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ORIGINAL PAPER

# A systematic approach of using green solvent for the extraction of Pb (II) from aqueous solution

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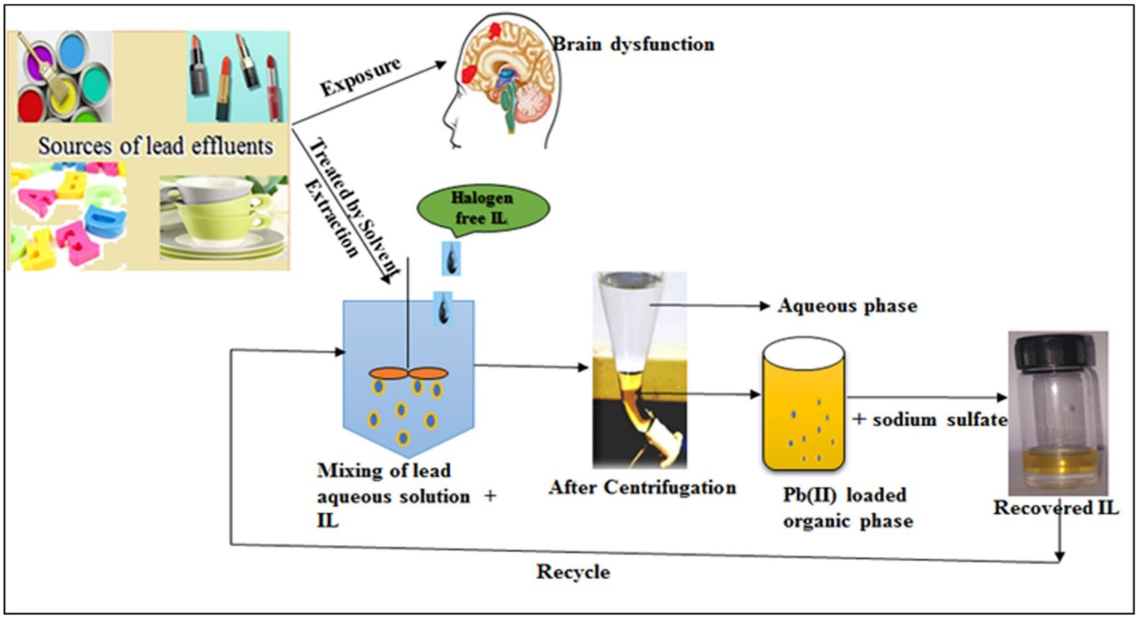
## Abstract

In this article, the extraction behavior of halogen-free ionic liquid, 1-butyl-3-methylimidazolium octyl sulfate, was investigated in the separation of lead from the aqueous solution. Experimental parameters include time, impact of pH, feed concentration, amount of ionic liquid, ionic strength, and temperature were optimized for the evaluation of the lead extraction. From the optimum conditions, it was emanated that the maximum extraction efficiency of lead was 97% with the feed concentration of 10 ppm in an equilibrium time of 60 min at the pH of 5 and 2 g of the ionic liquid, respectively. Furthermore, the extraction results revealed that the higher efficiency was achieved without the addition of salt and that the extraction process was spontaneous and endothermic in nature. The metal complexation was formed by the exchange of ionic liquid anion to the aqueous phase, and thereby, the extraction mechanism was proposed. The ionic liquid in the organic phase was stripped using sodium sulfate as a stripping agent. FTIR analysis confirmed the recoverable ionic liquid and effectively reused it five times in the course of extraction. From the analysis, it was authenticated that the ionic liquid, 1-butyl-3-methylimidazolium octyl sulfate, was an effective extractant for the elimination of lead (II) and could be employed for the tertiary treatment of industrial wastes.

### Graphic abstract



**Keywords** Ionic liquid · Liquid–liquid extraction · Lead · Aqueous solution · Recovery · Reuse

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## Abbreviations

| | |
|---|---|
| IL | Ionic liquid |
| [BMIM][$OCTSO_4$] | 1-Butyl-3-methylimidazolium octyl sulfate |
| $\Delta G^{\circ}$ | Change in standard Gibb's energy |
| $\Delta H^{\circ}$ | Change in enthalpy |
| $\Delta S^{\circ\circ}$ | Change in entropy |
| $D$ | Distribution coefficient |

## Introduction

Lead is a well-known highly toxic metal that reckons for 13 mg/kg of earth's crust. Among all the metals, lead is highly recycled and about 90% of lead is used in the batteries, radiation protection, sheathing for cables, and various applications like earthquake impediment and cathode ray tube (CRT) funnel glass (Wojciechowska et al. 2017). However, their widespread use at higher levels in the environment not only affects the ecosystem but also results in long-term health issues like birth defects, hepatitis, brain dysfunction, and kidney damage to humans (Arbabi and Hemati 2017; Parsons et al. 2019; Abraham and Venkateswarulu 2020). Major sources of lead pollution are the effluents from processing industries, such as the plastic industry, metal plating and finishing, paint industry, ammunition production, and glass industries (Wojciechowska et al. 2017; Korrapati et al. 2017). Besides, polyvinyl chloride (PVC) pipes also contain lead, which can percolate easily, therefore resulting in a high lead content in drinking water. Under the act of Environmental Protection, the standard concentration and the permissible limit for the lead discharge level in freshwater resources as well as in industrial effluents are 0.1 mg/L. Therefore, the separation or reduction of Pb (II) concentration is crucial and beneficial to the environment along with economic profits due to its demand in the metallurgical field.

So far, several efficient methods have been used to eliminate lead from the aqueous streams, which include chemical precipitation, coagulation, ion exchange, adsorption, photocatalysis, and membrane filtration (Guezzen and Amine Didi 2016; Platzer et al. 2017). However, these methods have several disadvantages such as the generation of toxic sludge, limited metal selectivity, a requirement of higher maintenance, and operational cost (Hajipour and Rafiee 2009). Solvent extraction offers excellent advantages over the competing techniques to mitigate the lead concentration in wastewaters, such as the ability to employ simple equipment under mild operating conditions, and to achieve large samples throughout with higher efficiency, and there is no need for an extra separation unit for the recuperation and recycle of consumed solvent (Shirani and Torkaman 2017). The extraction efficiency strongly depends upon the solvent and their physicochemical properties like density, viscosity, refractive index, and polarity (Egorov et al. 2010). As traditionally practiced water-immiscible volatile organic solvents, employed in the solvent extraction method, are highly toxic and hazardous causing a harmful impact on human health as well as the environment (Dietz 2006), ionic liquids (ILs) are recognized as hopeful substitutes of volatile organic solvents. They are environmentally benign, which consists of entirely organic cations and organic or inorganic anions that exhibit several properties such as non-flammability, high thermal stability over a lar2014ge range of temperatures, a near-absence of vapor pressure, and good solvating properties with spectral transparency (Dietz 2006; Valdes Vergara et al. ; Wang et al. 2016). The greatest advantages of using ILs over organic extractant are extraordinary tunability, recoverability, reusability, fastness, and reliability (Rajendran et al. 2011), which make them attractive as a potential basis for the solvent extraction process. Further, they have a strong ability to interact with metal ions in aqueous solutions through various mechanisms including π–π, dispersion, ionic exchange, and hydrogen bonding interactions. These interactions can be finely modified by the change of cation or anion of ILs, task-specifically bringing an elevated separation efficiency (Ren et al. 2011).

