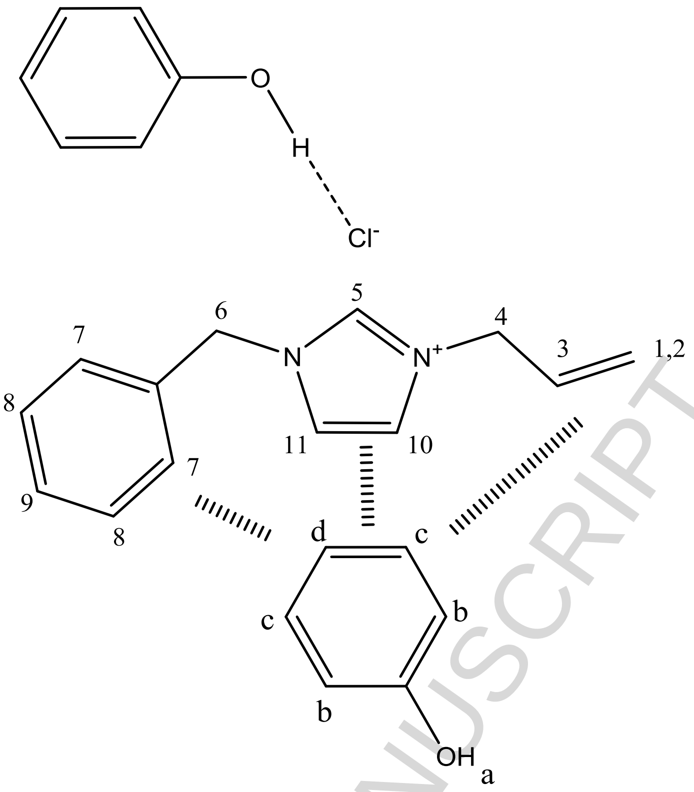


Fig. 10. The π-π interaction of aromatic benzene ring on phenol with aromatic and allylic moiety of [ABZIM]Cl as well as H-bonding of Cl^- with hydroxyl group on phenol

3.8 *Recyclability study*

To test the recyclability of [ABZIM]Cl, it is recovered after the first extraction and then reused for subsequent cycles. Ethyl acetate was used as an efficient back-extraction agent to recycle ILs due to the significant solubility difference between ILs and phenol in ethyl acetate. Upon addition of ethyl acetate to IL layer, the phenol reached equilibrium in ethyl acetate after shaking for 30 min. The ethyl acetate layer was then decanted and the process was repeated three times to ensure the recycled IL is free from impurities. The same processes were repeated for each cycle. The phenol removal efficiencies were finally calculated to evaluate the extraction ability of the recycled IL. Fig. 11 shows that the recycled IL can be reused several times and the phenol removal performance remains constant after 5 cycles. However, the efficiencies dropped gradually after 6th cycles but the efficiency is still maintained at approximately 90%.

