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Extraction of Pb(II) from water samples by ionic liquid-modified silica sorbents

Sarah Saleem[a], Ahmad Nauman Shah Saqib[a], Adnan Mujahid[b,*], Muhammad Hanif[a], Ghulam Mustafa[c], Tariq Mahmood[a], Amir Waseem[d], Abdur Rahman Khan[a,*]

[a]*Department of Chemistry, COSMATS Institute of Information Technology, Abbottabad 22060, Pakistan, Tel. +92 992 383591; Fax: +92 992 383441; emails: sarahsaleem@ciitlahore.edu.pk (S. Saleem), ahmadnauman@live.com (A.N.S. Saqib), muhammadhanif@ciit.net.pk (M. Hanif), mahmood@ciit.net.pk (T. Mahmood), khanar@ciit.net.pk (A.R. Khan)*

[b]*Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan, Tel. +92 42 99230463; Fax: +92 42 99230998; email: adnanmujahid.chem@pu.edu.pk*

[c]*Department of Environmental Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan, Tel. +92 51 90644138; email: ghulam.mustafa@univie.ac.at*

[d]*Department of Chemistry, Quaid-i-Azam University, Islambad 45320, Pakistan, Tel. +92 051 90642039; email: amir@qau.edu.pk*

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ABSTRACT

Removal of toxic heavy metals from water matrices is an important challenge in water pollution. In this study, a solid-phase extraction method based on physical adsorption is reported for the removal of Pb(II). Two modified silica sorbents were developed by direct immobilization of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C4) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C6), respectively, on silica surface. Surface modification and characterization of adsorbents were confirmed by FTIR and SEM. Both the sorbents showed enhanced sorption capacity for Pb(II), however, sorbent loaded with 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide showed relatively increased removal efficiency when compared to silica loaded with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide. Batch studies were performed to optimize different variables that influence adsorption process i.e. effect of sorbent dosage, pH, time of contact, sorbate concentration, and temperature. Langmuir, Freundlich, and Temkin isotherms were applied to study adsorption phenomenon.

Keywords: Adsorption; Ionic liquids; Silica; ICP-OES; Wastewater; Lead removal

1. Introduction

Water pollution is one of the major environmental issues with great concern across the globe. Among the many causes of water pollution, the major contribution is due to the presence of heavy metal ions. Human activities, for example, mining, plating, glass making, ceramics, and battery manufacturing lead to substantial increase in toxic metal contamination in water causing a persistent risk to the biosphere [1]. The non-planned progress, inefficient transformations, and non-sustainable processes have polluted the soils, water, and air drastically. As a result of the growing economy, a lot of wastewater is disposed to the environment without any prior treatment. Therefore, its

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*Corresponding authors.

treatment is necessary to lower the hazards and especially to minimize the concentration of heavy metals in water samples [2]. There are ongoing attempts to sought more active, selective, and environmentally benign protocols for wastewater treatment [3]. One of such practices is the use of environment friendly ionic liquids (ILs) known as green solvents [4].

ILs are organic salts which are made up of an equal number of organic cations and different anions to form an ionic media. In contrast to normal salts, which are solid at room temperature, these salts are liquid at room temperature. The composition and associated properties of ILs depend on the cation and anion combination [5]. One of the unique characteristics of ILs is their non-detectable vapor pressure which marks them as environment friendly solvents in contrast to volatile organic compounds [6–9]. The physicochemical properties of ILs e.g. melting temperature, density, viscosity, and solubility in solvents are readily optimized by simple changes in the nature of cation or anion. The incorporation of additional functionality through a side-chain appended to the cation is a common design theme [6–9]. By increasing the length of alkyl chain, the hydrophobicity of an ILs increases [10]. Hydrophilic cations are difficult to remove from wastewater using conventional solvents through liquid–liquid extraction, hence hydrophobic ILs are efficient solvents for this purpose [11].