In the solvent extraction process, some ILs are used as diluents with the chelating agent or commercial extractant and some are used as extractants to extract the various metal ions from aqueous solutions. Domańska and Rękawek (2009) studied the removal of $Ag^{2+}$ and $Pb^{2+}$ from aqueous solution using 1-alkyl-3-ethylimidazolium and 1-alkyl-3-methylimidazolium with $PF_6$ and $NTF_2$-based ILs in combination with dithizone as a metal chelator. It was reported that the more hydrophobic character of ILs based on 1-ethyl-3-ethylimidazolium and 1-butyl-3-ethylimidazolium cations with $NTF_2$ anions has a higher extraction efficiency in extracting $Ag^{2+}$ ions than $Pb^{2+}$ compared with $PF_6$-based ILs. The extraction of $Ni^{2+}$, $Cu^{2+}$, and $Pb^{2+}$ from water using 1-butyl-3-methylimidazolium hexafluorophosphate and chloroform with 2-aminothiophenol as a ligand was investigated by Lertlapwasin R et al. 2010. Their results revealed that IL has better extraction efficiency than chloroform. The same result was obtained by Fetouhi et al. 2016 for the extraction of the aforementioned metals except $Cu^{2+}$ but then $Co^{2+}$ using similar IL with N-salicylideneaniline as an extracting ligand. The studies of $Ni^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Fe^{2+}$ extraction from the tannery effluents using ammonium-based ILs by Rajendran et al. 2011 and these extractions using nine types of water-immiscible halogen-free ammonium-based ILs were also reported by Vergara et al. (2014). Zhou et al. (2015) reported that the betaine tri(n-butyl)[(2-ethoxy-2-oxoethyl] ammonium dicyanamide [BuGBOEt][Dca] has a higher extraction efficiency in extracting $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ from aqueous solution than [BuGBOEt][Br]. Furthermore, it was reported that these metals were recovered by aqueous EDTA solutions. Wojciechowska et al. (2017) investigated the extraction of lead (II) from chloride and chloride/nitrate solutions and also reported that chloride-based IL has better extraction efficiency for the lead among others.

The previous work reported that the prescreening of 25 halogen-free ILs using the COSMO-RS model (Vijayalakshmi et al. 2020) and the suitable IL, 1-butyl-3-methylimidazolium octyl sulfate [BMIM][$OCTSO_4$], was chosen for the extraction of $Pb^{2+}$ from wastewaters based on prescreening as well as their availability in the market. Also, to the best of our knowledge, there is no literature found for the removal of any metals using the above-mentioned IL, which therefore provoked the research toward lead extraction. This article will describe the extraction behavior of Pb (II) ion from aqueous solution using 1-butyl-3-methylimidazolium octyl sulfate [BMIM][$OCTSO_4$]. Dichloromethane was used as a chelating agent for [BMIM][$OCTSO_4$]. Extraction experiments were carried out to study the influence of equilibrium time, feed concentration, amount of IL, pH, salting effect, and temperature toward the extraction efficiency. In this work, the separation efficiency is greatly dependent on the cationic part of IL because its coordinating anion is hydrophilic. Therefore, IL cation has a strong ability to coordinate with Pb (II) solution to form a metal complex by the hydrogen bond interaction (Wang 2018). After the extraction process, the IL was recovered and reused effectively. This research work was carried out at Ionic Liquids Research Laboratory, Department of Chemical Engineering, A.C. Tech, Anna University, Chennai, from the period of October 2019–January 2020.

## Materials and methods

### Materials and reagents

Lead nitrate [$Pb(NO_3)_2$, 98% pure], HCl (98%), NaOH (98%), dichloromethane (99%) were procured from Sisco Research Laboratories Pvt. Ltd., Chennai. Dithizone (> 85%) and 1-butyl-3-methylimidazolium octyl sulfate (> 95%) were purchased from Sigma-Aldrich, Chennai. 1000 ppm of $Pb^{2+}$ in 1L of DI water stock solution was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ (Narayanan and Vetha 2017). The standard solutions were prepared by the dilution of the stock solution for instrument calibration at the time of extraction experiments. The pH of the aqueous solution was adjusted with 1 N HCl and NaOH buffer solutions.

### Instrumentation

A UV–Vis 1800 double-beam spectrophotometer (Shimadzu) was used for the determination of Pb (II) concentration in the aqueous phase monitored at 548 nm before and after the extraction processes. A mechanical shaker (Remi RS-12R) and centrifuge of R 24 model were used for agitation and centrifugation of solution, respectively. pH measurements were taken on a digital pH meter (IR-501 Roy Instruments) equipped with a glass electrode. Characterization of recovered IL was carried out on a Fourier transform infrared spectrophotometer (FTIR), Bruker model.

### Extraction experiment

The extraction procedure was performed as follows: 10 ml of the aqueous solution with known concentration and a known weight of [BMIM][$OCTSO_4$] was taken in an Erlenmeyer flask. A 5 ml of dichloromethane was added as a chelating agent. Then, the mixture was placed in a mechanical shaker at 180 rpm for a time interval of 30-180mins at room temperature. After homogenization, the solution was centrifuged at 4000 rpm for 10mins and then allowed to settle for separating the two phases in separating funnel (Valdes Vergara et al. 2014). Then, the aqueous phase was analyzed through a UV-visible spectrophotometer at the wavelength of 548 nm to determine the concentration of an unextracted lead in the solution. By using mass balance, the extracted Pb (II) ion concentration present in the organic phase was determined. The extraction efficiency (*E*) and distribution coefficient (*D*) on Pb (II) were determined by the following equations.

$$\text{Extraction efficiency } (E)\,\% = \frac{(\text{Ci})\text{ aq } - (\text{Cf})\text{ aq}}{(\text{Ci})\text{ aq}} \times 100$$

$$\text{Distribution coefficient } (D) = \frac{(\text{Ci})\text{ aq } - (\text{Cf})\text{ aq}}{(\text{Ci})\text{ aq}} \times \frac{\text{Volume of aqueous phase}}{\text{Volume of IL phase}}$$

where the initial and final concentrations (ppm) of Pb (II) ion in the aqueous phase are represented as (Ci) aq and (Cf) aq, respectively (Fetouhi et al. 2016). The molecular structure of IL with acronym is presented as shown in Fig. 1. Extraction studies were carried out by varying the parameters such as time, feed concentration, pH, amount of IL, and salt at 293 K except the experiment was done at variable temperatures for the determination of thermodynamic parameters. All the extraction experiments were executed at least in triplicate, and their average values were reported.

