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Adsorption behavior of lead onto a new class of functionalized silica gel



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Abstract In this study the surface of silica gel was functionalized with 2-thiophenecarbonyl, 2-furonyl and L-proline. The synthesized materials were characterized by fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM) with energy dispersive X-ray analyzer (EDX). Batch adsorption studies were carried out to analyze the adsorption of the lead ion from aqueous solution. The factors influencing % adsorption of Pb(II) onto the silica gel and functionalized silica gel such as initial pH value of the Pb(II) ion solution, adsorbent dose, initial Pb(II) ion concentration, contact time and temperature were investigated. Langmuir and Freundlich isotherm models were used to determine the isotherm parameters associated with the adsorption process. Kinetic data were analyzed considering pseudo-first order, pseudo-second order and intraparticle diffusion approaches. The latter two mechanisms seem to be significant in the rate-controlling step. Negative values of Gibb's free energy change (ΔG°) showed that the adsorption was feasible and spontaneous and negative values of enthalpy change (ΔH°) confirmed exothermic adsorption.

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1. Introduction

The release of heavy metals from many industrial processes leads to an increase in the concentration of heavy metals in the aquatic system and have created major global concern

because of their high toxicity. In fact, the presence of heavy metals in water supplies may cause serious environmental problems in view of human health and other living beings. Among the different heavy metals, lead is one of the common and most toxic pollutants released into the natural waters from various industrial activities such as metal plating, oil refining and battery manufacturing. Lead has been found to be acute toxic to human beings when present in high amounts (e.g. > 15 µg/L in drinking water) (Inglezakis et al., 2007). Lead can cause acute adverse effects on the liver, kidney and reproductive system, basic cellular processes and brain functions. Hence it is necessary to remove lead from water at least below the regulatory level.

Various processes have been proposed for the removal of lead from aqueous solution. The important ones are adsorp-

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tion (Sari et al., 2007a), ion exchange (Dabrowski et al., 2004), photocatalysis (Murruni et al., 2007), floatation, hyper-filtration, chemical precipitation, reverse osmosis etc. Among these the adsorption process is found to be quite suitable, cheap and effective for the removal of lead from aqueous solution. A number of adsorbents including clay (Abu-Eishah, 2008), zeolite (Nah et al., 2006), biosorbent (Akar and Tunali, 2006; Gundogdua et al., 2009; Sari et al., 2007b), agricultural wastes (Ayyappan et al., 2005), organic/inorganic composite (Solener et al., 2008; Tran et al., 2010) and alumina (Mahmoud et al., 2010) have been tried for the removal of lead from the aquatic system. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheaper and easily available adsorbents with high adsorption capacities.

Availability of silica is in plenty and its high potential toward the adsorption of organic and inorganic compounds has attracted the attention of many researchers to use it for the removal of pollutants. The presence of -OH groups on the surface of the silica gel (SG) create sites for adsorption of Pb(II). In order to get high adsorption capacity, a new class of functionalized silica gel was synthesised by loading it with 2-thiophenecarbonyl, 2-furoyl and L-proline. The adsorption properties of the activated silica gel (ASG), 2-thiophenecarbonyl loaded silica gel (TL SG), 2-furoyl loaded silica gel (FL SG) and L-proline loaded silica gel (PL SG) were investigated with lead as the target pollutant from aqueous solution as a function of pH, adsorbent dose, initial Pb(II) ion concentration, contact time and temperature. The adsorption capacity of all the adsorbents was compared with each other for getting a better adsorbent in order to get high adsorption efficiency for the removal.

2. Materials and methods

2.1. Adsorbent

Silica gel G (SG) was obtained from Sigma Aldrich Chemicals Pvt. Ltd., India. Activation of SG was done by adding 100 mL of 6 M HCl in 20 g of SG and the mixture was allowed to reflux with continuous stirring for 4 h. The resultant material was filtered and washed with double distilled water until the pH became 7 and dried at 150 °C for 5 h.

