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

Atakilt Abebe[1*], Sossina Tilahun[1], Mikias Mesfine[1] and Minaleshewa Atlabachew[1]

[1]Department of Chemistry, Bahir Dar University, Bahir Dar, 79, Ethiopia

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 (C_4mim][PF_6], [C_6mim][PF_6] , [C_8mim][PF_6] and [C_{10}mim][PF_6]) from water samples containing Cd^{2+} using very small ionic liquid to water ratio (1:6 and 1:12) from a solution of concentrations 0.005 mg/L with out 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 [C_6mim][PF_6] and [C_8mim][PF_6] 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.

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;

*Corresponding author: atakiltabebe1@gmail.com

Gunatilake, 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 draw backs. Replacement of the volatile organic solvents by non-volatile ones such as ionic liquids (ILs) is among such efforts (Wei *et al*., 2003; Domańska and Zhao, 2005; Platzer *et al*., 2015).

Ionic liquids (ILs) are low temperature melting salts (below 100 ^{0}C) (Villar-Garcia *et al*., 2012; Atakilt Abebe *et al.*, 2013). They are fundamentally different from salt solutions and molecular solvents. They are well characterized by unique properties, such as negligible vapor pressure, good thermal stability, tunable viscosity and designed miscibility with water and organic solvents, good extractability for various organic compounds as well as possession of cavities in their three dimensional microstructure (Huang *et al.*, 2005). For ionic liquids to be effectively used as solvents in liquid–liquid extractions, the knowledge of the mutual solubilities between ILs and the second liquid phase is fundamental. The mutual solubilities of water and imidazolium-based ILs were 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 PF_6^- are totally hydrophobic and the mole fractions of water in $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$ and $[C_{10}mim][PF_6]$ 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, $[C_4mim][PF_6]$, or 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6mim][PF_6]$ or other ILs with hexafluorophosphate, PF_6^-, or bis{(trifluoromethyl)sulfonyl}imide, NTf_2^-, 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 addtional 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 problemes combined. Taking this gap as an opportunity, herein, we investigate the extraction efficiencies of ILs, namely $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$ 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-Methylimmidazole, 1-chlorobutane, 1-bromohexane, 1-bromooctane and 1-bromodecane (Fairfield, OH, USA), potassium hexafluorophosphate (Rockford, IL, USA), acetone, ethyl acetate, diethyl ether, paraffin, tetra hydrated 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 $Cd(NO_3)_2.4H_2O$ in distilled water.

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 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 ($[C_4mim][PF_6]$) 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 ($[C_6mim][PF_6]$, $[C_8mim][PF_6]$, 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.

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 $[C_6mim]$ $[PF_6]$ 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 $[C_8mim][PF_6]$.

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.

Table 2. Working standards of the calibration curve for determinations of Cd^{2+} using ICP-OES.