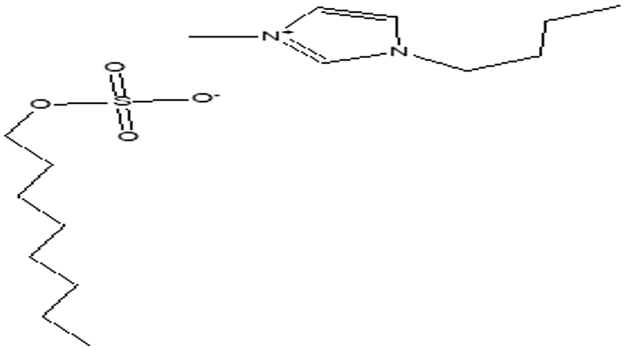


**Fig. 1** Structure of 1-butyl-3-methylimidazolium octyl sulfate [BMIM][OCTSO$_4$] IL

### Recovery of [BMIM][OCTSO$_4$ and Pb (II)

The lead ions was stripped out from the organic phase (IL phase) after extraction by the addition of 1gm of sodium sulfate. The lead was separated from the IL in the form of lead sulfate. The recovered IL was confirmed by the FTIR analysis. Through the confirmatory test, the aqueous phase containing lead (II) sulfate and sodium nitrate was analyzed. The regenerated IL was reused for five times in extraction experiments. The schematic representation of the extraction process for the lead ion removal is shown in Fig. 2.

## Results and discussion

Several experimental factors such as extraction time, feed concentration, pH, amount of IL, temperature, and ionic strength were examined to evaluate how these parameters affect the extraction process of Pb (II) ion.

### Effect of equilibrium time on Pb (II) extraction

Equilibrium time is one of the most important parameters in separation processes because the solute transfer needs to overcome the barrier energy between the two immiscible phases. This transport process takes time to occur and reach the equilibrium (Deng et al. 2011). In order to determine the optimum duration for full extraction of Pb (II) ion from the aqueous solution, the impact of optimal time was preliminarily studied. To achieve this aim, experiments were conducted by agitating a 10 ml of an aqueous solution containing 10 ppm feed concentration and 1 g of [BMIM][OCTSO$_4$] with 5 ml of dichloromethane at initial pH of 3 under room temperature. The shaking time

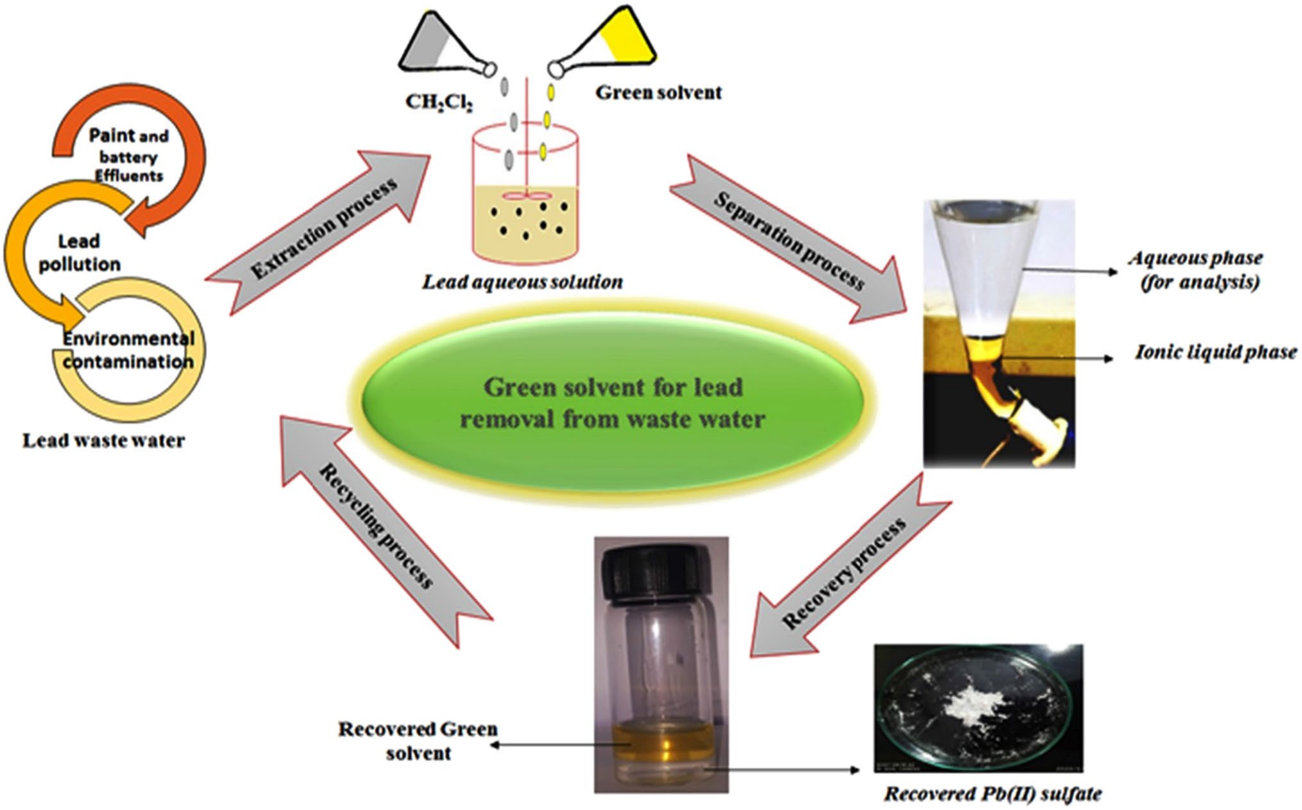


**Fig. 2** Schematic representation of lead (II) extraction from aqueous solution using [BMIM][OCTSO$_4$]

was varied from 30 to 180 min. As it is assured from the graph represented in Fig. 3, the maximum extraction of 93.82% was attained at 60 min. The reason behind this is the formation of a metal complex, which at this contact time achieves its optimum efficiency. After 60 min, however, the extraction efficiency decreased significantly with the increase in time, and new extraction equilibrium was established. This might be due to some degradation of the metal complex (Fetouhi et al. 2016). Therefore, 60 min was considered as an equilibrium time to obtain the maximum extraction efficiency for the lead from aqueous solution and was fixed to assure extraction equilibrium for further experimental studies.