Furthermore, ILs has been investigated for metal detection, separation, speciation, determination, and extraction studies [12–21]. Tricaprylmethylammonium chloride commercially known as Aliquat-336 is an important example of room temperature ionic liquid and has been used as a supported liquid membrane for the abatement of chromium [22]. Being a novel solvent, template, and a diffusion medium for extractant, ILs could be incorporated in silica matrix retaining their chemical activity [23]. Chemically modified silica is an attractive sorbent for the removal of metal ions because it does not swell or shrink as compared to typical polymer resins [24]. Direct interaction of chelating agents towards silica surface is difficult due to its relative inertness. However, surface activation or modification facilitates their direct bonding [25,26]. It actually activates the silanol groups (Si-OH) on the surface of silica which in turn act as precursors for further immobilization of organic ligands. Moreover, the modified silica has a good thermal stability and high-metal removal efficiency [27]. By loading of organic functional groups on silica surface, its organophillic properties are increased, which in turn increases the uptake of metal and improves the adsorption efficiency of silica [28]. In the present study, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C4) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C6)-loaded silica were utilized for Pb(II) extraction from aqueous solutions and compared their relative efficiencies for Pb(II) extraction through inductively coupled plasma-optical emission spectrometer (ICP-OES).

2. Experimental

2.1. Materials

ILs, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C4), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C6), and silica gel (particle size of 40–60 μm) were purchased from Merck. Sulfuric acid, hydrochloric acid, sodium acetate trihydrate, lead acetate trihydrate, and all the other chemicals of analytical grade were purchased from Sigma Aldrich.

Deionized water was used for the preparation of metal ion solutions. Buffer solutions having different pH values i.e.; 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 were prepared from 1.0 M hydrochloric acid and 1.0 M sodium acetate trihydrate solution. The pH meter (Hanna TH 211) was used for the adjustment of different pH values.

2.2. Instrumentation

Shimadzu FTIR 8400S double beam spectrometer was used to measure the FTIR of the adsorbents prepared for the removal of heavy metals from aqueous media. ICP-OES (Perkin Elmer AAnalyst 2100) was used for the determination of heavy metal ions concentration. Membrane filtration assembly was used for the filtration of acid-activated silica and that was loaded by ionic liquid. Scanning electron micrographs (Hitachi SU1500) were taken for both activated silica and ILs-loaded silica particles to examine the morphological changes on adsorbents surface. The micrographs were taken at different resolutions from 1 to 500X.

2.3. Preparation of sorbents

2.3.1. Acid activation of silica

Silica is not suitable for direct anchoring of ILs therefore, it was first activated. For this purpose, 20 g of silica gel particles mixed with 100 mL of concentrated sulfuric acid in a round-bottom flask and then stirred for 12 h. The activated silica powder was then subjected to washing with deionized water until it was acid free and dried in an oven at 100˚C for 10 h.

2.3.2. Adsorption of ionic liquid on activated silica

A suspension was obtained by the addition of activated silica powder in toluene and then IL was added to this suspension. The reaction mixture was subjected to stirring at room temperature for 6 h. The suspension was filtered and washed several times with ethanol and diethyl ether finally; it was dried in oven at 60˚C for 6 h. The same procedure was adopted for other ionic liquid.

2.4. Metal ion extraction

Both adsorbents were exposed to metal ion solutions and after an optimum contact time i.e. 30 and 60 min, the filtrate was analyzed by ICP-OES for the determination of residual metal ions concentration. Effects of various parameters that influence adsorption process such as adsorbent dose, contact time, pH, and temperature, and adsorbate concentration were investigated to optimize conditions.

The percent of adsorption by the adsorbent was calculated using the following Eq. (1).

$$\%\,\text{Sorption} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i and C_e are the initial and final concentrations, respectively, of metal ions expressed in $\mu g\,L^{-1}$.

2.4.1. Effect of adsorbent dosage

In order to investigate the effect of adsorbent dosage, different amounts of C6-loaded silica sorbent ranging from 5 to 50 mg were added in separate conical flasks. Each flask had 10 mL of Pb(II) solution with a concentration of 1,000 $\mu g\,L^{-1}$. Flasks were agitated on an orbital shaker for 30 min. The solutions were filtered and filtrates were subjected to analysis. The concentrations of sample solutions were calculated from calibration line obtained by plotting the emission against concentration of standard solutions. Same procedure was repeated for other adsorbent i.e. C4-loaded silica. ICP-OES was used for the concentration determination of Pb(II) at a wavelength 220.353 nm. The calibration of the instrument was carried out by standard methods.

2.4.2. Effect of contact time

In 10 mL Pb(II) solution of concentration 1000 $\mu g\,L^{-1}$, 30 mg of powdered C6- and C4-loaded silica sorbents were added separately, and agitated on the orbital shaker for different time intervals i.e. from 15 to 90 min. The effect of time interval on Pb(II) removal efficiency was monitored by respective adsorbents.

