Removal of cadmium ions from aqueous solution using very small ionic liquids to water ratio without metal chelator and pH modifications

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ABSTRACT

Solvent extraction is an energy-efficient technology which uses two immiscible phases. In this regard, solvents like hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate based ionic liquids have been used. The hydrophilicity of the metal ions is a challenge to use this method. Coordinating the metal ions by ligands, lowering the pH of the aqueous phase, modifying the ionic liquid itself in such a way that it can coordinate with the metal ions, employment of large ionic liquid to aqueous phase ratio (minimum of 1:1) were also the attempts made to improve the distribution coefficient of the ionic liquids. All these efforts are problematic in hindering the applications of ionic liquids in extraction. In this report, the extraction efficiencies of ionic liquids (C₄mim][PF₆], [C₆mim][PF₆], [C₈mim][PF₆] and [C₁₀mim][PF₆]) from water samples containing Cd²⁺ using very small ionic liquid to water ratio (1:6 and 1:12) from a solution of concentrations 0.005 mg/L without using any coordinating agent as an extractant and the need of changing the pH are disclosed. While ionic liquids to aqueous phase ratio 1:12 demonstrated extraction efficiencies of 75%, 83.75%, 87.50% and 100%, respectively; the 1:6 ratio extracted 87.50%, 100%, 100% and 100%, respectively which shows suitability of the later ratio for better extraction. Moreover, the recyclabilities of [C₆mim][PF₆] and [C₈mim][PF₆] was investigated and the result showed that they can be used at least for five cycles. A Linear calibration curve with good coefficient of determination was obtained during the analysis for determination of the metal in the extracts.

Key words: Cadmium(II), Ionic Liquids, Extraction, Recyclability, Small Ionic Liquid to Water Ratio.

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INTRODUCTION

The concentration of toxic heavy metals in natural water bodies has been increasing (Motsi et al., 2009; Hernandez et al., 2010; Pinto et al., 2011). Heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium are generated in electroplating, electrolysis depositions, conversion coating, and anodizing-cleaning, milling, and etching industries. Significant amount of heavy metals wastes like tin, lead, and nickel result from printed circuit board (PCB) manufacturing. Wood processing industries where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments contain chromium compounds and cadmium sulfide; petroleum refining generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment (Gunatilake, 2015). Consequently, they are accumulated in food chains that pose a threat to human health, animals and plants and ecological systems (Manahan, 2011;
Atakilt Abebe et al. (2015). Therefore, efficient treatment of water by removing toxic heavy metals has been one of the major concerns. A number of specialized processes have been developed for the removal of metals from waste discharges. These include chemical precipitation (Ku and Jung, 2001), coagulation/flocculation (Samrani et al., 2008), ion exchange (Kang et al., 2004), electrochemical operations (Wang et al., 2007), biological operations (Pavasant et al., 2006), adsorption (Fu and Wang, 2011), filtration, and membrane processes (Landaburu-Aguirre et al., 2009). The choice of method is based on the concentration of the metal ions in the solution and the cost of treatment (Richardson and Harker, 2002). Solvent extraction is an energy-efficient technology which uses two immiscible phases (conventionally an organic phase and an aqueous phase) (Alonso et al., 2006; de los Ríos et al., 2009). In this regard, different solvents have been used in the recovery and separation of metals from aqueous solutions. One way of removing metal ions from an aqueous phase is by dissolving extractants such as di(2-ethylhexyl) phosphoric acid, tris(2-ethylhexyl)amine, liquid phosphine oxides in an organic solvent such as kerosene and toluene. One disadvantage of this method of extraction is the loss of organic solvents via volatilization, which has a detrimental impact on the environment and human health (Lancaster, 2010). Consequently, different attempts have been implemented to minimize these drawbacks. Replacement of the volatile organic solvents by non-volatile ones such as imidazolium-based ILs was extensively studied and reported elsewhere. The results indicate that mutual solubilities are primarily defined by the anion followed by the cation alkyl side chain length. Methylimidazolium-based ILs with the anion PF₆⁻ are totally hydrophobic and the mole fractions of water in [C₄mim][PF₆], [C₆mim][PF₆], [C₈mim][PF₆] and [C₁₀mim][PF₆] at 298 K are reported to be 0.23%, 0.18%, 0.16% and 0%, respectively (Freire et al., 2007).