Standards	Concentration(µg/mL)	Intensity	Regression equation
1	0.1	435460.00	
2	1.0	435463.57	
3	2.0	436357.43	
4	3.0	437106.78	
5	4.0	438037.02	Y = 434630.3 + 843.7X
6	5.0	438842.40	R^2 = 0.99943
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(^1H) 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	δ (ppm)= 3.52(3H, s, CH$_3$-N), 6.88 (1H, d, N-C**H**-CH-N), 7.08 (1H, d, N-CH-C**H**-N), 7.47 (1H, s, N-CH-N).	δ (ppm)= 30.4, 120, 130, 138
[C$_4$mim][PF$_6$]	δ (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-C**H$_2$**-CH$_2$), 7.20 (1H, d, N-C**H**-CH-N), 7.21 (1H, d, N-CH-C**H**-N), 8.27 (1H, s, N-CH-N).	δ (ppm)= 12.97, 19.00, 31.49, 35.72, 49.45, 122.17, 123.42, 135.50
[C$_6$mim][PF$_6$]	δ (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-C**H$_2$**-CH$_2$), 7.22 (1H, d, N-C**H**-CH-N), 7.24 (1H, d, N-CH-C**H**-N), 8.3 (1H, s, N-CH-N)	δ (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$_6$]	δ (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-C**H**-CH-N), 7.27 (1H, d, N-CH-C**H**-N), 8.36 (1H, s, N-CH-N)	δ (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-C**H**-C**H**-N), 8.38 (1H, s, -N-CH-N)	δ (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
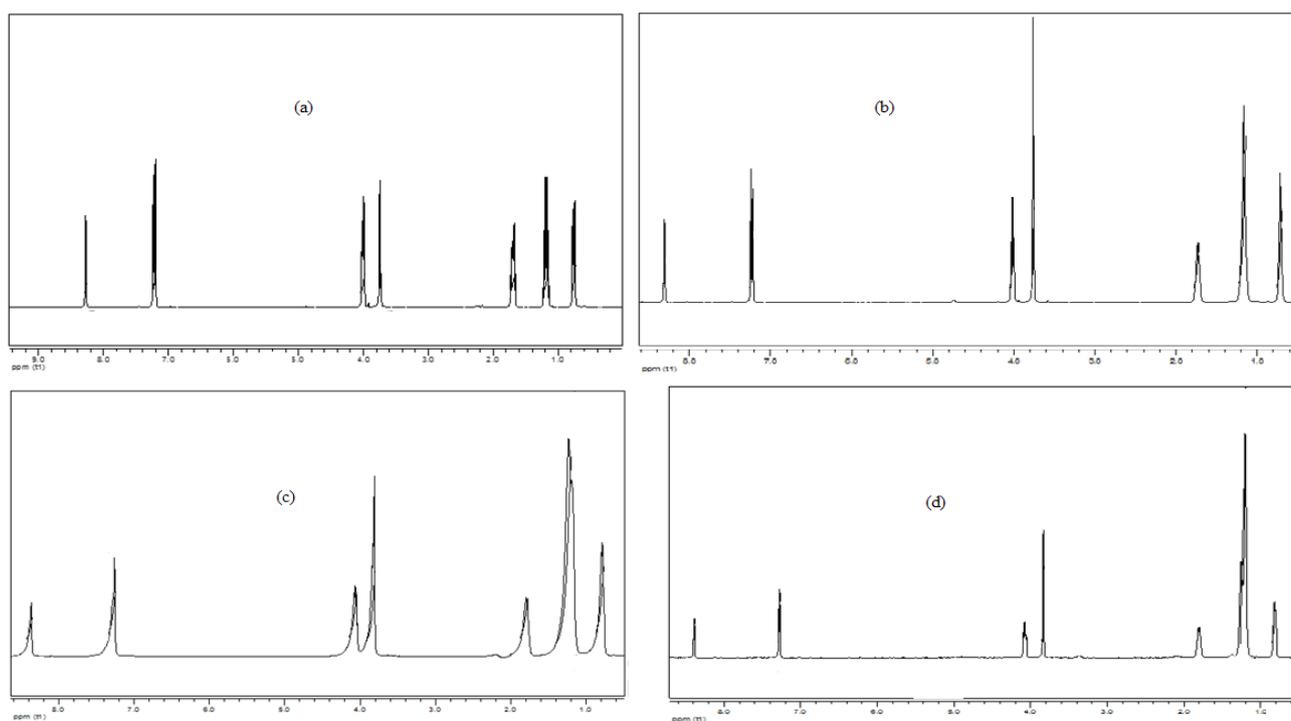
Figure 1. ^{1}H NMR spectrum of (a) [C$_4$mim][PF$_6$], (b) [C$_6$mim][PF$_6$], (c) [C$_8$mim][PF$_6$], (d)[C$_{10}$mim][PF$_6$]
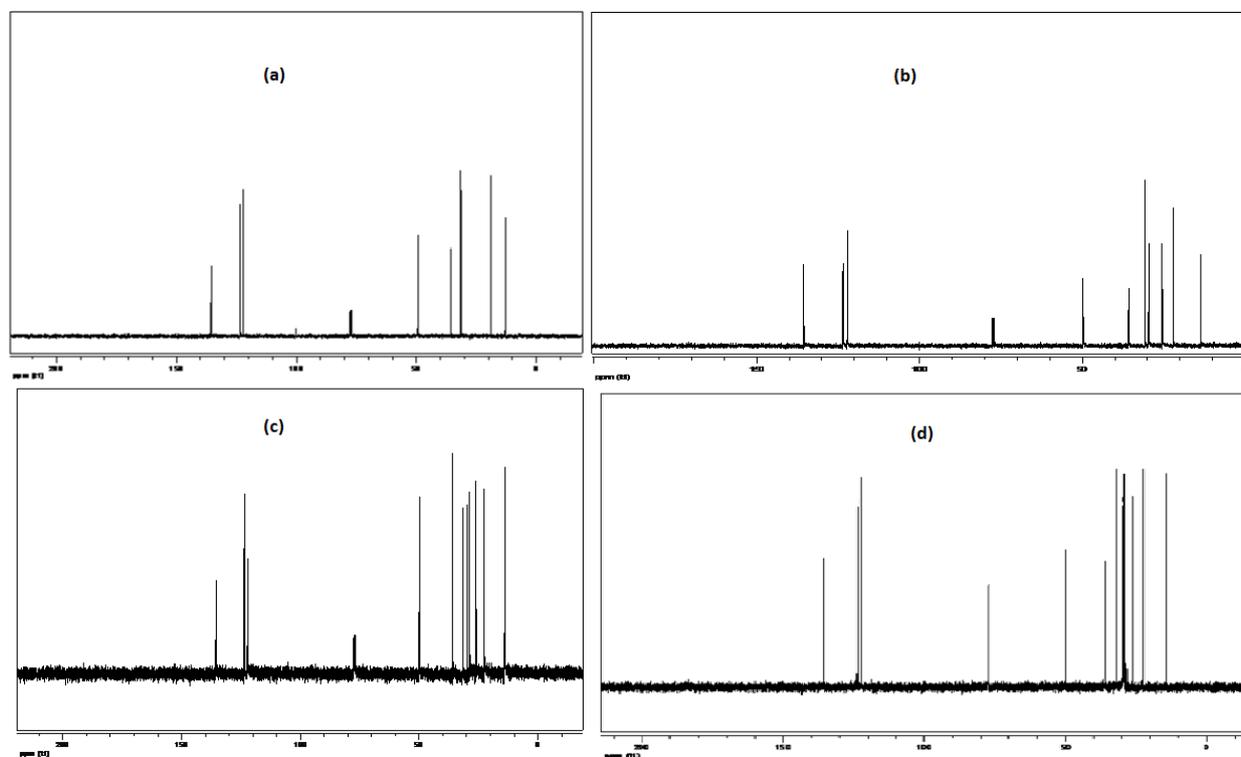
Figure 2. ^{13}C spectrum of (a)[C$_4$mim][PF$_6$], (b) [C$_6$mim][PF$_6$], (c)[C$_8$mim][PF$_6$], (d)[C$_{10}$mim][PF$_6$]