2.4.3. Effect of pH

For determining pH effect, 30 mg of C6- and C4-loaded silica sorbents were taken in different conical flasks. A 5 mL Pb(II) test solution of 1,000 $\mu g\,L^{-1}$ was then added, followed by addition of 5 mL buffer solutions of pH 1 to 7 and shaking it for 60 min. Maximum removal efficiency of Pb(II) was determined at respective pH by ICP-OES.

2.4.4. Effect of temperature

In order to find optimal temperature, 30 mg of C6- and C4-loaded silica sorbents were added to 10 mL Pb(II) solution (1,000 $\mu g\,L^{-1}$, pH 6) flasks separately. These flasks were shaken for 60 min, at different temperatures i.e. 10–50˚C. These samples were then filtered and filtrate was analyzed to determine the effect of temperature on extraction efficiency.

2.4.5. Effect of adsorbate concentration

Pb(II) solutions of different concentrations i.e. 500, 750, 1,000, 1,250, and 1,500 $\mu g\,L^{-1}$ were prepared. Ten milliliter of these solutions (pH 6), was added to 30 mg of C4- and C6-loaded silica respectively. The mixture was then shaken on an orbital shaker for 60 min before subjecting the samples to filtration. The filtrate was analyzed to determine the amount of Pb(II) extracted by the sorbents.

3. Results and discussion

3.1. Characterization by FTIR and SEM

Surface modification of silica particles was characterized by FTIR and SEM techniques. FTIR spectra were measured for pure silica as well as silica loaded with 1-hexyl-3-methylimidazolium bis(trifouro methyl sulfonyl)imide and 1-butyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imides. A comparison of functional groups from pure silica and IL-modified silica is highlighted in Table 1. The shift in absorption peaks indicated the modification of functional groups on surface of silica particles. For instance, significant change occurs at Si-OH functional group as the absorption is shifted from 3,450 to 3,315 cm^{-1}. The FTIR peaks such as (C–H stretching) at 2,974 cm^{-1}, (C=N stretching) at 1,629 cm^{-1}, (C=C stretching) at

Table 1
Comparison of functional groups in FTIR analysis of ILs-loaded and unloaded silica sorbents

Functional groups	Si–O-Si	S=O	C–F	C–N	C=C	C=N	C–H	Si-OH
Pure silica (cm^{-1})	822	–	–	–	–	–	–	3,450
IL-modified silica (cm^{-1})	800	1,070–1,100	1,100–1,200	1,342	1,463	1,629	2,974	3,315

1,463 cm^{-1}, (C–N stretching) at 1,342 cm^{-1}, (C–F stretching) at 1,100–1,200 cm^{-1}, and (S=O stretching) at 1,070–1,100 cm^{-1} clearly demonstrate that the silica surface is successfully modified by ILs.

The comparative study of scanning electron micrographs of acid-activated silica was shown in (Fig. 1(a)), and C4- and C6-loaded silica particles were shown in (Figs. 1(b) and 1(c), respectively. These images highlight an increase in the surface roughness of silica particles after loading of ILs. The side images of Figs. 1(a)–1(c), give a better view to compare their surface modifications. Some macro channels are also prominent on the surface of silica which may be responsible for the increased adsorption of metal ions. It can be stated that by loading IL on to activated silica particles led to increase in surface area and that in turn could increase the metal uptake capacity of the adsorbents [29].

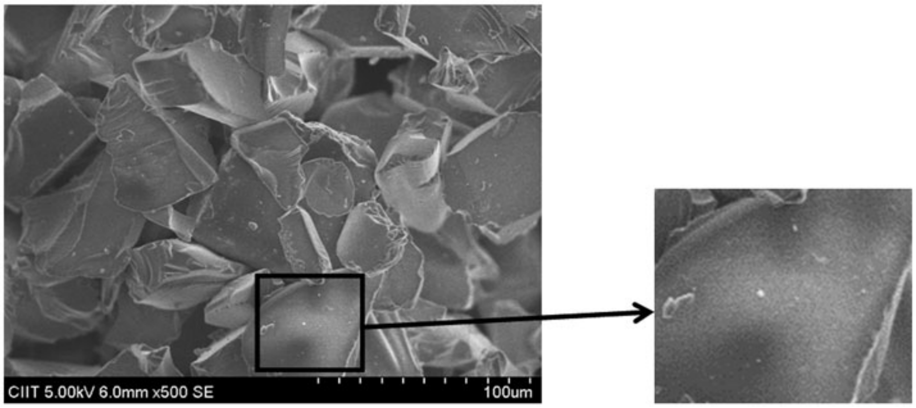

Fig. 1(a). SEM of acid-activated silica.