At present, ILs mostly used in extraction of metal ions from aqueous phase are the hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆], or 1-hexyl-3-methylimidazolium hexafluorophosphate, [C₆mim][PF₆] or other ILs with hexafluorophosphate, PF₆⁻ or bis{(trifluoromethyl)sulfonyl}imide, NTf₂⁻, anions (Visser et al., 2001; Wei et al., 2003; Dietz, 2006). Charged metal ions are usually insoluble in hydrophobic ionic liquids (IL), so extractants are necessary in the IL’s phase just as in organic solvent (Villemin and Didi, 2014). Therefore, researchers exerted different efforts to increase the distribution coefficients of the ILs by increasing the metal’s hydrophobicity. This included employment of extractants to form complexes with metal ions (Wei et al., 2003), grafting coordinating agents
on the cations of the ILs themselves (Visser et al., 2002), modifying the pH condition using hydrochloric acid solutions (Wei et al., 2003; Hernandez et al., 2010). Large IL to water ratio quantity (1:1) was also employed (Earle and Seddon, 2000; Sereshti et al., 2014). Moreover, the extraction activities using ionic liquids were carried out from water samples containing far greater concentrations (Hernandez et al., 2010) than the metal ions found in real samples (Xu et al., 2010). The additional steps in modifying the ILs were found to incur additional synthetic cost and elongated time. Moreover, the use of large IL (which are expensive) (Abbott et al., 2004; Hayyan et al., 2013) to aqueous phase ratio makes the employment of these types of ILs impractical.

There is no literature report on the extraction of toxic heavy metals in general and Cd$^{2+}$ in particular minimizing the above problems combined. Taking this gap as an opportunity, herein, we investigate the extraction efficiencies of ILs, namely [C$_4$mim][PF$_6$], [C$_6$mim][PF$_6$], [C$_8$mim][PF$_6$] and [C$_{10}$mim][PF$_6$], from water samples containing Cd$^{2+}$ using very small IL to water ratio (1:12 and 1:6) from a solution of concentrations nearly similar to its existence in the real samples with out using any coordinating agent as an extractant and the need of changing the pH. Moreover, the extent at which ILs can be used repeatedly as much as possible were investigated. These facts reported here may reduce the concern about the high cost of the solvent jointly with the problems associated with their disposal. Thus, the scientific and industrial community may be encouraged to be benefited from the attractive numerous properties of ILs from the implementation of this technology in research and production.

**EXPERIMENTAL**

**Materials**

The chemicals used in this investigation were 1-Methylimidazole, 1-chlorobutane, 1-bromohexane, 1-bromoocctane and 1-bromodecane (Fairfield, OH, USA), potassium hexafluorophosphate (Rockford, IL, USA), acetone, ethyl acetate, diethyl ether, paraffin, tetrahydrated cadmium nitrate were obtained from Sigma-Aldrich-Fluka Chemical Co, Madrid, Spain. $^1$H NMR and $^{13}$C NMR spectra were recorded on 400 MHz NMR spectrometer (Bruker Avance 400 NMR spectrometer at 400 MHz, Germany) by dissolving approximately 10 mL of the sample in CDCl$_3$.

Inductively coupled plasma optical emission (ICP-OES) spectroscopy (“ULTIMA-2” HORIBA scientific, Japan) was employed in the investigation of the extraction efficiency. The operating parameters of ULTIMA-2 ICP-OES spectrometer for the analysis of Cd$^{2+}$ is summarized as in the table below (Table 1).

**Synthesis of the ionic liquids (ILs)**

Three new ILs were synthesized and purified according to reported procedures (Bonhote et al., 1996). The ILs were synthesized in two steps. The first step involved synthesis of ILs with halide anions and the second step, exchange of the halide anions with hexafluorphosphate, PF$_6^-$ and characterized using $^1$H and $^{13}$C NMR.

**Sample preparation for extraction process**

A 0.005 mg/L Cd$^{2+}$ solution was prepared following appropriate dilution from 183 mg/L stock solution which was prepared by dissolving 0.5 g of Cd(NO$_3$)$_2$.4H$_2$O in distilled water.
Extraction of Cd\(^{2+}\) from the aqueous phase by ILs

Traditionally, large IL to water ratio (minimum of 1:1) is been reported for the extraction of metal ions from aqueous phase (Earle and Seddon, 2000; Sereshti et al., 2014). However, ILs are expensive that makes their application for this purpose expensive. To fill this gap, smaller IL to water ratios (1:6 and 1:12) were used to remove the metal ions which significantly minimizes the cost of extraction.