## Effect of pH on Pb (II) extraction

For any extraction process, the formation of the metal complex and their stabilities in the aqueous solution is strongly dependent on the strength of acid/base. Therefore, pH is an important parameter that governs the efficiency of the separation process (Guezzen and Amine Didi 2016; Stanisz and Zgoła-Grześkowiak 2013). The impact of pH on extraction of Pb (II) was studied by varying the pH ranging from 2 to 7. The extraction efficiency is displayed in Fig. 4. The lead extraction with IL was found to be increasing with an increase in pH. The reason could be that at low pH values, the acid is strongly competitive with a metal ion, which in turn inhibits the Pb (II) extraction (Rout and Binnemans 2014). At increasing pH values, the extractable metal complex was formed due to a higher protonation of IL (Swain et al. 2016). The maximum extraction efficiency was

**Fig. 3** Influence of equilibrium time on extraction of lead. Experimental conditions: volume of aqueous solution: 10 ml, volume of chelating agent: 5 ml, feed concentration: 10 ppm, pH: 3.5, volume of IL: 1gm at room temperature

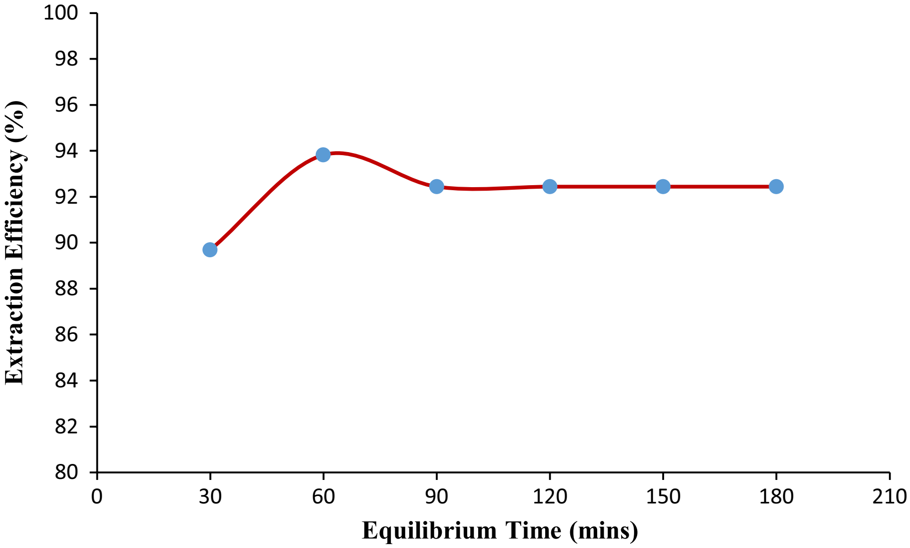
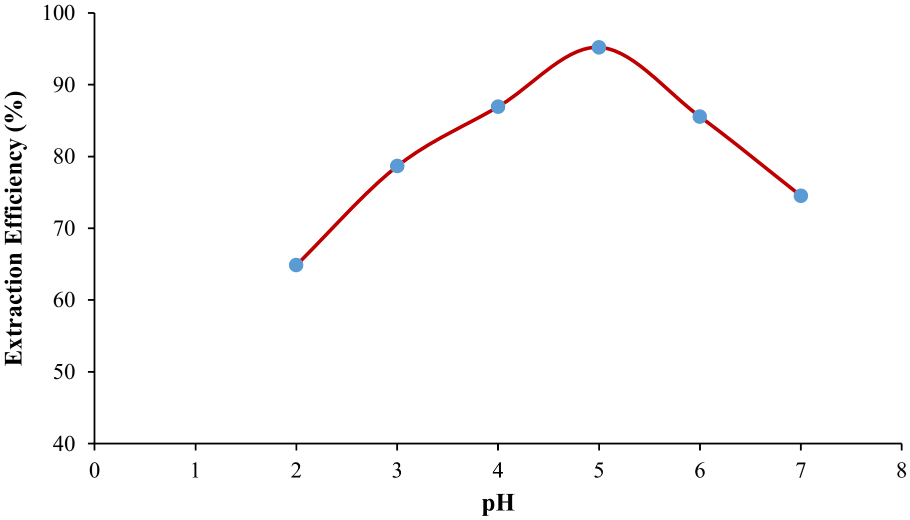


**Fig. 4** Effect of pH on extraction of lead. Experimental conditions: volume of the aqueous solution: 10 ml, the volume of chelating agent: 5 ml, shaking time: 60 min, feed concentration: 10 ppm, volume of IL: 1g at room temperature



obtained at pH 5, and the result was in good agreement with the report studied by Lertlapwasin et al. (2010) in the extraction of $Pb^{2+}$ using the same class of functionalized ILs with different anions. Further increasing the pH value, the extraction efficiency was decreased. Hence, pH 5 was fixed as an optimum value for obtaining a maximum extraction rate for lead and was used for the optimization of other parameters.

## Effect of feed concentration on extraction efficiency

The parameter of feed concentration plays a vital role to determine the ability of extractant in the separation process. For that reason, the effect of concentration of the lead aqueous solution was studied by performing the extraction experiments using 1 g of IL and 5 ml of dichloromethane for an optimum period of 60 min and pH of 5 at room temperature, respectively. The feed concentration can be varied ranging from 10 to 60 ppm, and the respective extraction efficiency is represented in Fig. 5. The result revealed that by increasing the feed concentration, the extraction rate on Pb(II) was gradually decreased from 93.82 to 52.60%, therefore reflecting the unavailability of coordinating sites of IL to form complex with $Pb^{2+}$ ions, i.e., a saturation of IL phase at a higher feed concentration was achieved (Zhou et al. 2015). The maximum extraction rate of 93.82% was attained at the feed concentration of 10 ppm. Therefore, 10 ppm was recommended as an optimum feed concentration and was fixed for further experimental studies on the extraction of lead.