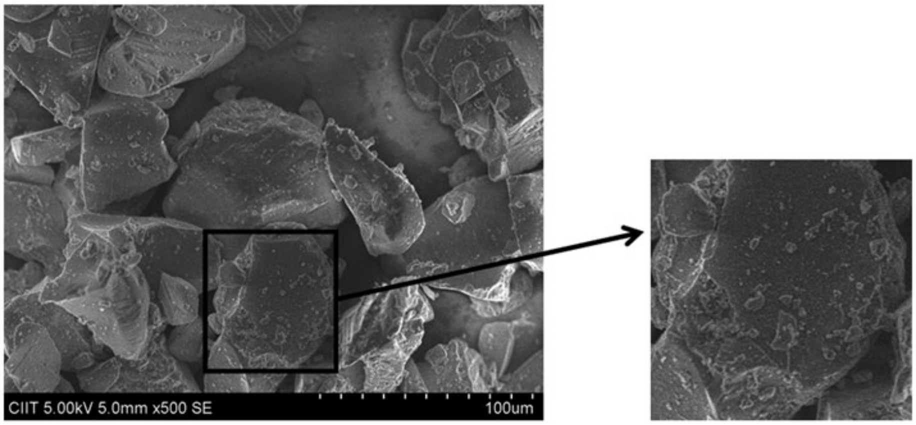

Fig. 1(b). SEM of C4 sorbent.

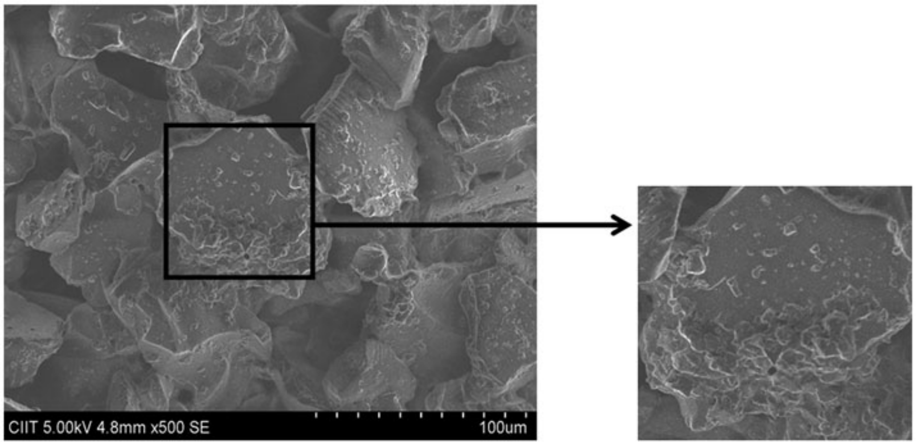

Fig. 1(c). SEM of C4 sorbent.

3.2. *Effect of adsorbent dose*

The study revealed that the adsorbent dosage has a direct effect on Pb(II) removal efficiency since the removal of Pb(II) increases with an increase in the mass of adsorbent. Maximum removal efficiency of 91 and 95% of Pb(II) was achieved by C6-loaded silica and C4-loaded silica sorbent, respectively, at an adsorbent dose of 30 mg (Fig. 2(a)). Further increase in the amount of adsorbent did not result in considerable increase in the removal efficiency. This could be explained in a way that after a certain concentration of adsorbent, the quantity of adsorbed and free metal ions remains constant in the solution.

The adsorption capacity is highly dependent on the surface area of adsorbent as the adsorption increases with an increase in surface area of adsorbent. The increase in surface area of adsorbent can be either achieved by decreasing the particle size or by increasing the amount of adsorbent material. Therefore, the amount of adsorbent was increased keeping the particle size same which resulted in an increase in the removal efficiency, due to increase in the number of available active sites of the adsorbent and increase in the surface area as well. While comparing the two different ILs, C4 is less hydrophobic as compare to C6, therefore, an increase in the hydrophobicity of the cation-like 1-hexyl-3-methylimidazolium decreases the extraction efficiency of the adsorbent. It is attributed to the lower probability of transfer of hydrophobic cation from IL to aqueous phase.

