



Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation

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ABSTRACT

A hydrophobic magnetic room temperature ionic liquid (MRTIL), trihexyltetradecylphosphonium tetrachloroferrate(III) ($[3C_6PC_{14}][FeCl_4]$), was synthesized from trihexyltetradecylphosphonium chloride and $FeCl_3 \cdot 6H_2O$. This MRTIL was investigated as a possible separation agent for solvent extraction of phenolic compounds from aqueous solution. Due to its strong paramagnetism, $[3C_6PC_{14}][FeCl_4]$ responds to an external neodymium magnet, which was employed in the design of a novel magnetic extraction technique. The conditions for extraction, including extraction time, volume ratio between MRTIL and aqueous phase, pH of aqueous solution, and structures of phenolic compounds were investigated and optimized. The magnetic extraction of phenols achieved equilibrium in 20 min and the phenolic compounds were found to have higher distribution ratios under acidic conditions. In addition, it was observed that phenols containing a greater number of chlorine or nitro substituents exhibited higher distribution ratios. For example, the distribution ratio of phenol (D_{ph}) was 107. In contrast, 3,5-dichlorophenol distribution ratio ($D_{3,5-DCP}$) had a much higher value of 6372 under identical extraction conditions. When compared with four selected traditional non-magnetic room temperature ionic liquids, our $[3C_6PC_{14}][FeCl_4]$ exhibited significantly higher extraction efficiency under the same experimental conditions used in this work. Pentachlorophenol, a major component in the contaminated soil sample obtained from a superfund site, was successfully extracted and removed by use of $[3C_6PC_{14}][FeCl_4]$ with high extraction efficiency. Pentachlorophenol concentration was dramatically reduced from $7.8 \mu g mL^{-1}$ to $0.2 \mu g mL^{-1}$ after the magnetic extraction by use of $[3C_6PC_{14}][FeCl_4]$.

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1. Introduction

Phenols are pollutants of major concern as a result of their widespread use, high toxicity and possible accumulation in the environment [1,2]. These compounds are present in wastewater of a great variety of industries, such as refineries, coking operations, coal processing, petrochemical manufacturing, coal gasification liquefaction processes, pharmaceutical plastics, wood products, paint, and pulp and paper industries [3,4]. Therefore, phenolic compounds should be removed before the water can be recycled or discharged into the environment [5]. Phenols can be degraded to harmless compounds by bacteria and fungi under aerobic or anaerobic conditions [6,7]. However, major disadvantages of biological degradation include the low survival of microorganisms under high phenol concentrations and extended exposure. In addition, thermal decomposition of phenols is limited to small scale wastew-

ater treatment [8–11]. Adsorption is an effective method that can be used to treat dilute phenols in wastewater [12–15]. However, this method may not be useful for treating high concentrated phenolic wastewater due to the high cost of sorbents [16–19]. Other approaches for phenol removal including electrochemical conversion [20], membrane filtration [21], and supercritical fluid extraction [22] have also been reported.

Liquid–liquid extraction is an effective separation technique for use in analytical science and chemical industry. In general, traditional solvent extraction employs a partitioning of a solute between two immiscible phases, typically an organic solvent and an aqueous solution. The solvent extraction method has the advantage of treating high concentrated phenolic wastewater [16]. However, the organic solvents used in traditional solvent extraction systems are usually volatile, toxic and flammable. Therefore, it is desirable and worthwhile to explore more effective and cleaner alternative extraction solvents for the development of new separation processes.

Room temperature ionic liquids (RTILs) are salts with a melting point close to or below room temperature. RTILs have recently been claimed as “green” solvents mainly due to their extremely low

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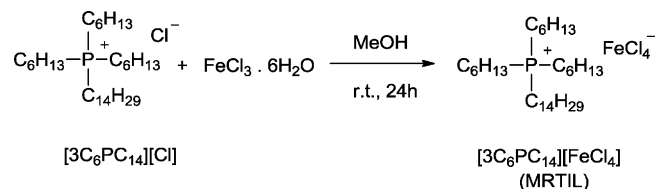
vapor pressure. In contrast to conventional volatile organic extraction solvents, RTILs are nonflammable, chemically and thermally stable, and have no detectable vapor pressure [23]. Therefore, as new alternative extraction solvents, RTILs have been successfully used to extract and separate various compounds from organic or aqueous solutions [24–30]. However, it is worth noting that RTILs used to date are non-magnetic and predominantly based on imidazolium and phosphonium salts. Recently, the development of magnetic room temperature ionic liquids (MRTILs) was reported [31,32]. These MRTILs are primarily based on high-spin d^5 iron(III) in the form of tetrachloro- or tetrabromoferrate(III) with various counter cations. Owing to the high single-ion magnetic moment, these MRTILs exhibit a strong response to external magnetic fields. Other MRTILs containing different transition metal ions such as gadolinium and dysprosium have also been reported [33,34]. However, to date there have not been any reports of these MRTILs as novel extraction solvents. In our view, the use of MRTILs as extraction solvents may provide a new separation technique which can capitalize on the magnetic property of MRTILs. A number of advantages should accrue from use of this novel magnetic solvent extraction approach. For example, the use of an external magnetic field to remove the extraction solvent and realize the phase contact and separation would be interesting for theoretical studies since this concept has not been previously explored. Such a study would yield useful information and knowledge about the novel magnetic separation process. In addition, magnetic extraction may overcome the formation of undesirable emulsification. The formation of emulsions, which frequently occurs in traditional extraction processes, has been reported to produce obstacles and inconveniences during phase separation and recovery of the extraction solvent. Herein, we report on the application of an MRTIL as an extraction solvent for the separation of various phenolic compounds from aqueous solution. Experimental measurements are performed to determine the distribution ratios of the phenols and thus to optimize this novel magnetic extraction process.