The thiophenecarbonyl loaded silica gel (TL SG) was prepared by mixing 3 mmol of 2-thiophenecarbonyl chloride with 1 g of activated silica gel (ASG) and the mixture was stirred vigorously for 5 h at reflux temperature. The resulting material was washed with toluene to remove unattached thiophenecarbonyl chloride and finally dried in a hot air oven at 80 °C. The 2-furoyl loaded silica gel (FL SG) was synthesized using a similar method given for the synthesis of TL SG. L-Proline loaded silica gel (PL SG) was prepared by mixing 3 mmol of L-proline solution with 1 g of activated silica gel (ASG) and the mixture was stirred vigorously for 30 min at 50 °C. The resulting slurry was poured onto a stainless steel tray and was kept at 50 °C for 24 h in forced air oven followed by an increase in temperature up to 120 °C, where thermochemical reaction between silica gel and L-proline takes place. After cooling, the material was washed with double distilled water and dried in a hot air oven at 80 °C. The resulting materials (ASG, TL SG, FL SG

and PL SG) were kept in a desiccator for use as an adsorbent.

2.2. Adsorption experiment

Batch adsorption experiments were carried out to determine the effects of pH, adsorbent dose, initial Pb(II) ion concentration, contact time and temperature by varying the parameter under study and keeping other parameters constant.

Stock solution (1000 mg/L) of Pb(II) was prepared by dissolving the requisite amount of Pb(NO₃)₂ (Merck) into double distilled water. It was subsequently diluted to different concentrations (5, 10, 15, 20 and 25 mg/L) and the pH of Pb(II) ion solutions were maintained by adding 0.1 M HNO₃ or 0.1 M NaOH. In each experiment a pre-weighed amount of adsorbent was added to 50 mL of Pb(II) ion solution in 150 mL conical flasks and stirred on a magnetic stirrer (Remi) at the speed of 200 rpm. The adsorption was monitored by determining the concentration of Pb(II) in solution by an atomic absorption spectrophotometer (ECIL 4141).

Percentage of Pb(II) adsorption and quantity of Pb(II) adsorbed on the adsorbent at the time of equilibrium (q_e) was calculated using Eqs. (1) and (2) respectively.

$$\% \text{Pb(II) adsorption} = 100(C_0 - C_e)/C_0 \quad (1)$$

$$q_e = (C_0 - C_e)V/W \quad (2)$$

where C_0 and C_e are the initial and the equilibrium concentrations (mg/L) of Pb(II) in solution, respectively. q_e is quantity of Pb(II) adsorbed on the adsorbent at the time of equilibrium (mg/g), V is volume (L) of solution and W is mass of adsorbent (g) taken for the experiment.

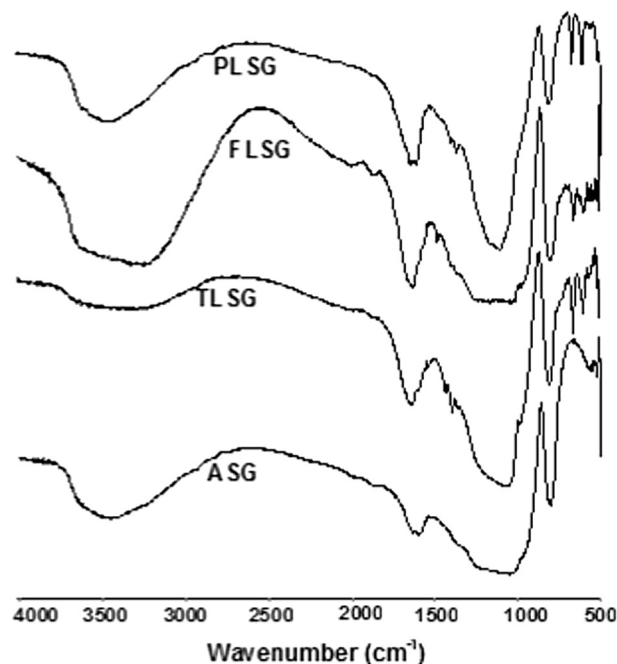


Figure 1 FT-IR spectra of ASG, TL SG, FL SG and PL SG.