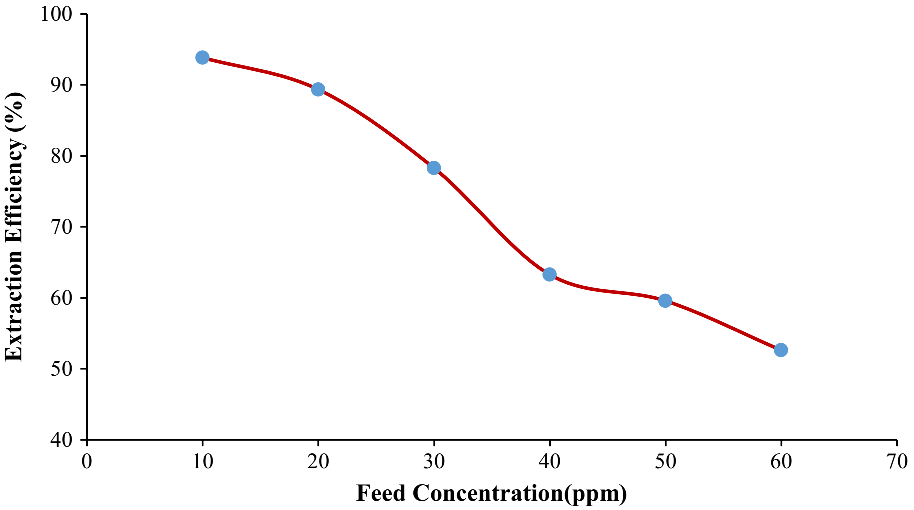
## Effect of the amount of IL ([BMIM][OCTSO$_4$])

Mass of extractant (IL) is one more important factor that affects the extraction efficiency. They exhibit not only a function of the number of metal ions in a solution but also the solubility of the IL phase. To predict the extraction behavior of Pb (II) ion over this parameter, experiments were conducted by stirring the sample solution at optimum feed concentration and IL ([BMIM][OCTSO$_4$]) in which the mass was varied from 1 to 3 g in 60 min and pH of 5 at room temperature, respectively. The extraction efficiency is shown in Fig. 6. The result showed that the rate of extraction rises with an increase in IL quantity and that the maximum extraction efficiency of 97.79% on Pb (II) was attained at 2 g of IL. Further, by increasing the amount, there are no drastic changes in their efficiency. This might be due to the migration of maximum metals toward the organic phase to form a metal complex at 2 g of IL. Therefore, the best ability of IL to extract lead from aqueous solution was achieved at 2 g of IL, which was taken as an optimal value and used for the optimization of further experimental parameters.

## Effect of ionic strength on Pb (II) extraction

The factor of salting effect in the extraction process helps to determine the activity of water in the aqueous phase (Foltova et al. 2019). Hence, the ionic strength effect on the extraction behavior of $Pb^{2+}$ ion using IL was examined by adding the sodium chloride into 10 ml of the aqueous solution. NaCl was varied over the range of 0.2–1.2 g under room temperature, while other experimental conditions were kept constant. The results are depicted in Fig. 7. The graph revealed that the extraction efficiency was slightly decreased by increasing the amount of sodium chloride to the aqueous solution. This might be due to the formation of chlorine gas in solution when the salt reacts with water in the aqueous phase. As a result, high pressure was created, and their effect was very high by the addition of a higher amount of salt in the aqueous solution, which somewhat disturbed the maximum yield on lead extraction. A similar extraction behavior was noticed for the separation of cobalt and nickel

**Fig. 5** Influence of feed concentration on extraction of lead. Experimental conditions: volume of the aqueous solution: 10 ml, the volume of chelating agent: 5 ml, shaking time: 60 min, pH: 5, the volume of IL: 1g at room temperature



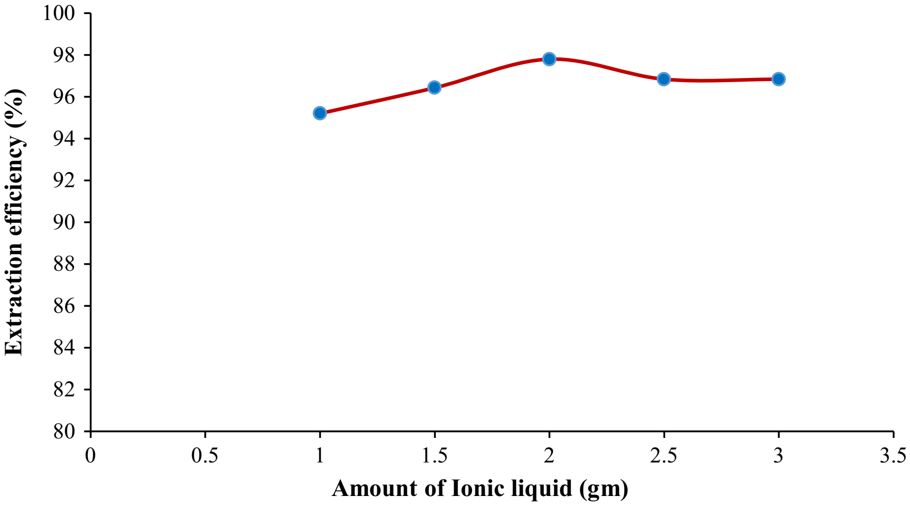


**Fig. 6** Effect of amount of ionic liquid on lead extraction. Experimental conditions: volume of aqueous solution: 10 ml, volume of chelating agent: 5 ml, shaking time: 60 min, pH: 5, feed concentration: 10 ppm at room temperature

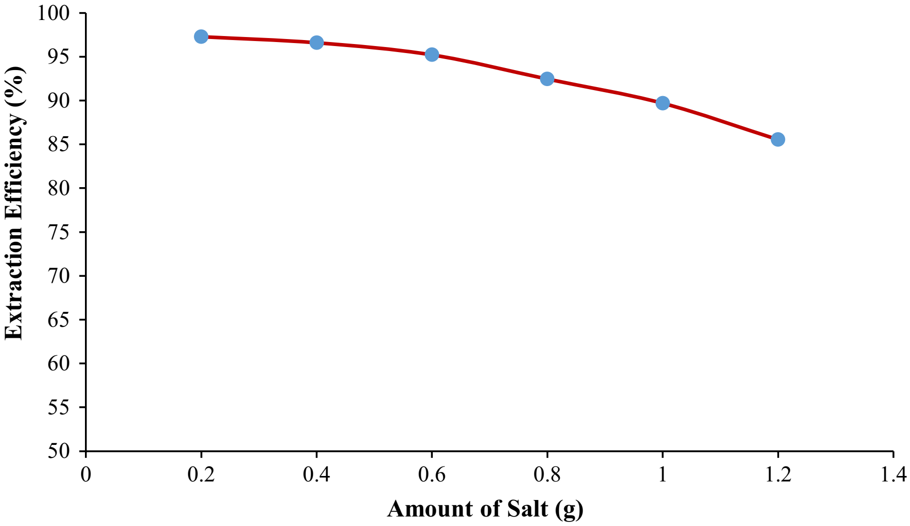


**Fig. 7** Effect of ionic strength on lead extraction. Experimental conditions: volume of the aqueous solution: 10 ml, the volume of chelating agent: 5 ml, shaking time: 60 min, pH: 5, feed Concentration: 10 ppm, volume of IL: 2g at room temperature

using another hydrophilic IL-based aqueous biphasic system (Chen et al. 2018). Therefore, no salt was recommended for further experimental studies.