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	$(Ci)_{aq}$ ($\mu g/L$)	$(Cf)_{aq}$ ($\mu g/L$)	C_{IL} ($\mu g/L$)	RSD%		% E
				$(Cf)_{aq}$	C_{IL}	
$[C_4mim][PF_6]$	0.80	0.20 ± 0.002	0.54 ± 0.0108	1.00	2.00	75.00
$[C_6mim][PF_6]$	0.80	0.13 ± 0.006	0.63 ± 0.033	4.61	5.23	83.75
$[C_8mim][PF_6]$	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	100.0

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

Table 5. Extraction of Cd^{+2} at T=298 K, using IL to aqueous phase ratio of 1: 6

ILs	$(Ci)_{aq}$ $(\mu g/L)$	$(Cf)_{aq}$ $(\mu g/L)$	C_{IL} $(\mu g/L)$	RSD%		% E
				$(Cf)_{aq}$	C_{IL}	
$[C_4mim] [PF_6]$	0.80	0.10 ± 0.0009	0.67 ± 0.037	0.9	5.522	87.50
$[C_6mim] [PF_6]$	0.80	0.00 ± 0.0	0.79 ± 0.055	0.0	5.696	100.0
$[C_8mim] [PF_6]$	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.
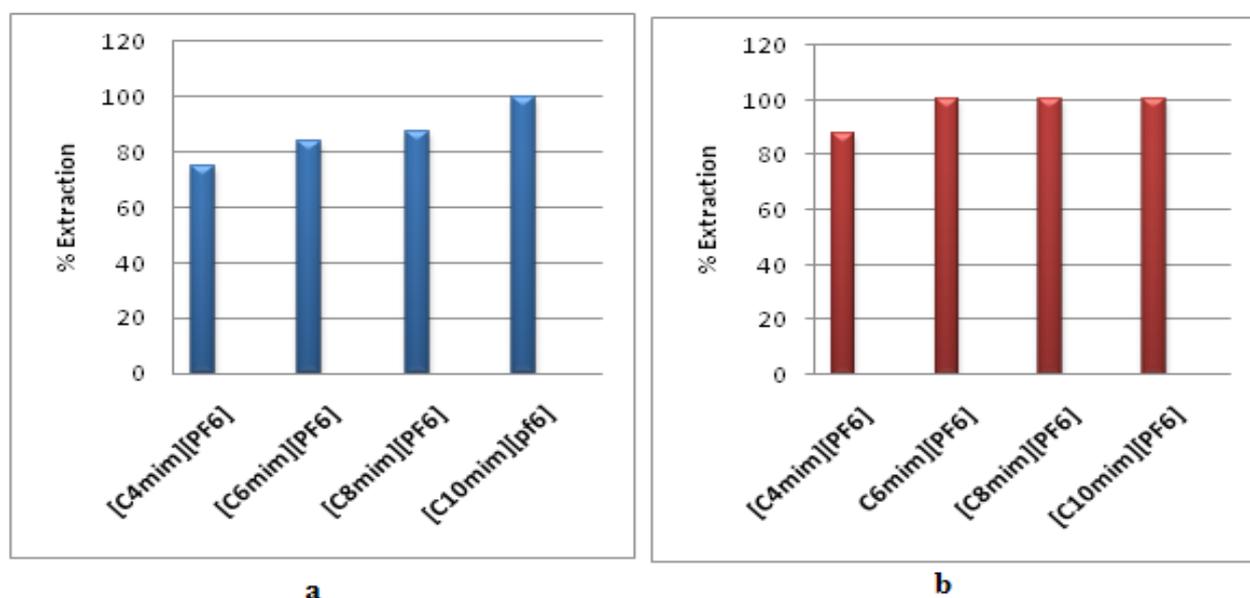

Figure 3: Trends of extractions at 298K, IL to aqueous phase ratio of a) 1:12, b)1:6

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 ($[C_6mim][PF_6]$ and $[C_8mim][PF_6]$) 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. 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 Cd^{2+} 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.

Table 6: The concentration of Cd^{2+} before and after the extraction in the aqueous phase for each cycle at 298K and IL to aqueous phase ratio 1:6 of a) $[C_6mim] [PF_6]$, b) $[C_8mim] [PF_6]$

a					b				
Cycle	$(Ci)_{aq}$ (mg/L)	$(Cf)_{aq}$ (mg/L)	RSD%	% E	Cycle	$(Ci)^*_{aq}$ (mg/L)	$(Cf)_{aq}^{**}$ (mg/L)	RSD%	% E
I	1.2	0.883 ± 0.025	2.862	26.43	I	1.2	0.767 ± 0.020	0.263	36.13
II	1.2	0.950 ± 0.037	3.848	20.83	II	1.2	0.839 ± 0.047	0.556	30.09
III	1.2	0.983 ± 0.035	3.602	18.11	III	1.2	0.846 ± 0.023	0.275	29.49
IV	1.2	1.039 ± 0.058	5.571	13.42	IV	1.2	0.966 ± 0.043	0.446	19.53
V	1.2	1.065 ± 0.036	3.407	11.25	V	1.2	1.03 ± 0.046	0.447	14.17

$^*(Ci)_{aq}$: concentration of the Cd^{+2} in the aqueous phase before extraction; $^{**}(Cf)_{aq}$: concentration of the Cd^{+2} in the aqueous phase after extraction