2. Experimental

2.1. Chemicals and materials

Trihexyltetradecylphosphonium chloride (95%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.9\%$), NaBF_4 (98%), KPF_6 (98%), lithium bis(trifluoromethanesulfonyl)imide (LiTf_2N) ($\geq 99\%$), phenol (Ph) (99%), 4-nitrophenol (4-NP) ($\geq 99\%$), 2-chlorophenol (2-CP) ($\geq 99\%$), 4-chlorophenol (4-CP) ($\geq 99\%$), 2,3-dichlorophenol (2,3-DCP) (98%), 2,4-dichlorophenol (2,4-DCP) (99%), 3,5-dichlorophenol (3,5-DCP) (97%), 3,4-dichlorophenol (3,4-DCP) (99%), pentachlorophenol (penta-CP) (98%), 2-benzyl-4-chlorophenol (2-Ben-4-CP) (95%), and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ($[\text{BM}_2\text{IM}][\text{PF}_6]$) ($\geq 97\%$) were obtained from Sigma–Aldrich (Milwaukee, WI, USA) and used without further purification. Ethanol, methanol, and chloroform were of anhydrous grade (Sigma–Aldrich, Milwaukee, WI), and all other organic solvents such as acetonitrile and water were of HPLC grade (J. T. Baker, Phillipsburg, NJ). Contaminated soil samples acquired from a superfund site were kindly donated by Professor Barry Dillinger in the Department of Chemistry at Louisiana State University.

By use of anion-exchange reactions, regular non-magnetic RTILs, trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide ($[\text{3C}_6\text{PC}_{14}][\text{Tf}_2\text{N}]$), trihexyltetradecylphosphonium tetrafluoroborate ($[\text{3C}_6\text{PC}_{14}][\text{BF}_4]$), and tetrahexylphosphonium bis(trifluoromethanesulfonyl)imide ($[\text{4C}_6\text{P}][\text{Tf}_2\text{N}]$) were synthesized according to the procedure previously reported [35,36]. The pH values of the aqueous solutions were adjusted by



Scheme 1. Synthesis of hydrophobic magnetic room temperature ionic liquid (MRTIL).

use of aqueous solutions of HCl or NaOH and were measured by use of a digital pH meter.

2.2. Synthesis of MRTIL $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$

$[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ was synthesized by use of a reaction between trihexyltetradecyl-phosphonium chloride ($[\text{3C}_6\text{PC}_{14}][\text{Cl}]$) and iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in anhydrous methanol at room temperature for 24 h (Scheme 1) [33]. A typical synthesis procedure is described as follows. To a solution of trihexyltetradecylphosphonium chloride in anhydrous methanol solution was added equal molar amount of iron(III) chloride hexahydrate, which was predissolved in anhydrous methanol. The resultant mixed yellow solution was stirred at room temperature for 24 h using a stirring rate of 400 rpm. After completion of the reaction, methanol was removed by rotavapor under vacuum. The resultant viscous brownish liquid was subsequently washed with a small amount of DI water. After careful removal of the upper water phase, the ionic liquid was further freeze-dried on a lyophilizer overnight. The final product, $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$, is a dark brown viscous liquid. Anal. Calcd for $\text{C}_{32}\text{H}_{68}\text{Cl}_4\text{FeP}$, C, 56.40; H, 10.06. Found: C, 57.21; H, 9.83. The pH of this compound is estimated to be acidic as a result of hydrolysis of FeCl_4^- and its density is 1.02 mg mL^{-1} .

2.3. Characterization of $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ by UV–Vis, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), superconducting quantum interference device (SQUID) and rheometer

To characterize $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$, its visible absorption spectrum was measured using a Shimadzu UV-3101PC UV–Vis–near-IR scanning spectrometer (Shimadzu, Columbia, MD). Absorption was collected using a 1.0 cm^2 quartz cuvette at room temperature with blank subtraction [32].

A TA Q50 thermal gravimetric analyzer (TA Instruments, New Castle, DE) was used to analyze the thermal stability of $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ and its thermal decomposition behavior [32]. The temperature was scanned from room temperature to 773 K under nitrogen flow (50 mL/min) with a heating rate of 10 K min^{-1} . The onset degradation temperature and peak temperature were determined using the derivative TGA curves. Glass transition behavior or melting point of $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ was investigated using a Q100 differential scanning calorimeter (TA Instruments, New Castle, DE). The sample was placed in a sealed aluminium crucible and analysis was performed under a nitrogen flow (50 mL/min). The sample was cooled to 207 K, kept isothermal for 3 min, and then heated to 333 K at a rate of 10 K min^{-1} .

The magnetic magnetization and susceptibility of $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ were measured using approximately 80 mg of the sample in a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer (San Diego, CA, USA) for fields between $-50,000$ and $50,000 \text{ Oe}$.