## Determination of thermodynamic parameter

In the extraction process, temperature plays a vital role that strongly influences the mass transfer rate of metal ions and increases the contact area between the extractant and aqueous solution (Zhang and Shi 2010). To study the temperature effect on the extraction of $Pb^{2+}$, experiments were carried out at various temperatures over the range of 303.15 K to 343.15 K using a water bath under optimum conditions. The result represented in Fig. 8 showed that a decreased extraction efficiency was due to the increasing temperature. As a result, the solution becomes homogenized at high temperatures, because of the low boiling point of a chelating agent (39.6˚C) present in the aqueous solution. Hence, the formation of metal complex migrates toward the aqueous phase, thereby decreasing the extraction efficiency. It was confirmed by the prediction of change in enthalpy, Gibb's free energy, and change in entropy at different temperatures during the extraction process.

The change in enthalpy ($\Delta H$) was calculated using the van's Hoff equation as follows

$$\log D = \frac{-\Delta H^{\circ}}{2.303R}\frac{1}{T} + C$$

The graph was plotted between $1/T \times 10^{-4}$ versus $\log D$ giving a linear relationship with a slope of $-\Delta H^{\circ}/2.303\ R$, from which the change in enthalpy ($\Delta H^{\circ}$) value was calculated. From the slope, $\Delta H^{\circ}$ was estimated to be 1.4686 kJ/mol, which indicates that it was endothermic. The change in standard Gibb's energy ($\Delta G^{\circ}$) and entropy ($\Delta S^{\circ}$) was determined using the following equations

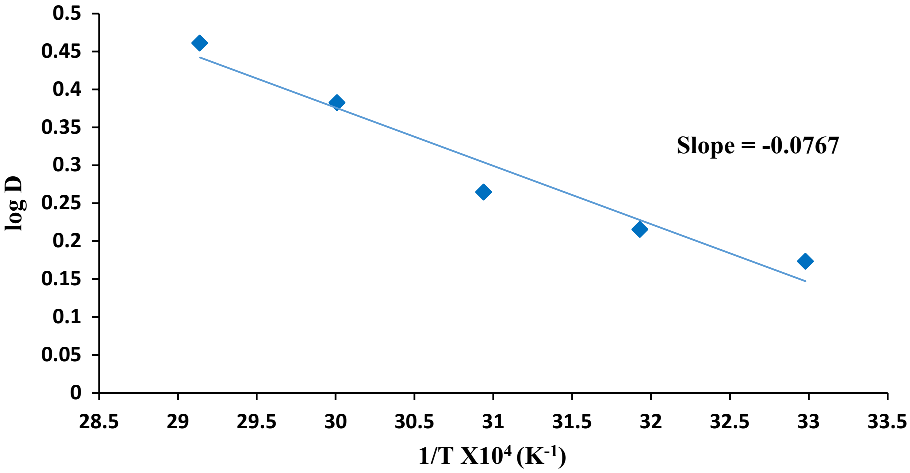


**Fig. 8** Effect of temperature on lead extraction. Experimental conditions: volume of the aqueous solution: 10 ml, the volume of chelating agent: 5 ml, shaking time: 60 min, pH: 5, feed Concentration: 10 ppm, volume of IL: 2gm

**Table 1** Values of thermodynamic constants obtained from temperature study for the lead extraction

| $T$ (K) | $\Delta G^\circ$ (KJ/mol) | $\Delta S^\circ$ (J/mol K) |
|---|---|---|
| 303 | − 1.00 | 81.47 |
| 313 | − 1.25 | 86.85 |
| 323 | − 1.53 | 92.84 |
| 333 | − 2.22 | 110.76 |
| 343 | − 2.67 | 120.66 |

$$[\mathrm{Pb(NO_3)_2}]^+_{(\mathrm{aq})} + \mathrm{nL}_{(\mathrm{IL})} + \{[\mathrm{C_4min}]^+[\mathrm{OCTSO_4}]^+\}_{(\mathrm{IL})} \rightleftharpoons [\mathrm{Pb(Ln)(NO_3)_2}](\mathrm{C_4min})_{(\mathrm{IL})} + [\mathrm{OCTSO_4}]^+_{(\mathrm{aq})}$$

$$\Delta G^\circ = -2.303RT \log D$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

The values of $\Delta G^\circ$ and $\Delta S^\circ$ of the extraction process at various temperatures are tabulated in Table. 1. The results show that the negative values of $\Delta G^\circ$ suggest that the extraction processes are spontaneous. The positive value of entropy $\Delta S^\circ$ designates that the reaction was favorable in nature. Most of the ILs need only an ambient temperature for getting the maximum extraction efficiency of metals from aqueous solution (Chaverra et al. 2020; Online and Binnemans 2020). Therefore, the ambient temperature (25°C) can be recommended as an optimum temperature for lead extraction from aqueous solution.

## Extraction mechanism

The extraction mechanism was proposed according to the anion of IL used in this work. The inorganic anions $[\mathrm{OCTSO_4}]^-$ are usually hydrophilic, due to its aliphatic side chain length which makes the IL, $[\mathrm{BMIM}]^+[\mathrm{OCTSO_4}]^-$water-miscible. Therefore, the cations of IL ($\mathrm{C_4mim^+}$) are capable of forming a coordinate bond with Pb (II) ion in the aqueous solution during the extraction process. Dichloromethane was used as a chelating agent for promoting the phase separation. By nature, it reacts readily with carbon atoms, so that it can be attracted by IL (usually contains 16 carbon atoms). From the stated above, it can be clearly understood that the anion exchange mechanism takes place in the extraction process, which can be written as follows.

where subscripts “aq” denotes the aqueous phase, “IL” denotes the organic phase, and L denotes the dichloromethane, respectively.

According to the anion exchange mechanism, the cationic part of IL exerts a direct influence on extraction efficiency. The metal complexes are formed by the transfer of lead nitrate from the aqueous phase to the hydrophobic sites of cation through the hydrogen bond interaction along with dichloromethane and anion is exchanged into the aqueous phase for charge neutrality. Both the metal complexation and extraction process are proceeded in a spontaneous and favorable in nature due to the evidence that the $\Delta G^\circ$ values are negative, which is derived from the thermodynamic parameter.

## Recovery of metal and IL, [BMIM][OCTSO$_4$]

After performing the extraction process, it is necessary to recover the IL to predict the repeated applicability in realistic treatment processes. Therefore, the IL-Pb (II) complex in the organic phase was collected separately from every parametric optimization step of the extraction process. Then, it was employed for stripping tests. For this purpose, a small amount of sodium sulfate as a stripping agent was dissolved in the lead-loaded organic phase. Then, the sample solution was well-mixed using an agitator for 10 min and then allowed to settle. In this way, the stripping agent strongly attracts the Pb (II) from IL, resulting in the formation of lead sulfate, which was collected at the bottom of the separating funnel. The lead sulfate solution was heated at 70°C for five minutes to get the powdered form, which is used as a positive active material for lead-acid batteries. The recovered IL was collected at the top layer and is represented in Fig. 9. The recovered IL was confirmed by the FTIR analysis. The lead present in the organic phase of the stripping solution was predicted by confirmatory tests.