a   b
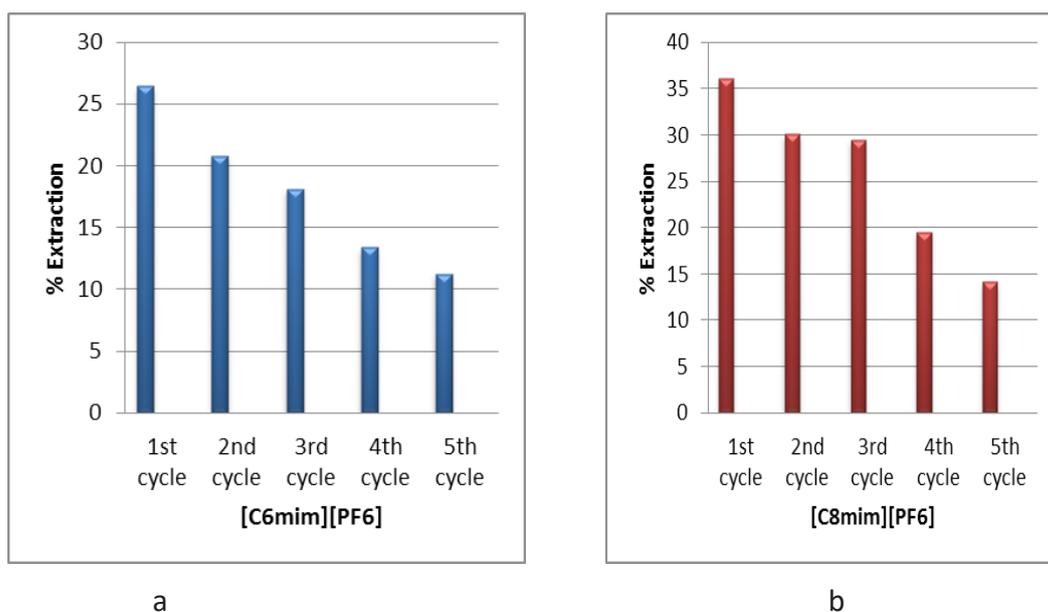
Figure 4: Trend of the extraction ability of the ILs at different cycles at 298K and IL to aqueous phase ratio 1:6 a) $[C_6mim] [PF_6]$, b) $[C_8mim] [PF_6]$

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+}.

ACKNOWLEDGMENTS

REFERENCES

Abbott, A.P., Boothby, D., Capper, G., Davies, D.L and Rasheed, R.K. (2004). Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society* **126**(29):9142-9147.

Atakilt Abebe, Shimelis Admassie , Villar-Garcia, I.J and Yonas Chebude (2013). 4, 4-Bipyridinium ionic liquids exhibiting excellent solubility for metal salts: Potential solvents for electrodeposition. *Inorganic Chemistry Communications* **29**:210-212.

Alonso, M., López-Delgado, A., Sastre, A.M and Alguacil, F.J. (2006). Kinetic modelling of the facilitated transport of cadmium (II) using Cyanex 923 as ionophore. *Chemical Engineering Journal* **118**(3):213-219.

Babel, S and Kurniawan, T.A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* **54**(7): 951- 967.

de los Ríos, A.P., Hernandez-Fernandez, F.J., Lozano, L.J., Sanchez, S., Moreno, J.I and Godinez, C. (2009). Removal of Metal Ions from Aqueous Solutions by Extraction with Ionic Liquids. *Journal of Chemical and Engineering Data* **55**(2):605-608.

Dietz, M.L. (2006). Ionic liquids as extraction solvents: Where do we stand?. *Separation Science and Technology* **41**(10):2047-2063.

Domańska, U. and Rękawek A. (2009). Extraction of metal ions from aqueous solutions using imidazolium based ionic liquids. *Journal of Solution Chemistry* **38**(6):739-751.

Earle, M.J and Seddon K.R. (2000). Ionic liquids. Green solvents for the future. *Pure and Applied Chemistry* **72**(7):1391-1398.

El Samrani, A. G., Lartiges, B. S and Villiéras, F. (2008). Chemical coagulation of combined sewer overflow: Heavy metal removal and treatment optimization. *Water Research* **42**(4):951-960.

Freire, M. G., Santos, L. M.N.B.F., Fernandes, A. M., Coutinho, J.A.P and Marrucho , I. M. (2007). *Fluid Phase Equilibria* **261**:449–454.

Fu, F and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management* **92**(3):407-418.

Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies* **1(1):12-18.**

Hayyan, M., Hashim, M. A., Hayyan, A., Al-Saadi, M. A., AlNashef, I. M., Mirghani, M. E and Saheed, O. K. (2013). Are deep eutectic solvents benign or toxic? *Chemosphere* **90**(7):2193-2195.

Hernández-Fernández, F. J., De los Ríos, A. P., Anzola, A. G and Godinez, C. (2010). Use of ionic liquids as green solvents for extraction of Zn (2+), Cd (2+), Fe (3+) and Cu (2+) from aqueous solutions. *Chemical Engineering Transactions* 21: 631-636.

Huang, X, Margulis, C.J., Li Y and Berne, B.J. (2005). Why is the partial molar volume of CO_2 so small when dissolved in a room temperature ionic liquid? Structure and dynamics of CO_2 dissolved in [Bmim$^+$][PF$_6^-$]. *Journal of the American Chemical Society* **127**(50):17842-17851.