A Rheometric Scientific RFSII rheometer (geometry: 25 mm cone and plate with a 25 mm diameter, 0.04 radians cone angle, 0.05 mm truncation) was used to measure the viscosity of $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$

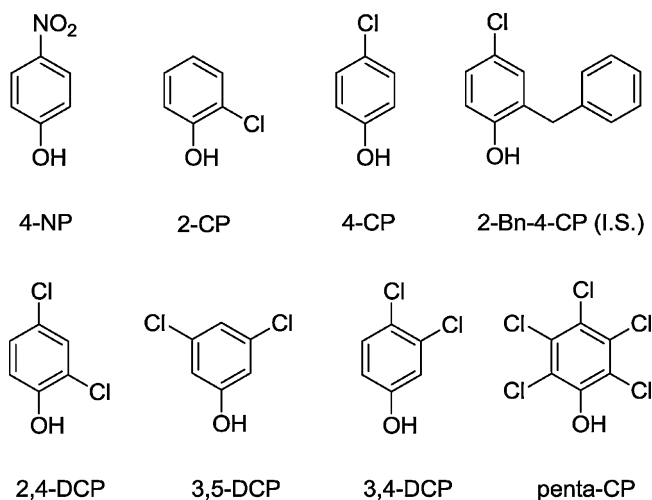


Fig. 1. Structures of nitro- or chlorophenols.

at room temperature. In the first measurement, the viscosity was measured at constant shear rates (0.02, 0.1, 0.5, 1.0, 10, 25, 50 and 100 s^{-1}). Each shear rate was held for 20 s and the measurement was averaged for a 2 s interval. In the second test, the shear rate was ramped from 0 to 100 s^{-1} , over 300 s time intervals. In each test, samples were loaded and allowed to thermally equilibrate for 15 s prior to test initiation.

2.4. Preparation of standard stock solution

Each phenol, including phenol (Ph), 4-nitrophenol (4-NP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 3,5-dichlorophenol (3,5-DCP), pentachlorophenol (penta-CP), and 2-benzyl-4-chlorophenol (2-Bn-4-CP) (Fig. 1) was dissolved in methanol to obtain a standard stock solution with a concentration of 2 mg mL^{-1} . The stock solutions were stored at 277 K. Mixed standard stock solutions containing various phenolic compounds were prepared similarly in methanol and stored at 277 K. Working solutions were prepared daily by diluting the standard stock solutions with DI water.

2.5. Magnetic extraction operation

In a capped glass vial (20 mL), $[3\text{C}_6\text{PC}_{14}][\text{FeCl}_4]$ ($50\text{ }\mu\text{L}$) was suspended in an aqueous phenolic solution (6 mL) with predeter-

mined concentration (Fig. 2). Due to its strong paramagnetism, $[3\text{C}_6\text{PC}_{14}][\text{FeCl}_4]$ responds to and moves in the presence of a neodymium magnet ($B = 1.4\text{ T}$). The magnet was moved circularly by use of an orbital shaker (S500, VWR, West Chester, PA, USA) and the suspended $[3\text{C}_6\text{PC}_{14}][\text{FeCl}_4]$ could move synchronously with the magnet in the aqueous phenolic solution (Fig. 2). After performance of magnetic extraction for a given time period, the phenol concentrations in the aqueous solution were determined by use of HPLC–UV.

2.6. HPLC analysis

Separation and quantitative analyses of phenolic compounds in aqueous solution were performed on a Shimadzu HPLC system (Kyoto, Japan) consisting of an SCL-10A system controller, two LC-10AD pumps, a DGU-14A degasser, a SIL-10AD autosampler and an SPD-10AV UV–Vis detector ($\lambda = 210\text{ nm}$). Separation of the analytes was performed at room temperature on a Phenomenex Luna C18 column, 100 Å pore size, $4\text{ }\mu\text{m}$ particle size, $250\text{ mm} \times 4.6\text{ mm}$ i.d. column containing a guard column (Phenomenex, Torrance, CA, USA). The analytes were eluted isocratically at a flow rate of 0.4 mL/min using an acetonitrile/water mobile phase (65/35, v/v). The water was pre-adjusted to pH 3 by use of phosphoric acid. The sample injection volume was $20\text{ }\mu\text{L}$ and 2-Bn-4-CP was used as an internal standard for the quantification of other phenolic compounds. The concentrations of phenolic compounds in the ionic liquid phase were calculated by use of mass balance.

2.7. Calculations

Distribution ratios (D) of the phenolic compounds between $[3\text{C}_6\text{PC}_{14}][\text{FeCl}_4]$ and aqueous solution were calculated using the following Eq. (1) and the extraction percentages (E) were calculated according to Eq. (2).

$$D = \frac{C_{\text{IL}}}{C_{\text{w}}} = \frac{C_{\text{w}}^0 - C_{\text{w}}}{C_{\text{w}}} \times \frac{V_{\text{w}}}{V_{\text{IL}}} \quad (1)$$

$$E = \frac{m_{\text{IL}}}{m} = \frac{C_{\text{IL}} \times V_{\text{IL}}}{C_{\text{w}}^0 \times V_{\text{w}}} = \frac{D}{D + (V_{\text{w}}/V_{\text{IL}})} \quad (2)$$

where C_{w}^0 and C_{w} are the initial and equilibrium concentrations of the solute (phenols) in aqueous phase, respectively (mg L^{-1}), and V_{w} and V_{IL} denote the volumes of aqueous and IL phases, respectively (mL). The concentrations in aqueous solution were measured in triplicate by use of HPLC and their average values were reported. The key to increase of the extraction efficiency