**Extraction using 1:6 IL to aqueous phase ratio**

Exactly 6 mL of a 0.005 mg/L cadmium ion (Cd\(^{2+}\)) solution was transferred to a 25 mL conical-flask, to which 1 mL IL ([C\(_4\)mim][PF\(_6\)]) was added and two phases were formed. The mixture was shaken mechanically for 1 h at room temperature and then allowed to stand to attain equilibrium and phase separation. Then, 4 mL aqueous phase was taken from the mixture and diluted to 25 mL using distilled water. The concentration of cadmium ion that was left in the aqueous phase (not extracted by the IL) was determined by ICP-OES. The IL phase was placed in a clean and dry beaker, to which 10 mL, 69–72 % HNO\(_3\) was added and the content was heated gently until a few drops remained in the beaker. The latter step was repeated three times until the entire organic portion was removed. Then the residue was dissolved and diluted using distilled water in a 25 mL volumetric flask. Similar procedure was followed for the remaining ILs ([C\(_6\)mim][PF\(_6\)], [C\(_8\)mim][PF\(_6\)], and [C\(_10\)mim][PF\(_6\)]) for the control solution, exactly 4 mL of 0.005 mg/L of Cd\(^{2+}\) solution was taken, diluted to 25 mL using distilled water and analyzed by ICP-OES. Each experiment was repeated three times. The precision of the method was evaluated by calculating standard deviation (SD) and relative standard deviation (RSD) of the replicate measurements. For all the data obtained, the %RSD values were below 5% which signifies the repeatability of the procedure.

The extraction ability of the ILs from the aqueous phase was investigated by measuring the concentration of Cd\(^{2+}\) in the aqueous phase before and after the extraction process and in the ILs after the extraction.

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Table 1. The operating parameters of ULTIMA-2 ICP-OES for the analysis of Cd\(^{2+}\).

| Parameters                                      | Value   |
|------------------------------------------------|---------|
| RF generator plasma power (W)                   | 1500    |
| Plasma gas flow rate (L/min)                    | PL1     |
| Auxiliary gas flow rate (L/min)                 | 0.3     |
| Nebulizer or carrier gas flow rate (L/min)      | 0.53    |
| Nebulizer pressure                              | 1.76    |
| Spectra line (analytical wave length) (nm)      | 228.802 |
| Sample replicates                               | 3       |
| Maximum integration times (sec.)                | 5       |
Extraction using 1:12 IL to aqueous phase ratio
Similar procedure as above was employed except that 0.5 mL of IL was used as extractant.

Recyclability of the ILs
The reusability of the ionic liquid was evaluated by taking solution of cadmium metal ion. The same ionic liquid was used repeatedly after stripping Cd$^{2+}$ from the ionic liquid after each extraction step was carried out. In this case, 1 mL of [C$_6$ mim][PF$_6$] was transferred to 25 mL conical flask and mixed with 6 mL aqueous phase containing 1.2 mg/L cadmium metal ion. It was shaken for 1 hr and left to stand for 40 minute. The cadmium metal ion concentration in the aqueous phase was determined. Then after 3 mL of 0.1 M HNO$_3$ acid solution was added to the ionic liquid phase and shaken to strip the Cd$^{2+}$ from ionic liquid. The acid was removed from the IL washing with 5 mL distilled water three times and then extraction was carried out as above. The extraction and stripping was repeated five times. The same procedure was followed for [C$_8$ mim][PF$_6$].

Calibration of the ICP-OES instrument
The ICP-OES was calibrated using standard solutions of cadmium ion concentrations indicated in Table 2. The results clearly show that the calibration curve with good coefficient of determination was obtained during the analysis.

| Standards | Concentration(µg/mL) | Intensity   | Regression equation          |
|-----------|----------------------|-------------|-----------------------------|
| 1         | 0.1                  | 435460.00   | Y = 434630.3 + 843.7X       |
| 2         | 1.0                  | 435463.57   | R$^2$ = 0.99943             |
| 3         | 2.0                  | 436357.43   |                             |
| 4         | 3.0                  | 437106.78   |                             |
| 5         | 4.0                  | 438037.02   |                             |
| 6         | 5.0                  | 438842.40   |                             |
| 7         | 6.0                  | 439692.41   |                             |