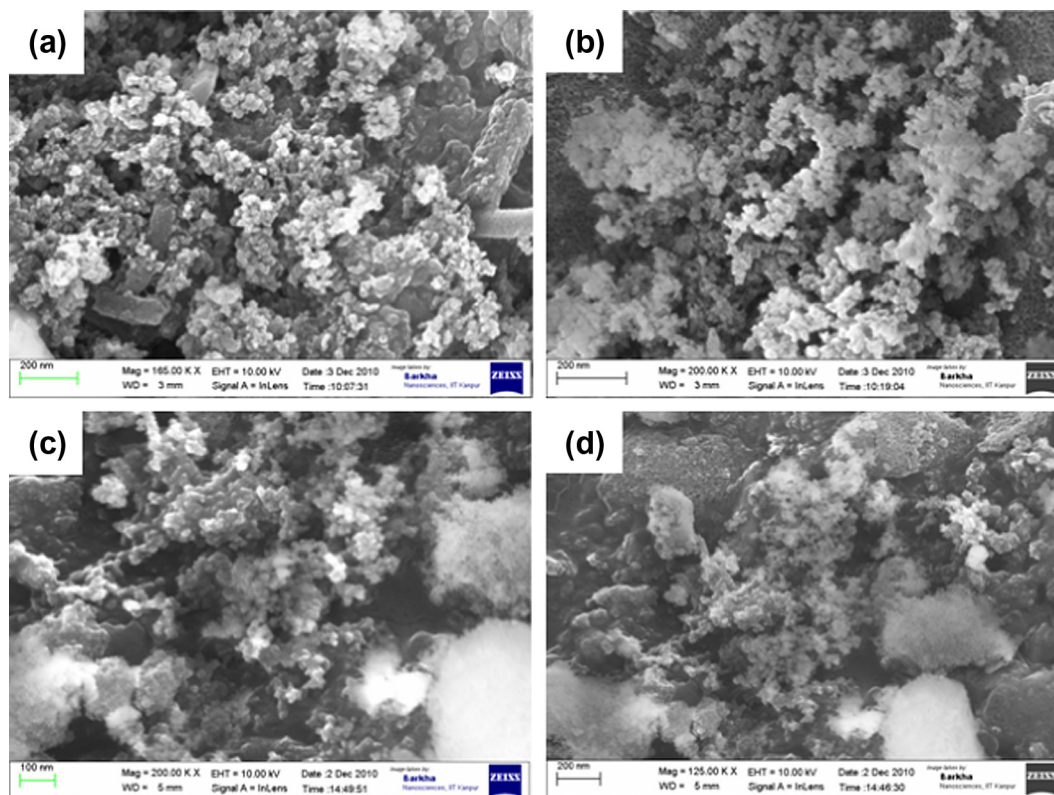


Figure 2 SEM images of ASG (a), TLSG (b), FLSG (c) and PLSG (d).

3. Results and discussion

3.1. Characterization of adsorbents

The FT-IR spectra of ASG, TLSG, FLSG and PLSG were recorded by FTLA2000 spectrophotometer using KBr disc method and are shown in Fig. 1. FT-IR spectra of ASG showed a band at 1027 cm^{-1} due to asymmetric stretching of Si–O–Si and corresponding symmetric stretching was observed at 805 cm^{-1} . The Si–O–Si bending mode was positioned at 502 cm^{-1} . The peaks at 3473 cm^{-1} and 1594 cm^{-1} were due to the stretching and bending of O–H groups present in silica respectively. The FT-IR spectra of TLSG, FLSG and PLSG showed a band at 1350 cm^{-1} which was due to the bending of C–H group and the band around 1740 cm^{-1} was due to the stretching of C=O group of ester which confirms loading of ASG with 2-thiophenecarbonyl in TLSG, 2-furoyl in FLSG and L-proline in PLSG.