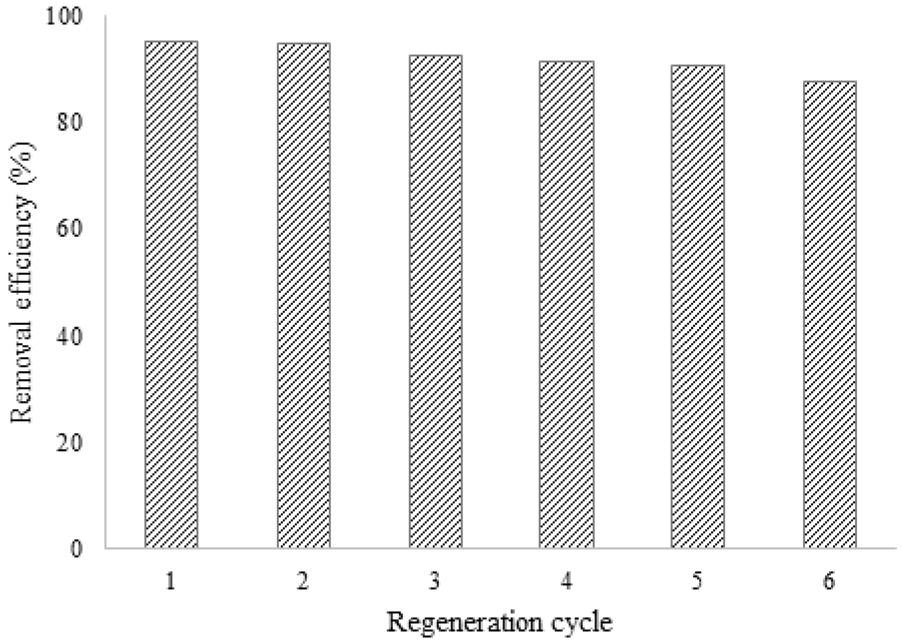


Fig. 11. Phenol removal efficiency versus regeneration cycle of RTIL

To confirm the structure of the recycled RTIL, ^{1}H NMR and FT-IR analyses were carried out. In Fig. 12, the characteristic absorption peaks of the recycled [ABZIM]Cl were identical to those of pure [ABZIM]Cl. The identity of the recycled [ABZIM]Cl was also confirmed by the ^{1}H NMR spectrum shown in Fig. 13.

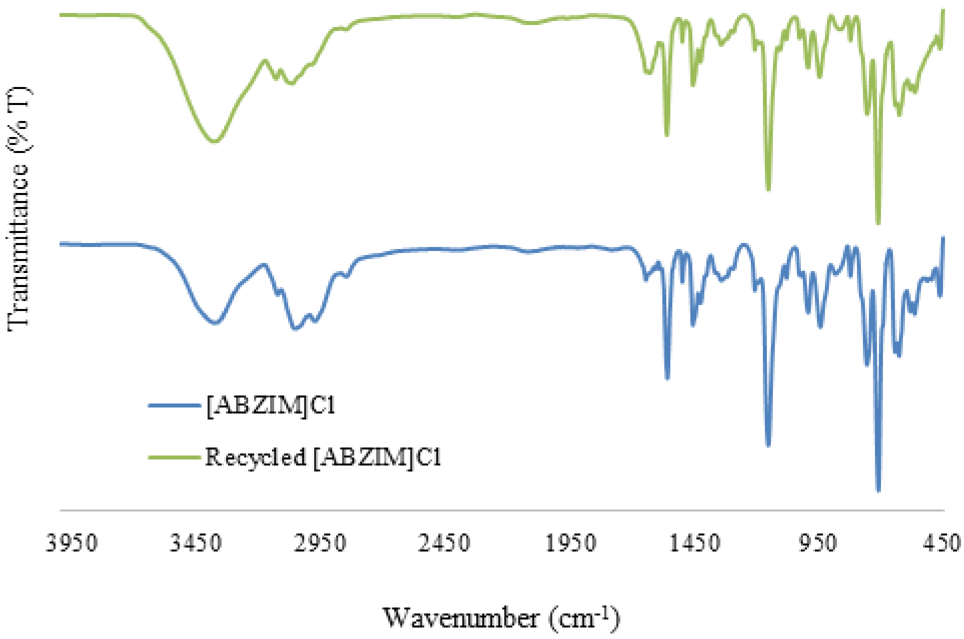


Fig. 12. FT-IR spectra of pure [ABZIM]Cl and recycled [ABZIM]Cl.