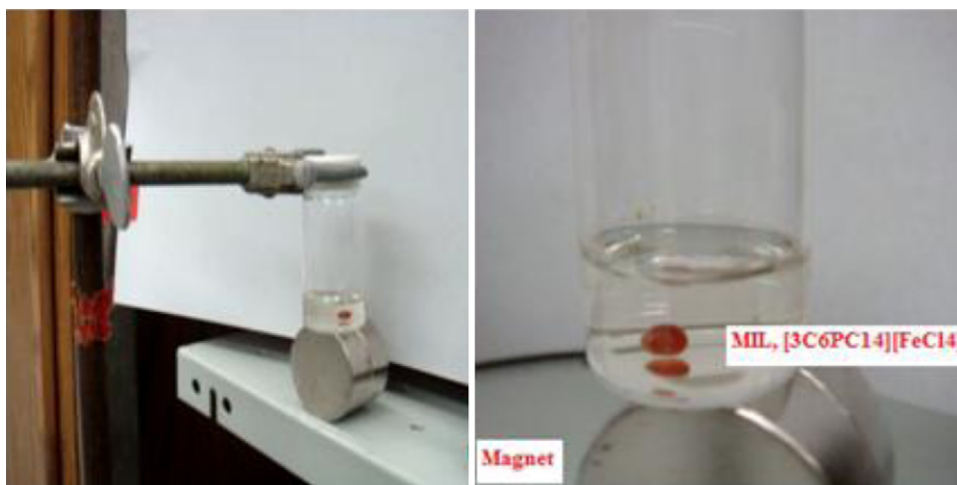


Fig. 2. Experimental set-up of magnetic extraction.

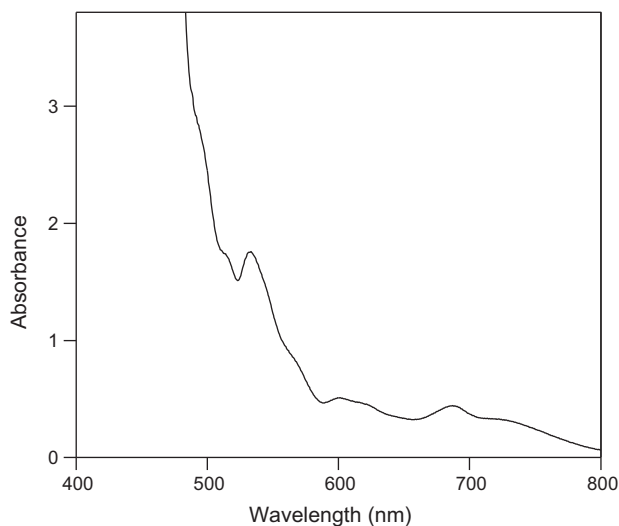


Fig. 3. Visible absorption spectrum of $[3C_6PC_{14}][FeCl_4]$.

is to enhance the distribution ratio. Studies of distribution ratio and extraction equilibrium may provide insightful understanding of this novel separation process and ultimately aid in optimizing separation efficiencies [30].

3. Results and discussion

3.1. Characterization of $[3C_6PC_{14}][FeCl_4]$

The absorption spectrum of the MRTIL $[3C_6PC_{14}][FeCl_4]$ was measured using a UV–Vis–NIR spectrometer (Fig. 3). Three major peaks at 531, 613, and 687 nm were observed. These peaks are well known to be characteristic of the tetrachloroferrate(III) anion. These very similar absorption behaviors and peak wavelengths were also observed previously for the reported magnetic ionic liquids such as 1-butyl-3-methylimidazolium tetrachloroferrate(III) [31].

The thermal properties of $[3C_6PC_{14}][FeCl_4]$ including thermal stability and phase transition behavior were investigated by use of TGA and DSC. From the TGA curve (Fig. 4) it can be seen that $[3C_6PC_{14}][FeCl_4]$ is thermally stable up to temperatures nearing 623 K under nitrogen atmosphere. In addition, a one-stage thermal decomposition process was observed for $[3C_6PC_{14}][FeCl_4]$. The compound $[3C_6PC_{14}][FeCl_4]$ exhibits high storage stability under ambient conditions. As a matter of fact, $[3C_6PC_{14}][FeCl_4]$ can still be used for magnetic extraction after it has been stored over one year at room temperature. According to the DSC result (data not shown), a major endothermic peak at 285 K was observed, which could be assigned to the melting point of $[3C_6PC_{14}][FeCl_4]$.

The MRTIL $[3C_6PC_{14}][FeCl_4]$ contains tetrachloroferrate(III) anions with $3d^5$ configuration and displays paramagnetic behavior at room temperature. Its magnetic susceptibility was measured using a Quantum Design superconducting quantum interference device (SQUID). The magnetization at 300 K was measured in the magnetic field range of $-50,000$ to $50,000$ Oe. The magnetization showed an expected linear dependence on the applied magnetic field (Fig. 5). From the slope of the linear fits to the data, the molar magnetic susceptibility of $[3C_6PC_{14}][FeCl_4]$ was obtained as $\chi_M = 0.0135 \text{ emu mol}^{-1}$, which conformed well to the value expected for Fe(III) [31,33].