RESULTS AND DISCUSSION

Characterization of the ILs
Nuclear magnetic resonance (NMR) spectroscopy is one of the powerful techniques by which the synthesis and purity of ILs is investigated. Therefore, proton($^1$H) and carbon ($^{13}$C) NMR spectra were employed to check the synthesis and purity of the ILs used to carry out the extraction experiments. The synthesis of the ILs by alkylation of N-methylimidazole using the different alkyl halides was evident from the appearance of the characteristic picks representing each type of H and C on their corresponding chemical shifts in the NMR spectra. The appearance of more number of peaks in the up field in the NMR justifies the successful alkylation of N-methylimidazole (Table 3, Figures 1 and 2).
Table 3. $^1$H NMR and $^{13}$C NMR chemical shifts of the ILs in CDCl$_3$

| IL(Compound)      | $^1$H NMR chemical shift (ppm) | $^{13}$C NMR chemical shift (ppm) |
|-------------------|--------------------------------|----------------------------------|
| Non quaternized mim | $\delta$ (ppm)= 3.52 (3H, s, CH$_3$-N), 6.88 (1H, d, N-CH-CH-N), 7.08 (1H, d, N-CH-CH-N), 7.47 (1H, s, N-CH-N). | $\delta$ (ppm)= 30.4, 120, 130, 138 |
| [C$_4$mim][PF$_6$] | $\delta$ (ppm)= 0.70 (3H, t, CH$_3$), 1.13 (2H, m, CH$_2$), 1.70 (2H, m, CH$_2$), 3.72 (3H, s, CH$_3$-N), 4.01 (2H, t, N-CH$_2$CH$_2$), 7.20 (1H, d, N-CH-CH-N), 7.21 (1H, d, N-CH-CH-N), 8.27 (1H, s, N-CH-N). | $\delta$ (ppm)= 12.97, 19.00, 31.49, 35.72, 49.45, 122.17, 123.42, 135.50 |
| [C$_6$mim][PF$_6$] | $\delta$ (ppm)= 0.71 (3H, t, CH$_3$), 1.16 (6H, m, 3(CH$_2$), the consecutive three CH$_2$ groups next to the up field CH$_3$ group), 1.72 (2H, m, CH$_2$), 3.76 (3H, s, CH$_3$-N), 4.02 (2H, t, N-CH$_2$CH$_2$), 7.22 (1H, d, N-CH-CH-N), 7.24 (1H, d, N-CH-CH-N), 8.3 (1H, s, N-CH-N) | $\delta$ (ppm)= 13.37, 22.12, 25.49, 29.88, 30.80, 35.78, 43.78, 122.14, 123.48, 136.61 |
| [C$_8$mim][PF$_6$] | $\delta$ (ppm)= 0.78 (3H, t, CH$_3$), 1.2 (10H, m, the five consecutive CH$_2$ groups attached with the up field CH$_3$ group), 1.79 (2H, m, CH$_2$ which is attached with the down field CH$_2$, i.e N-CH$_2$), 3.82 (3H, s, CH$_3$-N), 4.05 (2H, t, N-CH$_2$), 7.25 (1H, d, N-CH-CH-N), 7.27 (1H, d, N-CH-CH-N), 8.36 (1H, s, N-CH-N) | $\delta$ (ppm)= 13.97, 22.48, 26.00, 28.77, 28.89, 29.81, 31.59, 35.93, 49.93, 122.18, 123.60, 136.63 |
| [C$_{10}$mim][PF$_6$] | 0.814 (3H, t, CH$_3$ up field), 1.23 (16H, 8(CH$_2$)), 1.8 (2H, m, CH$_2$, which is attached to the down field CH$_2$-N group), 3.83 (3H, s, CH$_3$-N), 4.07 (2H, t, N-CH$_3$), 7.27 (2H, s, N-CH-CH-N), 8.38 (1H, s, N-CH-N) | $\delta$ (ppm)= 14.05, 22.82, 28.09, 28.90, 29.29, 29.31, 29.45, 29.87, 31.81, 35.98, 49.95, 122.19, 123.83, 138.88 |
Figure 1. $^1$H NMR spectrum of (a) $[\text{C}_4\text{mim}][\text{PF}_6]$, (b) $[\text{C}_6\text{mim}][\text{PF}_6]$, (c) $[\text{C}_8\text{mim}][\text{PF}_6]$, (d) $[\text{C}_{10}\text{mim}][\text{PF}_6]$

Figure 2. $^{13}$C spectrum of (a)$[\text{C}_4\text{mim}][\text{PF}_6]$, (b) $[\text{C}_6\text{mim}][\text{PF}_6]$, (c)$[\text{C}_8\text{mim}][\text{PF}_6]$, (d)$[\text{C}_{10}\text{mim}][\text{PF}_6]$
Extraction efficiency of the ILs

The Concentrations of Cd\(^{2+}\) in the aqueous and ILs phases before and after the extraction are indicated in Table 4. The trend of the extraction efficiencies are indicated in Figures 3.