Surface morphology of adsorbents and wt.% of elements was studied using SEM-EDX (Carl Zeiss NTS GmbH, Oberkochen, Germany; Model: SUPRA 40VP). SEM micrograph (Fig. 2a–d) of adsorbents showed a rough and porous nature, indicating that the materials present good characteristics to be employed as an adsorbent for metal ion uptake. There was no significant change observed in surface morphology of ASG after its loading with 2-thiophenecarbonyl, 2-furoyl and L-proline. This indicated that the differences in adsorption capacity depend on functional groups present on its surface and not due to the morphology of adsorbents. EDX spectra (Fig. 3a–d) were recorded and wt.% of elements

is shown in Table 1. Results showed carbon/silica (C/Si) ratio in ASG, TLSG, FLSG and PLSG as 0.007, 0.24, 0.32 and 0.358, respectively. EDX analysis yielded direct evidence for the functionalization of silica gel surface with 2-thiophenecarbonyl, 2-furoyl and L-proline.

3.2. Influence of pH

The pH of the aqueous solution has a significant effect on the adsorptive uptake of metal ions presumably due to its impact on both the surface binding-sites of the adsorbent and the presence of hydrogen ion in solution. The influence of pH on adsorption of Pb(II) ion was studied over the pH range 2–5.5. Fig. 4 shows that the adsorption of Pb(II) ion increased as pH increased from 2 to 5.5. At lower pH values, hydrogen ion concentration in solution increased, which competes with Pb(II) ions for the binding sites of the adsorbent and reduced the adsorbed amounts of Pb(II) ion. At higher pH values, the presence of hydrogen ions in the solution decreased and the adsorbent surface also deprotonated, resulting in increased adsorption of Pb(II). Further increase in pH causes precipitation of Pb(II) due to the formation of hydroxide, therefore, a pH higher than 5.5 was avoided.

3.3. Effect of adsorbent dose

The effect of adsorbent dose on adsorption was studied in the range of 0.5–4 g/L. Fig. 5 shows that the adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG increased from 42% to 76%, 43% to 85%, 49% to 89% and 54% to 95.4% respec-