Viscosity tests of $[3C_6PC_{14}][FeCl_4]$ based on shear stress/shear rate ratio showed a linear relationship indicating that this magnetic ionic liquid behaves as a Newtonian fluid over this shear rate

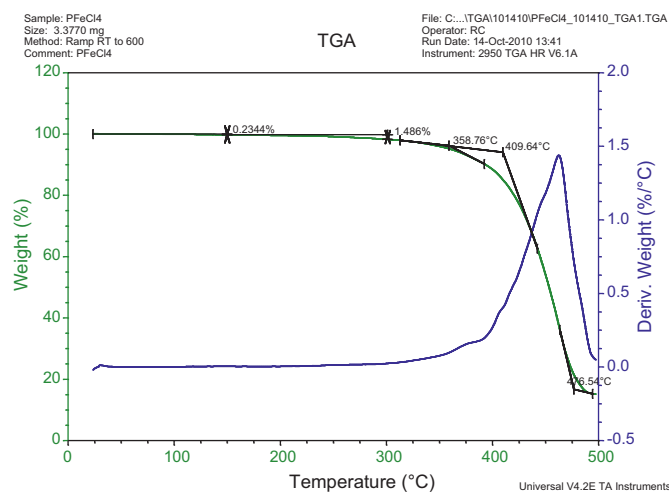


Fig. 4. Thermal gravimetric analysis scan of $[3C_6PC_{14}][FeCl_4]$.

range. Linear regression of the results showed that the viscosity of $[3C_6PC_{14}][FeCl_4]$ obtained is 0.914 Pa s at room temperature.

3.2. Effect of extraction time

Extraction time is one of the most important factors in most extraction processes because mass transfer of analytes between the two immiscible phases needs to overcome phase barrier energy [30]. This transport process takes time to occur and to reach equilibrium [37]. Therefore, the effect of extraction time on the distribution ratios of the phenols was studied. Four different phenolic compounds were extracted by use of $[3C_6PC_{14}][FeCl_4]$ for various durations of time. The distribution ratios of the four phenols displayed a similar trend, i.e. they increased in the beginning of the extraction process (Fig. 6). However, the distribution ratios reached a plateau after 20 min extraction. Further increase of extraction time to 60 min did not significantly affect the phenol distribution ratios. These results may suggest that the extraction of phenols reached equilibrium in 20 min. In addition, phase contact time required for the extraction of phenols into $[3C_6PC_{14}][FeCl_4]$ does not depend significantly on the molecular structures of phenols. Therefore, a phase contact duration of 20 min was employed as the optimum extraction time for all the phenols in the following investigations.

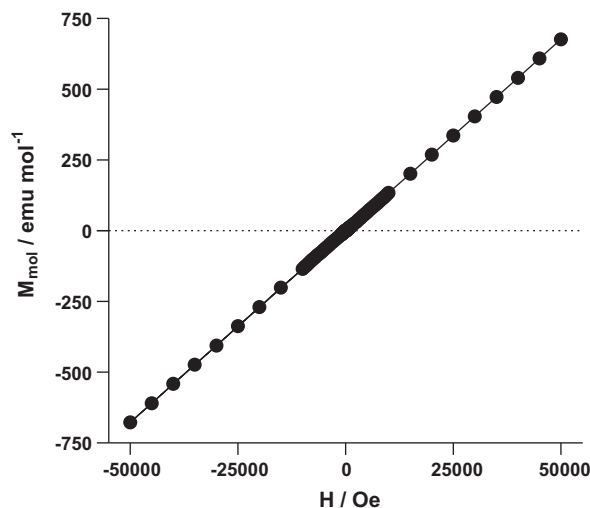


Fig. 5. Field dependence of molar magnetization of $[3C_6PC_{14}][FeCl_4]$ at 300 K.

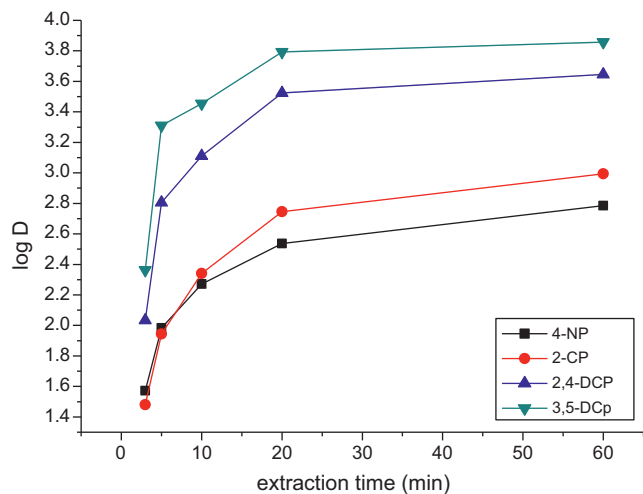


Fig. 6. Effect of extraction time on distribution ratios of phenols.

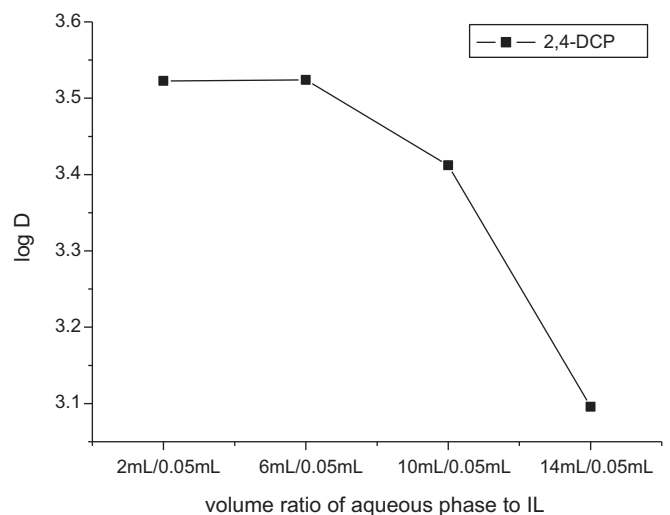


Fig. 7. Effect of volume ratios between water and MRTIL on distribution ratios of phenols.