3.3. *Effect of contact time*

The maximum adsorption was observed for contact times of 30 and 60 min for C4- and C6-modified silica sorbents, respectively. Further increase in contact time had no pronounced effect on the removal efficiency as indicated in Fig. 2(b). This rapid adsorption process indicates the availability of large number of available active sites and high surface area. High metal uptake and rapid equilibrium were established for C4 adsorbent when compared to C6 adsorbent. This could be explained that C4 is comparatively less hydrophobic and can interact more rapidly thus, takes much less time in developing equilibrium. However, C6 is more hydrophobic and requires more time for interaction with metal ions.

3.4. *Effect of pH*

The pH of solution plays a key role in the removal of metal ions through adsorption as it affects the active sites and charge distribution on the adsorbent surface, solubility characteristics, ionization, and most importantly the speciation of adsorbate in the reaction solution [13,30]. Adsorption capacity for both the adsorbents increased with an increase in the pH with maximum adsorption efficiency observed at pH 6 for both adsorbents as shown in Fig. 2(c), however, C4 showed higher metal uptake affinity when compared to C6. At low pH values, the extraction efficiency of both modified sorbents is low which could be due to the protonation of functional groups containing lone pairs. Batch studies were performed in the pH range from pH 1 to 7. Further, higher pH values were not tested due to possible precipitation of Pb(II) hydroxide at higher pH values. In general, the large Pb(II) extraction capacity by modified silica adsorbents revealed the direct extraction capability of immobilized ILs on silica particles.

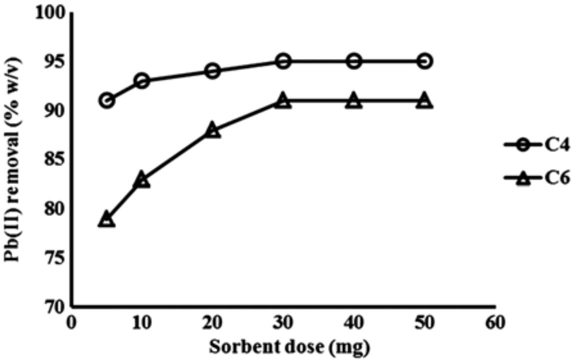

Fig. 2(a). Effect of adsorbent dosage of C4 and C6 sorbents on Pb(II) extraction.

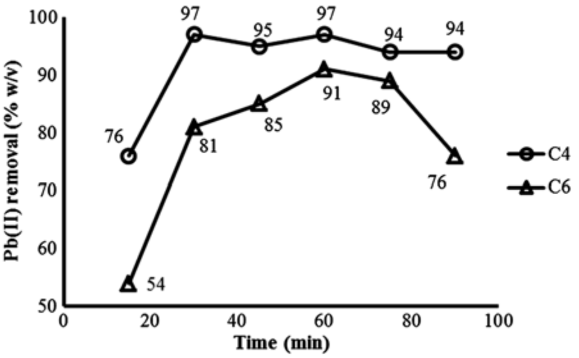

Fig. 2(b). Effect of contact time on adsorption of Pb(II) by C4 and C6 sorbents.

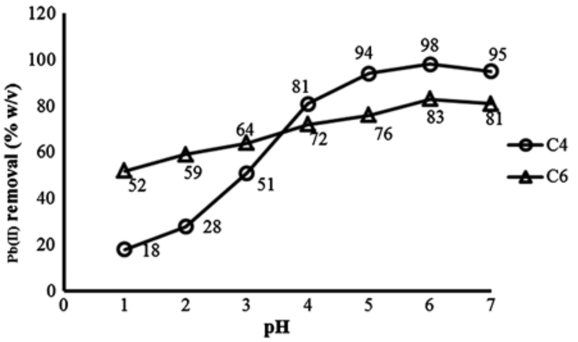

Fig. 2(c). Effect of pH on adsorption of Pb(II) by C4 and C6 sorbents.