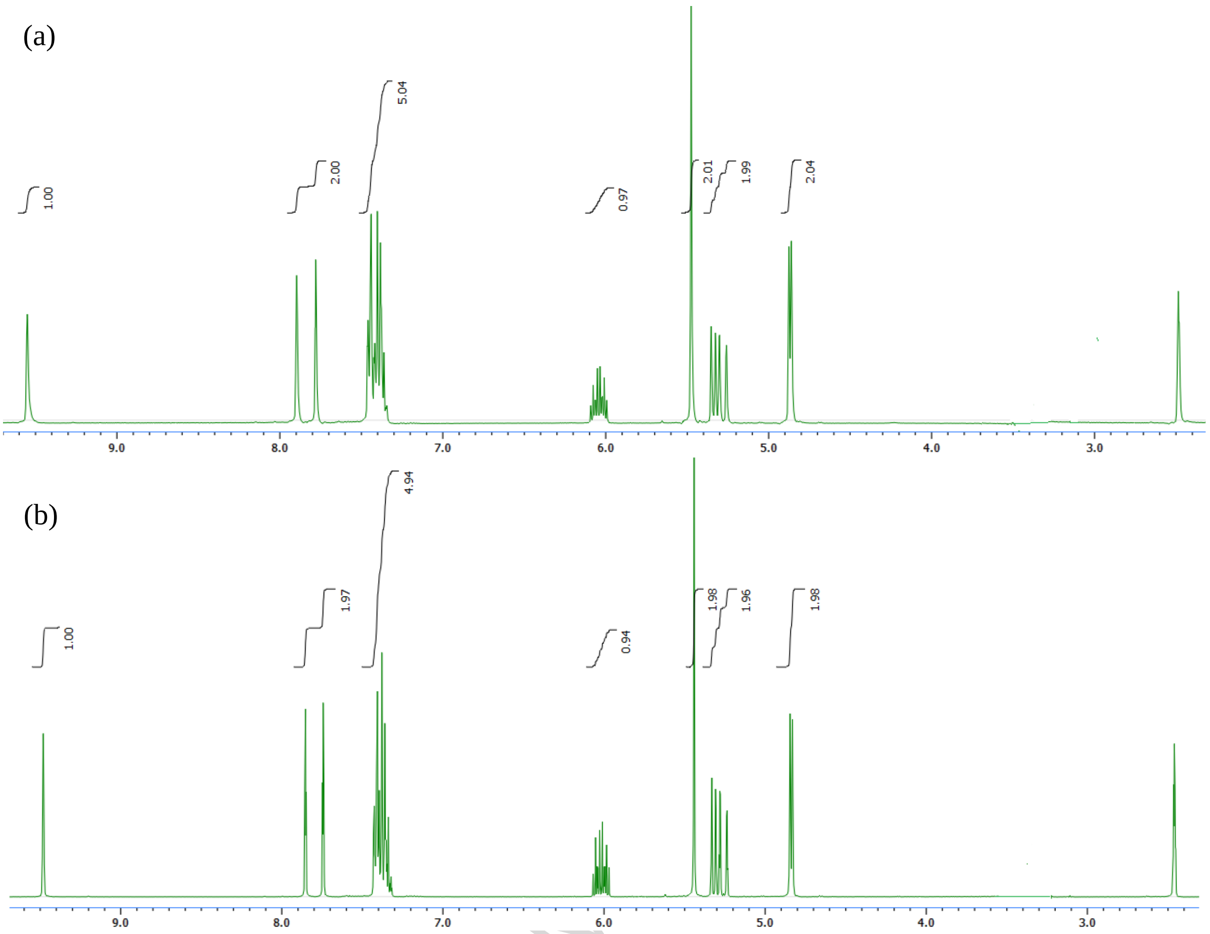


Fig. 13. ^{1}H NMR spectra of (a) pure [ABZIM]Cl and (b) recycled [ABZIM]Cl.

3.9 Extraction of phenols in synthetic oil

The calculated HPLC chromatogram peak area of the synthetic oil before and after the extraction showed that [ABZIM]Cl was able to remove about 87.72% of phenol, 64.77% of 2,4-DNP and 63.47% of 2,4-DCP. This result proved that the performance of [ABZIM]Cl is excellent even in the presence of different types of phenolic compounds and polyaromatic hydrocarbons (PAHs). The % removal of fluorene and fluoranthene was found to be negligible. Thus, we concluded that benzyl imidazolium-based ionic liquid is only selective towards phenolic compounds and not selective to polyaromatic hydrocarbons.

4. Conclusion

It was found that benzyl imidazolium-based IL is a potential alternative extraction medium for separating phenols from model oil. The presence of benzyl and double bond groups significantly improve the ability of ILs to remove phenol via hydrogen bonding and enhanced π-π interaction of aromatic moieties. As revealed by the ^{1}H NMR of [ABZIM]Cl-Phenol mixture, the benzene ring on phenol interacts with both allylic and benzylic substituents of [ABZIM]Cl as well as the imidazolium ring. Thus, it can be concluded that [ABZIM]Cl form strong bonds with phenol under optimized conditions with good recyclability up to 6 cycles without significant loss in mass. This study also revealed that the long double bond group on the benzyl imidazolium IL allow strong interaction with the phenol due to the freely moving chloride anion forming hydrogen bonds with phenol compared to the shorter double bond due to the tightly-attached chloride anion to the C(2)-H on imidazolium ring.

Acknowledgement

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Highlights

- The effects of the main parameters in liquid-liquid extraction were investigated.
- Allyl substituted RTIL showed 95% removal efficiency.
- The mechanistic interaction of phenol removal by RTILs was proposed.
- π-π interaction and hydrogen bonding were found to be the ultimate removal mechanism.
- The recyclability of RTIL was also discussed.