3.3. Effect of phase volume ratio

In order to determine the effect of phase volume ratio between the aqueous solution and $[3C_6PC_{14}][FeCl_4]$ on phenol distribution ratios, additional magnetic extraction experiments were conducted using 2,4-DCP as a representative phenolic compound. In all these magnetic extractions, aqueous solution volumes were increased while keeping the $[3C_6PC_{14}][FeCl_4]$ volume constant (50 μ L) at the same time. The results from these studies demonstrate that the distribution ratio of 2,4-DCP between $[3C_6PC_{14}][FeCl_4]$ and aqueous solution exhibited no significant change when the volume ratio was increased from 40 (2 mL/0.05 mL) to 120 (6 mL/0.05 mL) (Fig. 7). However, 2,4-DCP distribution ratios dramatically dropped with further increase of phase volume ratios (aqueous solution volume). The decrease in distribution ratios could possibly be due to the much greater volumes of aqueous phase as compared to the ionic liquid phase used in this extraction, which may enhance the dissolution of the IL into the aqueous phase. Due to the extremely high extraction efficiency of the MRTIL, we used only a small volume of MRTIL in order to develop our magnetic extraction process, which lowers consumption of MRTIL and fully capitalizes on its high extraction capacity. Therefore, a phase ratio of 120 (6 mL/0.05 mL) was selected as the optimal value to increase the extraction capacity to the maxim, while still maintaining high distribution ratios.

3.4. Effect of pH of aqueous solution

It is well known that the pH of a sample solution could significantly influence extraction efficiency particularly when acidic or basic solutes are extracted. The target phenols are weak acids with low ionization constants. For example, the pKa values of 4-NP, 2-CP, and 2,4-DCP are 7.15, 8.56, and 7.85, respectively. Therefore, the pH was varied from pH 4 to 10 to investigate the effect on phenol distribution ratios (Fig. 8). Higher distribution ratios were achieved at acidic conditions for all three phenols investigated. In contrast, the distribution ratio of 2,4-DCP significantly decreased when it was extracted in basic solutions. This typical partition behavior of phenolic compounds has been previously observed when quaternary ammonium salt-based ionic liquids were used [26,38]. Under acidic conditions, the disassociation of phenols was suppressed and phenols exist predominantly as neutral species. This observed pH dependence of extraction efficiency clearly suggests that phenols are preferably partitioned into MRTIL as non-dissociated species. However, it should be noted that even at pH 10, the extraction of 2-CP into

$[3C_6PC_{14}][FeCl_4]$ is still quite significant. It has been reported that in the case of extraction of hydrophobic phenols, the effect of pH on distribution ratios into imidazolium- and quaternary ammonium-based ionic liquids was small [30]. Pletney and coworkers also observed that when pH was higher than 10, 4-chlorophenol (4-CP) could still be significantly extracted into 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]. They proposed that extraction of anionic phenolate may proceed through an alternative pathway, *i.e.* anion exchange [39]. Therefore, the two different trends mentioned above suggest that in addition to the extraction of phenol in molecular form, the extraction of anionic phenolate into $[3C_6PC_{14}][FeCl_4]$ through an anion-exchange mechanism may also occur.

3.5. Effect of structures of the phenolic compounds

Five phenols with different chlorine or nitro substituents were tested as solutes for magnetic extraction. In acidic aqueous solutions, distribution ratios of the phenols increased in the order of Ph < 4-CP < 2-NP < 2-CP < 3,4-DCP < 2,4-DCP < 3,5-DCP under the same experimental conditions (Fig. 9). Higher distribution ratios

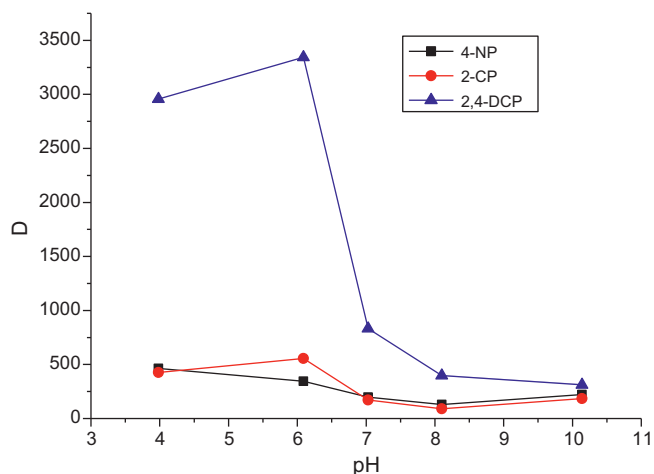


Fig. 8. Effect of pH on distribution ratios of phenols.