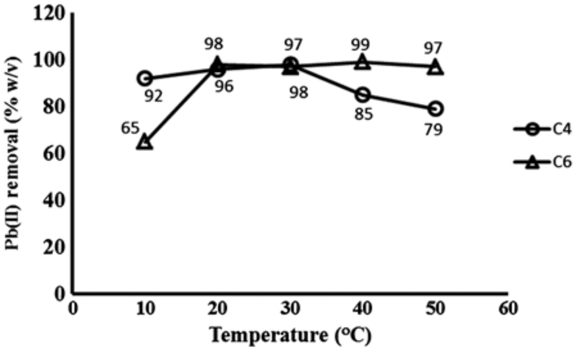

Fig. 2(d). Effect of temperature on adsorption of Pb(II) by C4 and C6 sorbents.

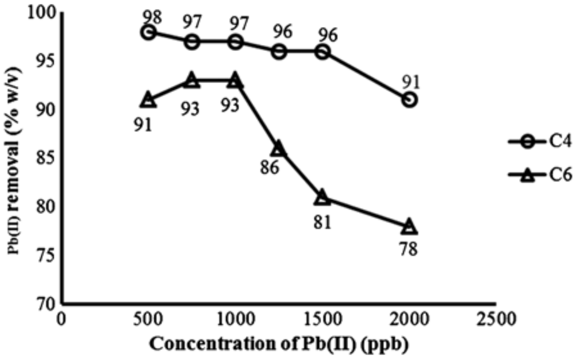

Fig. 2(e). Effect of adsorbate concentration on Pb(II) extraction by C4 and C6 sorbents.

The extraction of Pb(II) by C4- and C6-loaded silica particles could be attributed to the different factors. For example, one is the direct interaction of metal ions with ILs; the second possibility could be an ion-exchange relationship between surface functional groups and metal ions [30]. The functional groups of ILs containing lone pair from oxygen and nitrogen develop strong electrostatic interactions with sorbate ions which result in significant metal ions adsorption.

3.5. Effect of temperature

The adsorption efficiency is greatly affected by variation in temperature. The optimum temperature range was found to be 20–30˚C for C4 sorbent and 20–40˚C for C6 sorbent. The maximum uptake capacity for C4 and C6 adsorbents was observed at 30 and 40˚C, respectively, as shown in Fig. 2(d). Both the sorbents showed great affinity towards the Pb(II) ions at room temperature and no adjustment in temperature is required. Binding forces of adsorbate with the adsorbent may become weak with an increase in temperature above 50˚C therefore; an increase in temperature above 50˚C does not favor the adsorption process for either of the adsorbent.

3.6. Effect of adsorbate concentration

The removal efficiency was more than 90% for both C4 and C6 sorbents up to a concentration of 1,000 μg L^{-1}. Efficiency of C4 remains above 90% even though the Pb(II) ion concentration increased up to 2,000 μg L^{-1}, however, in the case of C6, with an increase in sorbate concentration above 1,000 μg L^{-1}, the Pb(II) extraction efficiency decreases continuously down to 78% at 2,000 μg L^{-1}. The results are displayed in Fig. 2(e). This indicates that binding sites of C6 are much earlier saturated in contrast to C4 thus, leading to reduced efficiency at higher concentration of metal ions.

3.7. Adsorption isotherms

Adsorption isotherms are the mathematical models used for adsorption studies and these isotherms give information about the relative metal ion concentration between liquid phase and adsorbent, amount of sorbate adsorbed by the sorbent, and mechanism of interaction among the adsorbate species and adsorbent [31,32]. In this study, Langmuir, Freundlich, and Temkin isotherms were applied to the experimental data and the results are summarized in Figs. 3(a)–3(f). In specific volume of known concentration of metal ion solution, various amounts of sorbents were added and the amount of metal ions extracted was calculated. The same data were used for Langmuir, Freundlich, and Temkin isotherms.

Langmuir isotherm model is based on the assumption that number of active sites is fixed in a monolayer and only one ion can be adsorbed by each active site and the adsorbed ions have no interaction with each other [33]. The Langmuir isotherm is given by Eq. (2).

$$\frac{1}{q} = \frac{1}{q_m . k_{\text{ads}}} \left(\frac{1}{C}\right) + \frac{1}{q_m} \qquad (2)$$

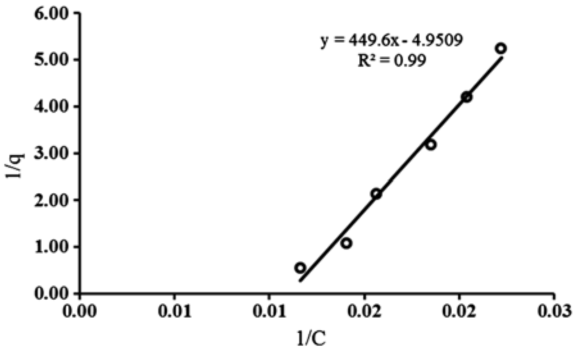

Fig. 3(a). Langmuir isotherm plot of C4 sorbent.