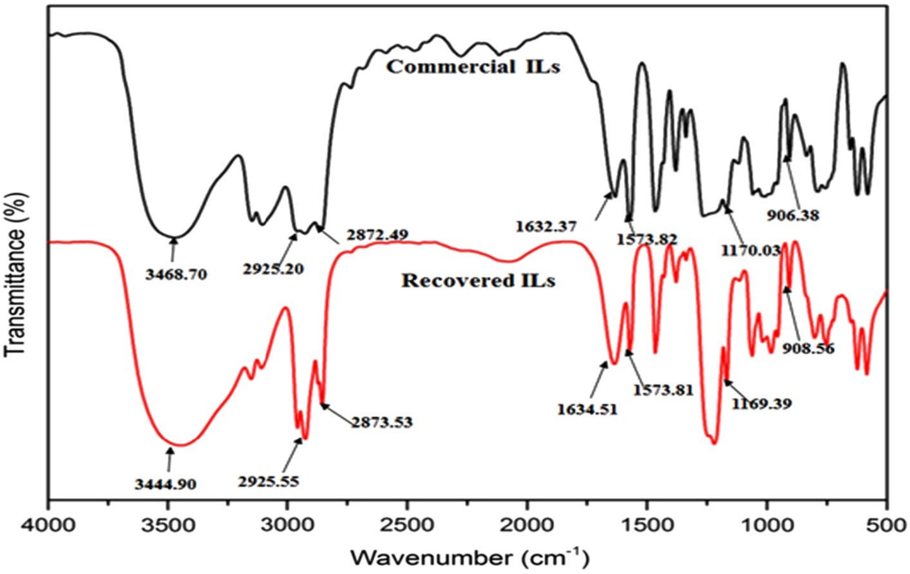
## FTIR analysis

The FTIR spectrum obtained for recovered IL was in accordance with the commercial IL. The results were almost similar to each other, which are reflected in Fig. 10. The band at 1573 cm$^{-1}$ is attributed to the vibration of C=N stretching, and the band at 1632 cm$^{-1}$ was assigned to C=C stretching vibration, which was the characteristic peaks of the imidazole group. Peaks at 2925 and 2870 cm$^{-1}$ were attributed to the vibrations of aliphatic

Microcrystalline form of
lead (II) sulfate

**Fig. 9** Recovered IL and metal salt after extraction

**Fig. 10** FTIR spectrum of commercial ILs and recovered IL



asymmetric and symmetric C–H stretching owing to the methyl groups. The peaks of wave numbers like 1169 and 908 $cm^{-1}$ were the asymmetric and symmetric vibrations that correspond to $SO_4$ (Dharaskar et al. 2013). Through the analysis, it was confirmed that the recovered liquid was IL, [BMIM][$OCTSO_4$].

## Confirmatory tests for lead

The presence of lead in the aqueous phase of the stripping solution was confirmed by laboratory tests. The first test was carried by the addition of a small amount of concentrated hydrochloric acid to the aqueous phase, and subsequently, the formation of a white precipitate was confirmed by the presence of lead. The second test was dissolving a little amount of potassium chromate to the aqueous phase, therefore resulting in the formation of yellow precipitate consisting of slightly soluble lead chromate, which is represented in Fig. 11.

## Extraction after recovery

To better examine the feasibility of the IL-based separation process, their reusability over-extraction efficiency on a metal ion is of great importance (Regel-Rosocka 2009). Therefore, the recovered IL was subjected to recycle process for predicting its extracting ability for lead (II) after recovery. To succeed in this target, extraction experiments were carried out using recovered IL at optimized parametric conditions (time—60mins, pH 5, feed concentration—10 ppm, amount of IL—2 g) for the separation of lead from aqueous solution. The recovered IL was reused for five cycles. The extraction efficiencies and amount of IL recovered were evaluated as represented in Table. 2. It was found that the extraction rates were slightly decreased from 97.65 to 95.85% with increasing consecutive cycles. This could be due to a small amount of IL getting lost during the recovery process in every cycle. From the obtained results, it was revealed that the IL, [BMIM][$OCTSO_4$] have a great tendency to remove $Pb^{2+}$ without lowering their efficiencies after the recovery.

**Table 2** Extraction rate on lead (II) using regenerated [BMIM][$OCTSO_4$]

| Cycles | Amount of IL (g) | Extraction efficiency (%) |
|---|---|---|
| 1 | 1.83 | 97.65 |
| 2 | 1.70 | 97.43 |
| 3 | 1.64 | 97.11 |
| 4 | 1.59 | 96.25 |
| 5 | 1.45 | 95.85 |

## Comparative study of [BMIM][$OCTSO_4$] with other ILs for lead extraction

The studied IL, [BMIM][$OCTSO_4$], was compared with ILs found in the literature for the extraction of lead from the aqueous solution, which is tabulated in Table 3. The extraction rate of Pb (II) was 97% using [BMIM][$OCTSO_4$], and it concurs with those found in the