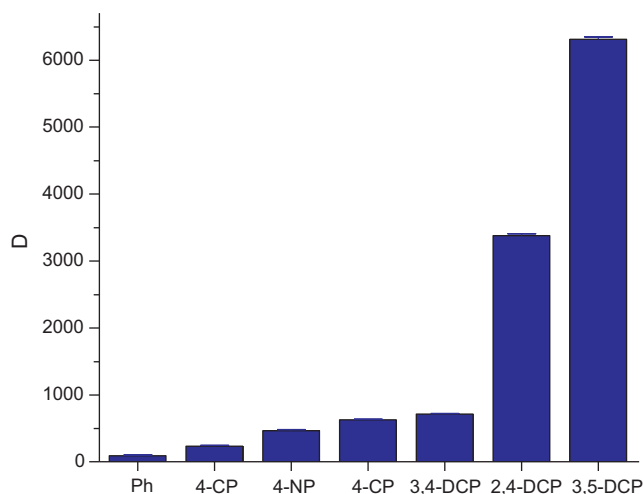


Fig. 9. Distribution ratios of various phenols.

were observed for phenols containing more chlorine substituents. This trend may suggest that the increased distribution ratios of phenols with more chlorine substituents could be due to their greater hydrophobic interactions with $[3C_6PC_{14}][FeCl_4]$. Botsaris and coworkers reported the extraction of chlorophenols containing different number of chlorine substituents by imidazolium-based RTILs such as $[BMIM][PF_6]$ [40]. They found that partitioning of chlorophenols between the ionic liquid and water phase was significantly increased when chlorophenols containing more chlorine substituents were extracted. This behavior was similar to the trend that 1-octanol/water partition coefficients of chlorophenols exhibited [40].

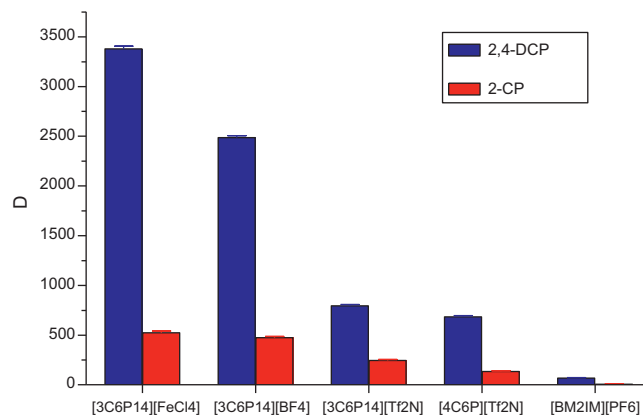


Fig. 10. Distribution ratios of 2,4-DC and 2-CP in different ILs.

3.6. Effect of the structures of ionic liquids

Four traditional non-magnetic RTILs were also investigated as extraction solvents for comparison with the MRTIL. The distribution ratios of both 2-CP and 2,4-DCP were significantly higher in the MRTIL $[3C_6PC_{14}][FeCl_4]$ than in the four non-magnetic RTILs (Fig. 10). Among the four non-magnetic RTILs, higher distribution ratios of phenols were obtained when the phosphonium-based hydrophobic ionic liquids with long alkyl chains such as $[3C_6PC_{14}][BF_4]$ and $[3C_6PC_{14}][Tf_2N]$ were used. In contrast, the imidazolium-based RTIL $[BM_2IM][PF_6]$ with shorter alkyl chain showed the lowest extraction efficiency. Increased extraction efficiency by use of ionic liquids containing longer alkyl chain was previously observed in a study where an ionic liquid-based headspace single-drop microextraction with GC for sensitive

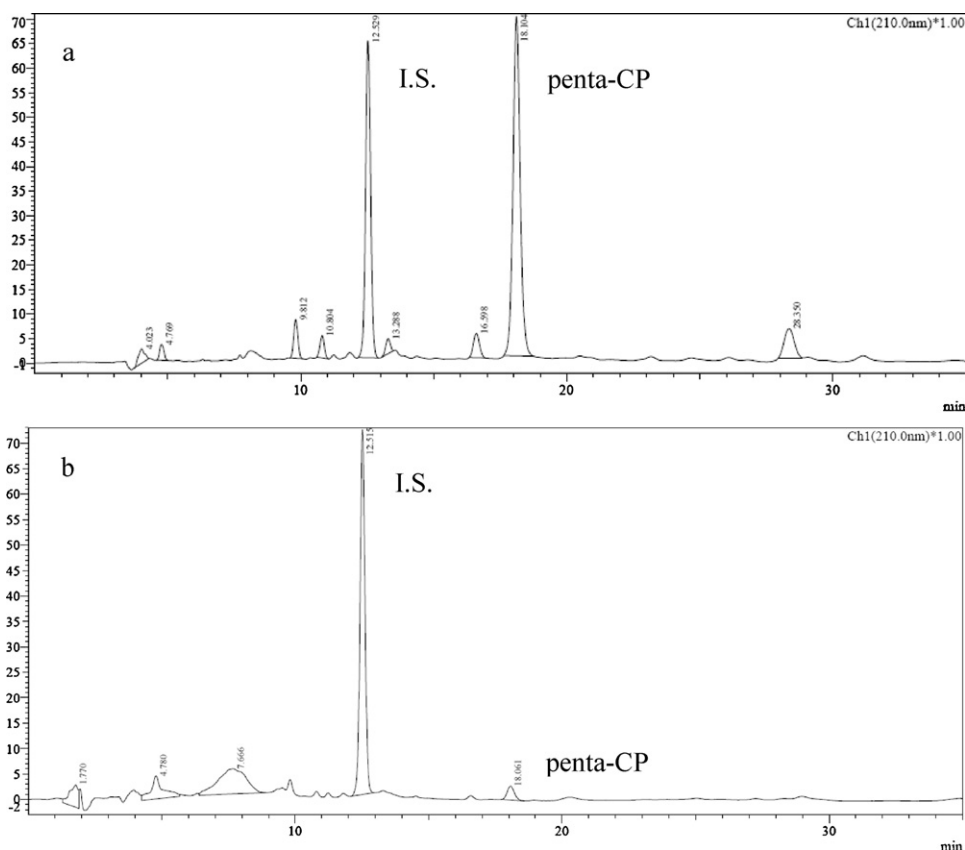


Fig. 11. HPLC chromatograms of contaminated soil sample obtained from a superfund site, (a) before extraction, (b) after extraction by $[3C_6PC_{14}][FeCl_4]$.