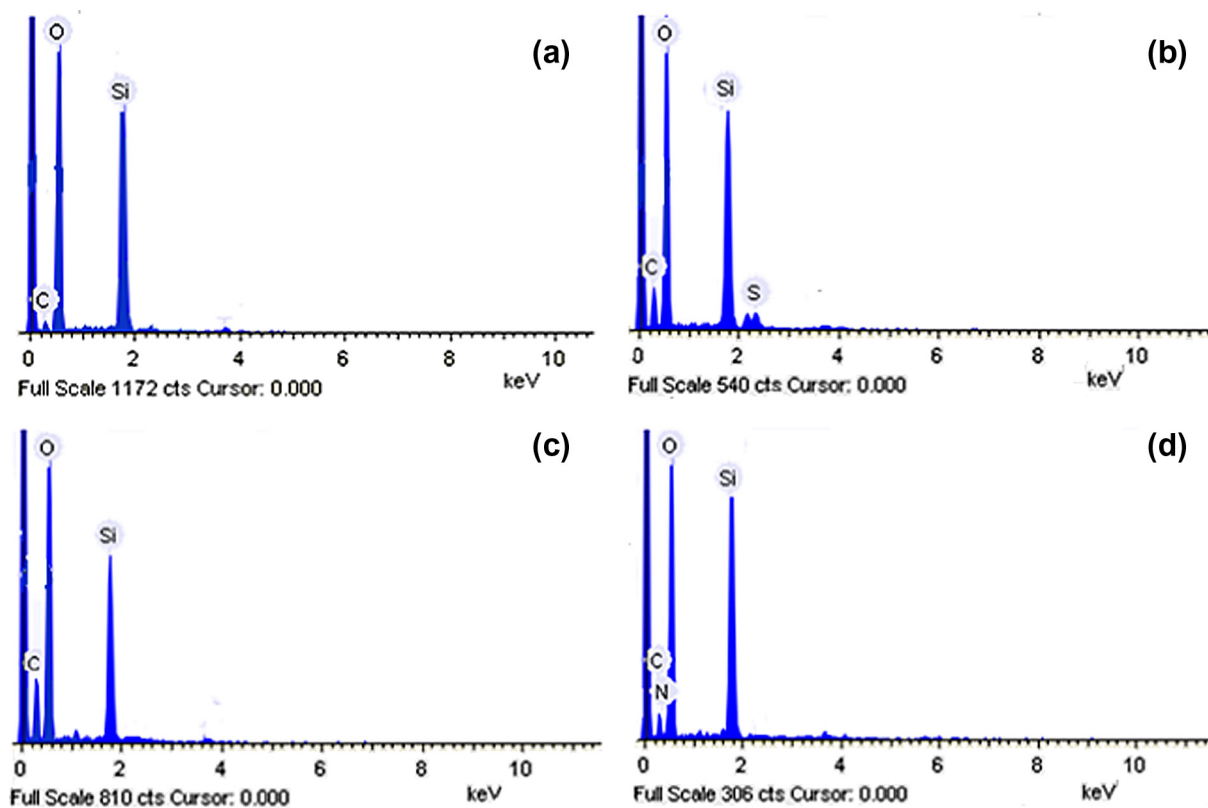


Figure 3 EDX spectra of ASG (a), TLSG (b), FLSG (c) and PLSG (d).

Table 1 Wt.% of elements present in adsorbents.

Adsorbents	Wt.% of elements				
	Si	O	C	S	N
ASG	41.65	58.04	0.3	–	–
TLSG	33.6	55.05	8.15	3.2	–
FLSG	32.43	57.1	10.4	–	–
PLSG	31.7	54.64	11.35	–	2.3

tively, when the adsorbent dose increased from 0.5 to 2 g/L. This increase in adsorption was due to an increase in the adsorptive surface area and the availability of more active adsorption sites. A Further increase in the adsorbent dose did not cause any significant change because equilibrium was achieved between the solid and the solution phase.

3.4. Effect of initial Pb(II) ion concentration

To observe the effect of initial Pb(II) concentration on adsorption, the experiments were conducted over the range of initial Pb(II) ion concentration (5–25 mg/L) (Fig. 6). The % removal of Pb(II) decreased from 78 to 66.4%, 86 to 76.8%, 90.6 to 83.2% and 95.8 to 92.4% onto ASG, TLSG, FLSG and PLSG respectively as initial Pb(II) ion concentration increased from 5 to 25 mg/L. In spite of this, the absolute amount of Pb(II) adsorbed at equilibrium increased in all cases, from 1.9 to 8.2 mg/g, 2.1 to 9.5 mg/g, 2.2 to 10.3 mg/g and 2.3 to 11.4 mg/g onto ASG, TLSG, FLSG and PLSG, respectively, with an increase in the initial concentration of Pb(II) from 5 to

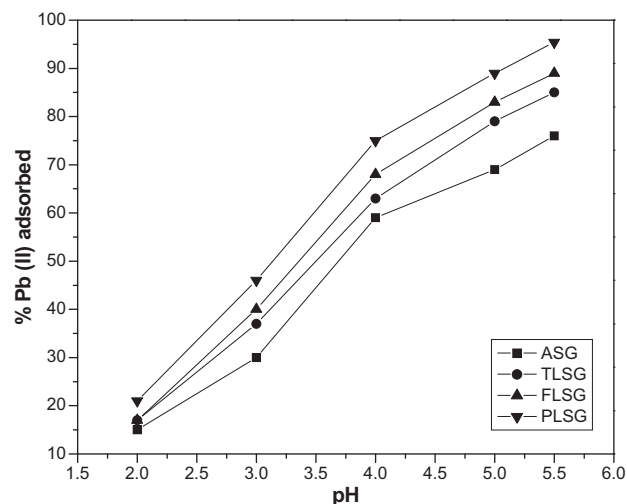


Figure 4 Influence of pH on adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; contact time: 90 min; temperature: 303 K).