Kang, S. Y., Lee, J. U., Moon, S. H and Kim, K. W. (2004). Competitive adsorption characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere* **56**(2):141-147.

Ku, Y and Jung, I. L. (2001). Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. *Water Research* **35**(1):135-142.

Kuo, C.Y and Lin, H.Y. (2009). Adsorption of aqueous cadmium (II) onto modified multiwalled carbon nanotubes following microwave/chemical treatment. *Desalination* **249**:792- 796.

Lancaster, M. (2010). **Green chemistry: an introductory text**. RSC Publishing, Cambridge, UK, pp340

Landaburu-Aguirre, J., Garcia, V., Pongracz, E and Keiski, R.L. (2000). The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments. *Desalination* **240**:262-269

Manahan, S.E. (2011). **Fundamentals of environmental chemistry**. CRC press, New York. Pp75-114.

Motsi, T., Rowson, N.A and Simmons, M.J. (2009). Adsorption of heavy metals from acid mine drainage by natural zeolite. *International Journal of Mineral Processing* **92**(1):42-48.

Pavasant, P., Apiratikul, R., Sungkhum, V., Suthiparinyanont, P., Wattanachira, S and Marhaba, T. F. (2006). Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga Caulerpa lentillifera. *Bioresource Technology* **97**(18):2321-2329.

Pinto, P.X., Al-Abed, S.R and Reisman, D.J. (2011). Biosorption of heavy metals from mining influenced water onto chitin products. *Chemical Engineering Journal* **166**(3):1002-1009.

Platzer, S., Sap, O., Leyma, R., Wallner, G., Jirsa, F., Kandioller, W., Krachler, R and Keppler, B.K. (2015). Extraction of natural radionuclides from aqueous solutions by novel maltolate-based task-specific ionic liquids. *Journal of Radioanalytical and Nuclear Chemistry* **303**(3):2483-2488.

Richardson, J.F. and Harker, J.H., (2002), Coulson and Richardson's **Chemical Engineering**. 5th ed. Butterworth Heinemann, Oxford, UK.pp721-769.

Sereshti, H., Eskandarpour, N., Samadi, S and Aliakbarzadeh, G. (2014). Investigation on Dracaena Sanderiana PhytoremeDiation Ability for Hg and Cd using Multivariate Optimized Task Specific Ionic liquid-based Dispersive liquid-liquid Microextraction. *International Journal of Environmental Research* **8**(4):1075-1084.

Villar-Garcia, I.J., Atakilt Abebe and Yonas Chebude. (2012). 1, 10-Phenanthrolinium ionic liquids exhibiting excellent solubility for metal complexes: Potential solvents for biphasic and supported ionic liquid phase (SILP) catalysis *Inorganic Chemistry Communications* **19**:1-3.

Villemin, D and Didi, M.A. (2014). Extraction of rare earth and heavy metals, using ionic solvents as extraction medium (A Review). *Oriental Journal of Chemistry* **29**(4):1267-1284.

Visser, A.E., Swatloski, R.P., Griffin, S.T., Hartman, D.H and Rogers, R.D. (2001). Liquid/liquid extraction of metal ions in room temperature ionic liquids. *Separation Science and Technology* **36**(5-6):785-804.

Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davis, J.H. and Rogers, R.D. Task-specific ionic liquids incorporating novel cations for the coordination and extraction of Hg^{2+} and Cd^{2+}: synthesis, characterization, and extraction studies *Environmental Science and technology* **36**(11):2523-2529.

Wang, L.K., Hung, Y.T and Shammas, N.K. (2007). Advanced physicochemical treatment technologies. In: **Handbook of Environmental Engineering**, vol. 5. Humana, New Jersey. Pp55-106.

Wasserscheid, P and Welton T. (2008). Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, Germany.

Wei, G.T., Yang, Z and Chen, C.J. (2003). Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Analytica Chimica Acta* **488**(2):183-192.

Xu, Y., Yang, L and Yang, J. (2010). Removal of cadmium (II) from aqueous solutions by two kinds of manganese coagulants. *International Journal of Engineering, Science and Technology* **2**(7):1-8.

Zhao, H., Xia S and Ma P. (2005). Use of ionic liquids as 'green'solvents for extractions. *Journal of Chemical Technology and Biotechnology* **80**(10):1089-1096.