detection of phenols was reported [41]. These results suggest that for a given phenolic solute, its distribution ratios increase with increasing alkyl chain length on the cations of the ionic liquids used as extractants under acidic conditions. The trend of increasing extraction efficiency with increasing linear alkyl chain length can be attributed to the increase in hydrophobicity of the cation. Hydrophobicity, along with hydrogen bonding of the cation, plays a major role in the selective extraction of phenols from aqueous solution under acidic conditions [26]. In addition, according to a quantum chemical based “conductor-like screening model for real solvents” (COSMO-RS), an increase of the alkyl chain enhances the volume size of the channels formed by the interaction of the phosphonium-based cations and anions. The increased interaction thus facilitates the accommodation of the phenol molecules by ionic liquids [42].

When the same cation, trihexyltetradecylphosphonium, was used, BF_4^- -containing ionic liquid displayed higher extraction efficiency than Tf_2N^- -containing IL (Fig. 10). It has been reported that distribution ratios of phenols generally were found to decrease with increase in total screening charge values of anions [42]. This trend indicates that anions with low screening charges have a higher affinity for phenol in aqueous solution. This trend is also consistent with the fact that the higher the screening charge, the lower will be the polarizability of the molecule and the smaller will be the possibility of hydrogen bonding with phenols. Another manuscript from the literature reports on the separation of 1-hexene from n-hexane by use of ionic liquids. In that study, the authors also found that suitable ionic liquids should have small molecular volumes, unbranched groups, and a sterical shielding effect around the anion charge center. Headspace-gas chromatography verified that the anion with sterical shielding around the anion charge center is favorable for increasing selectivity [43]. The anion BF_4^- has a smaller steric shielding effect around its charge center than the anion Tf_2N^- . Therefore, higher extraction efficiency in the BF_4^- -containing IL was obtained compared with that in the Tf_2N^- -containing IL.

3.7. Extraction of pentachlorophenol from contaminated soil samples

A Superfund site is a hazardous waste site which has been placed on the National Priorities List (NPL), a list of polluted sites requiring cleanup which is maintained by the United States Environmental Protective Agency (EPA). Chlorinated phenols are toxic chemicals frequently found in hazardous wastes at superfund sites. Upon heating or burning they can be converted into even more toxic polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) by both gas-phase and metal catalyzed pathways [44]. Pentachlorophenol is a manufactured chemical which is restricted in use as a pesticide and is used industrially as a wood preservative for utility poles, railroad ties, and wharf pilings. Exposure to high levels of pentachlorophenol can cause increases in body temperature, adverse liver effects, and damages to the immune system [45]. This substance has been found in at least 313 of the 1585 National Priorities List sites identified by the EPA. The EPA has set a limit for drinking water of 1 part of pentachlorophenol per billion parts of water (1 ppb).

The HPLC chromatogram of a contaminated soil sample obtained from a superfund site is shown in Fig. 11a. The peak at 18.10 min was identified as pentachlorophenol (penta-CP) by both spiking standard pentachlorophenol and by use of LC-MS. The original concentration of penta-CP was determined as $7.8 \mu\text{g mL}^{-1}$ by use of an internal standard method. After extraction by $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ using our novel magnetic extraction technique, the concentration of penta-CP was dramatically reduced to $0.2 \mu\text{g mL}^{-1}$. An HPLC chromatogram of the same sample after extraction is shown in

Fig. 11b. Thus, the penta-CP peak significantly decreased due to the extraction. The extraction or removal efficiency under this optimized conditions is 97.4%, which indicates that the majority of penta-CP was removed.

4. Conclusions

In summary, we have developed a novel magnetic extraction technique for removal of phenolic compounds using a magnetic room temperature ionic liquid as a highly efficient extraction solvent. The distribution ratios of phenols were significantly influenced by pH of the aqueous phase, nature of the ILs, and chemical structure of the phenols themselves. Moreover, our MRTIL exhibited much higher extraction capacity than traditional nonfunctionalized RTILs under the same conditions used in this work. It can be expected that these results are promising for the liquid-liquid extraction, separation, and preconcentration of phenols in analytical and separation science. In addition to the contaminated soil samples obtained from superfund sites, application of this new magnetic extraction technique to remove phenolic compounds from other real samples such as industrial river and lake water samples is currently in progress. At the same time, we are currently attempting the development of an efficient approach to recovery and recycling our MRTIL. For example, we have explored centrifugation for separation of the magnetic ionic liquids from bulk aqueous phenolic solution. Another possible approach is to use a strong magnet for forcing MRTIL to the bottom of the glassware. The bulk solution can then be decanted out. The recovered MRTIL will then be recycled and tested for the next extraction of phenolic compounds.

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