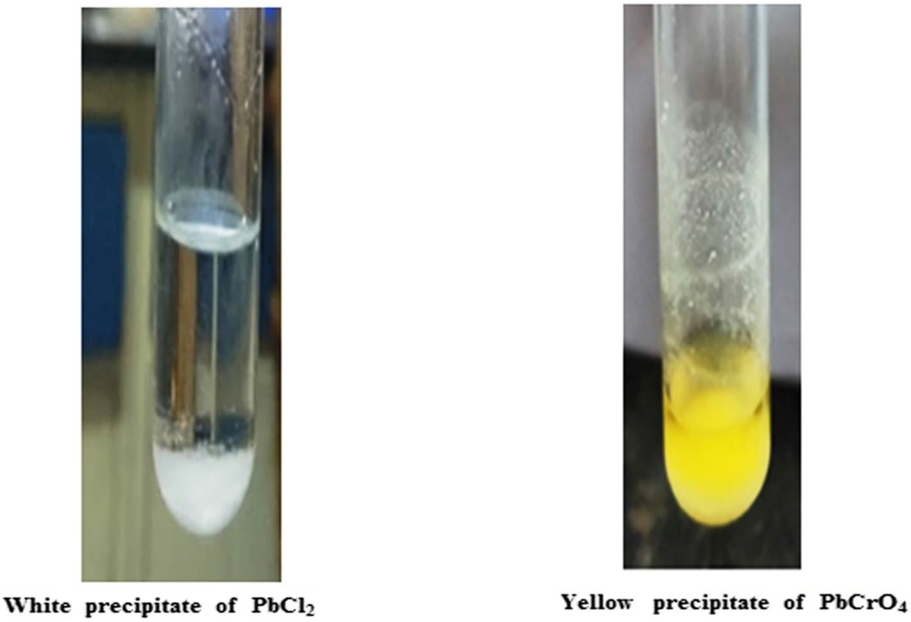


**Fig. 11** Confirmatory tests for lead

**Table 3** Comparison of maximum extraction rate of lead using various ILs

| S.no. | Name of the ionic liquids | Chelating agent/ligand | Concentration used (ppm) | Extraction efficiency (%) | Remarks | References |
|---|---|---|---|---|---|---|
| 1 | 1-Alkyl-3-ethylimidazolium hexafluorophosphate<br>1-Alkyl-3-ethylimidazolium bis {(triflurometyl) sulfonyl} imide<br>1-Butyl-3-methylimidazolium hexafluorophosphate (alkyl – C$_2$, C$_4$, C$_6$,) | Dithizone | 30 | 59.8–81 | Increase in alkyl chain length from ethyl to hexyl decreases the extraction efficiency<br>[EMIM][NTF$_2$] has better extractor for Pb$^{2+}$ removal than [EMIM][PF$_6$] | Domańska U, Rękawek (2009) |
| 2 | 1-Butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$] | 2-aminothio phenol | 5 | | Lead was extracted via proton transfer mechanism<br>Stripping of Pb$^{2+}$ was done by HNO$_3$ | Lertlapwasin et al. 20201010 |
| 3 | Tetrapropylammonium benzoate (ILA)<br>Tetrapropylammonium salicylate (ILB)<br>Tetrapropylammonium anthranilate (ILC)<br>Tetrabutylammonium benzoate (ILD)<br>Tetrabutylammonium salicylate (ILE)<br>Tetrabutylammonium anthranilate (ILF)<br>Tricaprylmethylammonium benzoate (ILG)<br>Tricaprylmethylammonium salicylate (ILH)<br>Tricaprylmethylammonium anthranilate (ILI) | – | – | 88.2 | Among nine water-immiscible ILs, ILC and ILH were found to be a better extractant for Pb removal<br>Proven to be an excellent extractor of heavy metals like Zn, Ni, Pb, Fe, and Cu from the tannery effluents | Rajendran et al. 2011 |
| 4 | Trihexylmethylammonium methyl carbonate<br>Trioctylmethylammonium methyl carbonate<br>Trihexylmethylammonium adipate<br>Trihexylmethylammonium salicylate<br>Trihexylmethylammonium azelate<br>Trioctylmethylammonium dodecanedioate<br>Trioctylmethylammonium oxalate<br>Trioctylmethylammonium azelate<br>Trioctylmethylammonium thiosalicylate | – | 25 | 93–96 | The maximum efficiency for lead extraction was obtained from the ILs 4,5,6,7 and 8 | Vergara et al. 2014 |

**Table 3** (continued)

| S.no. | Name of the ionic liquids | Chelating agent/ligand | Concentration used (ppm) | Extraction efficiency (%) | Remarks | References |
|---|---|---|---|---|---|---|
| 5 | Betaine tri(n-butyl) [2-ethoxy-2-oxoethyl] ammonium bis {(trifluromethyl) sulfonyl} imide [BuGBOEt][$NTF_2$] | –- | 2000 | 97 | [BuGBOEt][Dca] have a higher | Zhou et al. 2015 |
| 6 | Trioctylmethyl ammonium camphorate<br>Trioctylmethyl ammonium dodecanedioate | – | 50–100 | 76-81 | Water-immiscible halogen free ILs were synthesized for the extraction of Cd2+, Cu2+ and Pb2+<br>Addition of sodium salt to IL which reduces their weight loss<br>Recovery of ILs using acetone and ethylic alcohol | Valdes Vergara et al. 2014 |
| 7 | 1-butyl-3-methylimidazolium hexafluorophosphate | N-Salicylideneaniline (SA) | – | 70–90 | The % extraction was higher for Pb (II) using IL with SA than chloroform<br>The association constant for Pb (II) complex in ionic liquid was 2.08 x 103 | Fetouhi et al. 2016 |
| 8 | 1-(3-pyridyl)undecan-1-one oxime [3PC10]<br>3-[1-(hydroxyimine) undecyl]-1-propylpyridinium chloride [3PC10-PrCl]<br>3-[1-(hydroxyimine) undecyl]-1-propylpyridinium bromide [3PC10-PrBr] | Toluene | 5 | 70–75 | Among the three ILs, [3PC10-PrCl] has better extractor towards lead removal from aqueous solution<br>The extraction efficiency strongly dependent on chloride and extractant concentration and its structure | Wojciechowska et al. 2017 |
| 9 | 1-butyl-3-methylimidazolium octyl sulfate [BMIM][OCTSO4] | Dichloromethane | 10 | 97 | Water-miscible halogen free ILs was used for the extraction of lead<br>Recovery of IL and metal using sodium sulfate | This work |

literature. From the results in Table 3, it can be emanated that the halogen-free ILs gave the maximum removal rate with the efficiency ranging from 85 to 99% for lead extraction compared with halogenated ILs.

## Conclusion

Experimental investigations on the elimination of potentially toxic $Pb^{2+}$ pollutant from aqueous solution using halogen free-IL, [BMIM][$OCTSO_4$] by solvent extraction were studied. The results showed that the extraction efficiency was strongly dependent on the feed concentration, salting out effect and working temperature, respectively. Increasing the concentration of Pb (II) ion in aqueous solution, the extraction efficiency was decreased. Moreover, the effect of ionic strength significantly decreased the extraction rate on lead. Regarding the thermodynamic investigation, it was found that the extraction process was endothermic and spontaneous as confirmed by the positive value of $\Delta H^{\circ}$ (1.4686 kJ/mol) and negative value of $\Delta G^{\circ}$ (81.47 kJ/mol). Also, it suggests that the higher temperature exhibits a negative effect on the extraction efficiency. Sodium sulfate has proven to be a suitable agent for stripping off the lead in the form of lead sulfate from the IL phase. The regenerated IL was confirmed by FTIR analysis and thereafter reused five times successfully in back extraction process without the loss of separation efficiency. The proposed anion exchange mechanism of

Pb (II) from aqueous phase to hydrophilic IL in the presence of chelating agent was discussed. Overall, the extraction results evidence that the IL was an effective extractant for the removal of lead from aqueous solution with the removal efficiency of 97%. It also suggested that this process with this novel halogen-free solvent can be recommended for the tertiary treatment of industrial effluents, which has a significant positive effect on the environment. Further work regarding this research is in progress.

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## Compliance with ethical standards

**Conflict of interest** None.

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