Extraction of Cd\(^{2+}\) from the aqueous phase was achieved using all ionic liquids. Even though Cd\(^{2+}\) is hydrophilic, a good amount was found transferred to the IL phase up on shaking. The metal ions are transferred to the ILs probably being trapped by the cavities in the microstructures of the ILs (Huang et al., 2005). It is also clear that the extraction ability of the ILs increases with the alkyl chain length on the cation (Table 4, Figure 3). This is speculated to be due to the increase in the three dimensional cavity size and density as the alkyl chain length increases. For a given IL, better extraction was achieved when the IL to aqueous phase ratio is 1:6 (Table 5) compared to 1:12 (Table 4). This may be due to the larger number of cavities in the IL in the former ratio.

However, complete (100%) extraction is observed by [C\(_{10}\)mim][PF\(_6\)] from both IL to aqueous phase ratios (1:6 and 1:12) in consistence with the significant increase in the three dimensional cavity density increase following the alkane chain length increase in the cation. Nevertheless, since viscosity is a function of alkane chain length on charge carrying head (Wasserscheid and Welton, 2008), [C\(_{10}\)mim][PF\(_6\)] has the highest viscosity among the ILs tested here and hence limit its ease of application. Previous experiments on extraction of toxic heavy metal ions from aqueous environment showed %E as high as 99.3%. This was achieved after employing several modifications including using coordinating molecules Dithizone to lower the hydrophilicity of the metal ion, lowering of pH, modification of the ILs by grafting coordinating appendages on the cation (Domanska and Rekawek, 2009). Compared with the latter, this work is far cost and time effective.

Table 4. Extraction of Cd\(^{2+}\) at T=298 K, using IL to aqueous phase ratio of 1:12.

| ILs               | (C\(_i\))\(_{aq}\) (µg/L) | (C\(_f\))\(_{aq}\) (µg/L) | C\(_{IL}\) (µg/L) | RSD% | (C\(_f\))\(_{aq}\) | C\(_{IL}\) | % E  |
|-------------------|--------------------------|--------------------------|------------------|------|-------------------|------------|------|
| [C\(_4\)mim][PF\(_6\)] | 0.80                     | 0.20 ± 0.002             | 0.54 ± 0.0108    | 1.00 | 2.00              | 75.00      |
| [C\(_6\)mim][PF\(_6\)] | 0.80                     | 0.13 ± 0.006             | 0.63 ± 0.033     | 4.61 | 5.23              | 83.75      |
| [C\(_8\)mim][PF\(_6\)] | 0.80                     | 0.10 ± 0.0014            | 0.69 ± 0.007     | 1.40 | 1.020             | 87.50      |
| [C\(_10\)mim][PF\(_6\)] | 0.80                     | 0.0 ± 0.0                | 0.80 ± 0.0220    | 0.0  | 2.72              | 100.00     |

Where (C\(_i\))\(_{aq}\): concentration of the Cd\(^{2+}\) in the aqueous phase before extraction; (C\(_f\))\(_{aq}\): concentration of the Cd\(^{2+}\) in the aqueous phase after extraction; and

C\(_{IL}\): concentration of the Cd\(^{2+}\) in the ionic liquid phase
Table 5. Extraction of Cd\(^{2+}\) at T=298 K, using IL to aqueous phase ratio of 1:6

| ILs            | (Ci\(_{aq}\)) (µg/L) | (Cf\(_{aq}\)) (µg/L) | C\(_{IL}\) (µg/L) | RSD\% | (Cf\(_{aq}\)) | C\(_{IL}\) | % E |
|----------------|----------------------|----------------------|-------------------|-------|--------------|-----------|-----|
| [C\(_4\)mim][PF\(_6\)] | 0.80 | 0.10 ± 0.0009 | 0.67 ± 0.037 | 0.9 | 5.522 | 87.50 |
| [C\(_6\)mim][PF\(_6\)] | 0.80 | 0.00 ± 0.0 | 0.79 ± 0.055 | 0.0 | 5.696 | 100.0 |
| [C\(_8\)mim][PF\(_6\)] | 0.80 | 0.00 ± 0.0 | 0.80 ± 0.009 | 0.000 | 1.123 | 100.0 |
| [C\(_{10}\)mim][PF\(_6\)] | 0.80 | 0.00 ± 0.0 | 0.80 ± 0.042 | 0.000 | 5.024 | 100.0 |