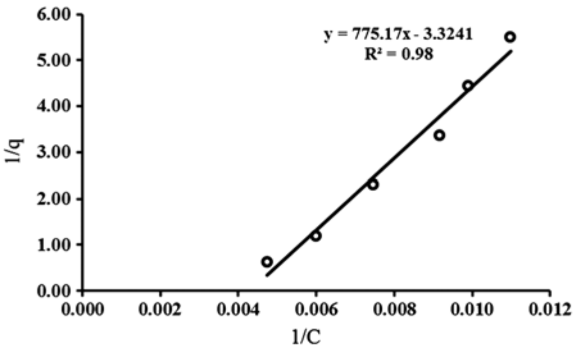

Fig. 3(b). Langmuir isotherm plot of C6 sorbent.

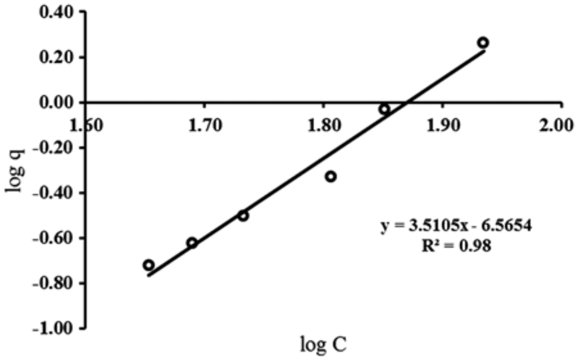

Fig. 3(c). Freundlich isotherm plot of C4 sorbent.

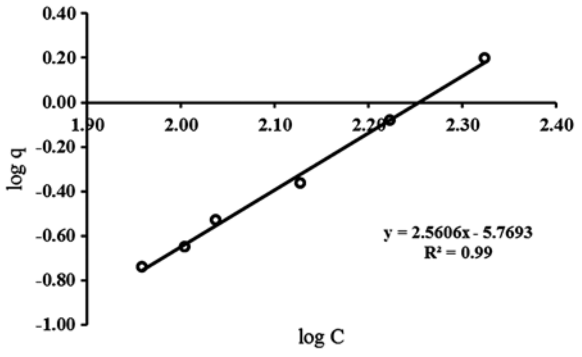

Fig. 3(d). Freundlich isotherm plot of C6 sorbent.

where q and q_m are equilibrium and monolayer sorption capacities of the sorbents (μg mg^{-1}), respectively, C is equilibrium concentration (mass per unit volume) (mol L^{-1}), and k_{ads} is the energy constant related to heat of adsorption.

A plot of $1/q$ against $1/C$ (C4 sorbent) produced a straight line with an r^2 value of 0.99. Slope ($1/q_m$) of the plot was found to be 449.6 and an intercept ($1/q_m k_{ads}$) value of −4.9. While a plot of $1/q$ against

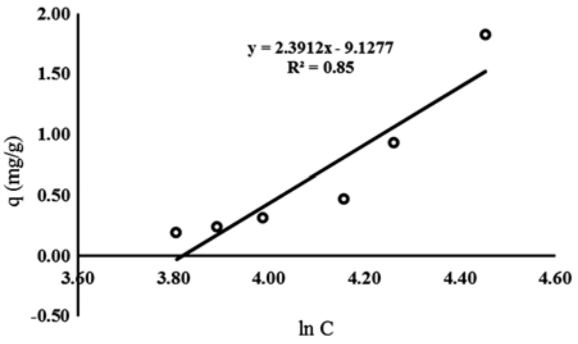

Fig. 3(e). Temkin isotherm plot of C4 sorbent.