Where (Ci\(_{aq}\)) : concentration of the Cd\(^{2+}\) in the aqueous phase before extraction; (Cf\(_{aq}\)) : concentration of the Cd\(^{2+}\) in the aqueous phase after extraction; and C\(_{IL}\) : concentration of the Cd\(^{2+}\) in the ionic liquid phase.

Figure 3: Trends of extractions at 298K, IL to aqueous phase ratio of a) 1:12, b)1:6

The re-usability of two ILs was tested by recycling five times each. The concentration of Cd\(^{2+}\) before and after the extraction in the aqueous phase for each cycle is indicated in Table 6. The trend of the extraction ability of the ILs for each cycle is showed in Figure 4a-b. The reusability investigations was conducted employing ILs with intermediate alkane chain length ([C\(_6\)mim][PF\(_6\)] and [C\(_{10}\)mim][PF\(_6\)]) in order to have a good picture of their reusability. The reusability investigations (Table 6, Figure 4a-b) indicate that ILs can be recycled for reuse in liquid-liquid extraction of metal ions by freeing the cavities where the metal ions are trapped out from the aqueous phase.
phase. However, the efficiency decreases for each subsequent extraction in all the ILs employed here. This may be due to the interference of H⁺ on the adsorption cavity of the IL from the acid employed to leach the adsorbed Cd²⁺ from the subsequent solution. For each cycle of extraction in the recyclability experiment, the extraction efficiency is found to increase with the alkyl chain length on the cation. The recovered ionic liquid was reused successively to the same kind of extraction method.

| Cycle | (Ci)_{aq} (mg/L) | (Cf)_{aq} (mg/L) | RSD% | % E |
|-------|------------------|------------------|------|-----|
| I     | 1.2              | 0.883 ± 0.025    | 2.862| 26.43|
| II    | 1.2              | 0.950 ± 0.037    | 3.848| 20.83|
| III   | 1.2              | 0.983 ± 0.035    | 3.602| 18.11|
| IV    | 1.2              | 1.039 ± 0.058    | 5.571| 13.42|
| V     | 1.2              | 1.065 ± 0.036    | 3.407| 11.25|

**Cycle** (Ci)_{aq} **(Cf)_{aq}** RSD% % E

a) 

| Cycle | (Ci)_{aq} (mg/L) | (Cf)_{aq} (mg/L) | RSD% | % E |
|-------|------------------|------------------|------|-----|
| I     | 1.2              | 0.767 ± 0.020    | 0.263| 36.13|
| II    | 1.2              | 0.839 ± 0.047    | 0.556| 30.09|
| III   | 1.2              | 0.846 ± 0.023    | 0.275| 29.49|
| IV    | 1.2              | 0.966 ± 0.043    | 0.446| 19.53|
| V     | 1.2              | 1.03 ± 0.046     | 0.447| 14.17|

*(Ci)_{aq}*: concentration of the Cd²⁺ in the aqueous phase before extraction; ***(Cf)_{aq}**: concentration of the Cd²⁺ in the aqueous phase after extraction.

**Table 6**: The concentration of Cd²⁺ before and after the extraction in the aqueous phase for each cycle at 298K and IL to aqueous phase ratio 1:6 of a) [C₆mim][PF₆], b) [C₈mim][PF₆]

**Figure 4**: Trend of the extraction ability of the ILs at different cycles at 298K and IL to aqueous phase ratio 1:6 a) [C₆mim][PF₆], b) [C₈mim][PF₆]
CONCLUSION

The experiment result indicated that merely shaking mixture of very small ionic liquid to aqueous phase ratio as low as 1:12 for an hour is capable of extracting Cd$^{2+}$ with 75-100% efficiency from the aqueous phase depending on the alkyl chain length on the cation of the IL. Each IL could extract the metal ion for more than five cycles even though a continuous decrease in the efficiency is observed due to the inability to completely remove the H$^+$ used to leach the Cd$^{2+}$ from each succeeding step. These results demonstrate that ILs are good alternatives in the treatment of polluted water by toxic trace heavy metals such as Cd$^{2+}$.

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