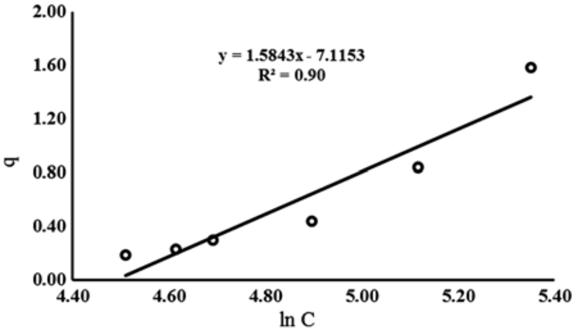

Fig. 3(f). Temkin isotherm plot of C6 sorbent.

$1/C$ for C6 sorbent produced a Langmuir plot with a straight line and an r^2 value of 0.98. Slope ($1/q_m$) of the plot was 775.1 and an intercept ($1/q_m k_{ads}$) value of −3.32 (Table 2).

The Freundlich isotherm model assumes that active sites on the adsorbent have different energies and behave differently for different adsorbents [32]. This isotherm model can be derived from Langmuir model. The mathematical expression of Freundlich isotherm is expressed in Eq. (3).

$$q = KC^{1/n} \tag{3}$$

where K is Freundlich constant/capacity measurement of adsorbent and n is the indicator of adsorption capacity. If $n < 1$, it indicates that there is strong interaction between metal and adsorbate. All active sites on the adsorbent surface have the same affinity for the adsorbate and results in a linear isotherm. However, the value of $n > 1$ shows that with an increase in adsorption density, the affinity for adsorbate decreases [32]. The linearized form of the equation can be written as follows.

Table 2
Adsorption isotherm data

	Linear regression coefficient (r^2) values		
	Langmuir Isotherm	Freundlich Isotherm	Temkin Isotherm
C4	0.99	0.98	0.85
C6	0.98	0.99	0.90

$$\log q = \log k + \frac{1}{n}\log C \tag{4}$$

With C4 sorbent, Freundlich isotherm plot with a linear regression coefficient (r^2) value of 0.98 was obtained by plotting log q against log C. Slope ($1/n$) of the plot was found to be 3.5 and an intercept (*log k*) value of −6.5. While in C6, a plot of log q against log C produced a straight line with r^2 value of 0.99, slope ($1/n$) of 2.56, and an intercept (log k) value of −5.76 (Table 2).

Temkin isotherm is expressed in the following form in Eq. (5).

$$q_e = B\,\ln(AC_e) \tag{5}$$

where B and A are Temkin isotherm constants related to capacity and intensity of adsorption. According to Temkin isotherm, active sites on the adsorbent surface are energetically different, and more energetic active sites are preferentially occupied by the adsorbate. Plot of ln C vs. q (mg g^{-1}) for C4 produced a straight line with an r^2 value of 0.85. Slope (b) of the plot was found to be 2.39 and an intercept (a) value of −9.12. In case of C6 sorbent, an r^2 value of 0.90 was obtained by plotting ln C and q (mg g^{-1}), with a Slope (b) of 1.584 and an intercept (a) value of −7.11 (Table 2).

The regression coefficient values revealed that both the adsorbents followed Langmuir and Freundlich isotherms but Temkin isotherm was not strictly followed and thus it can be said that most of the sorption is not through chemical attachment. The physical adsorption has pronounced share in overall sorption process [34]. Therefore, by sorption model studies it is evident that Pb(II) ions are physically adsorbed onto the surface of ILs-immobilized silica particles and there were different active sites on the adsorbent surface that have different affinities for different adsorbate.

4. Conclusion

Green chemistry introduces a new approach towards developing methodologies for industrial and chemical processes. In this study, the ability of two room temperature ILs to adsorb on modified acid-activated silica was monitored. Both the sorbents showed an excellent adsorption capacity for Pb(II), however, C4-modified silica sorbent exhibited a faster and higher efficiency in Pb(II) removal when compare to C6-modified sorbent. They are suitable for metal ions extraction from aqueous solutions at various pH values. These adsorbents do not require temperature modification as they showed an efficient adsorption capacity even at room temperature. Both sorbents followed Langmuir and Freundlich isotherms, however, Temkin isotherm was not strictly obeyed which suggests that adsorption of Pb(II) by IL-modified silica sorbents is a more physical phenomena. In general, the straightforward synthesis, excellent removal efficiency for metal ions, and their environment friendly character make these materials highly suitable in wastewater treatment.

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