25 mg/L, attesting to the efficacy of the removal process. Apparently, the initial Pb(II) concentration plays an important role in affecting the capacity of adsorbents to adsorb Pb(II). The higher the initial concentration of Pb(II), stronger the driving force of the concentration gradient and therefore the higher the adsorption capacity (Weng et al., 2009).

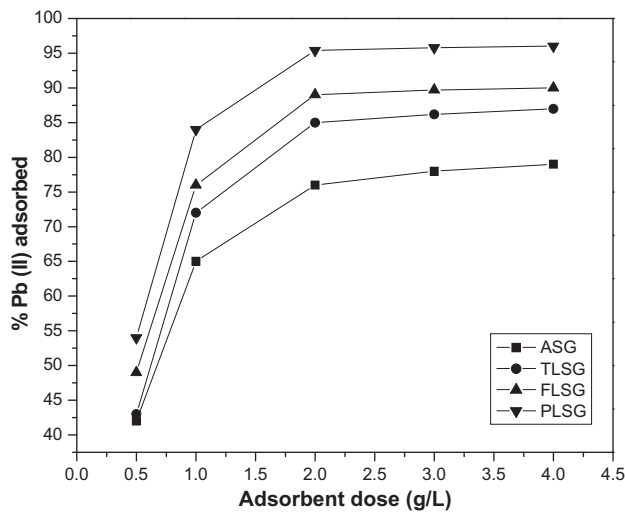


Figure 5 Effect of adsorbent dose on adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (pH: 5.5; initial Pb(II) concentration: 10 mg/L; contact time: 90 min; temperature: 303 K).

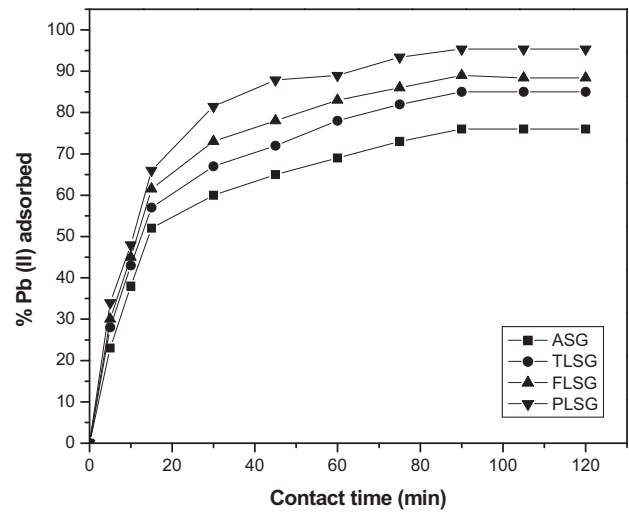


Figure 7 Adsorption kinetics of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; pH: 5.5; temperature: 303 K).

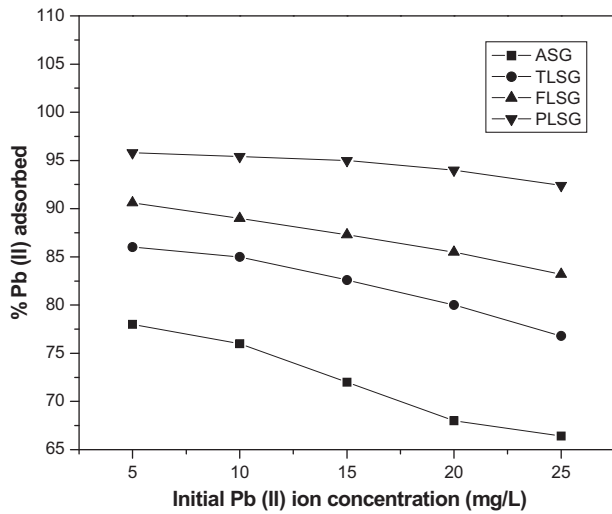


Figure 6 Effect of initial Pb(II) ion concentration on adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; pH: 5.5; contact time: 90 min; temperature: 303 K).

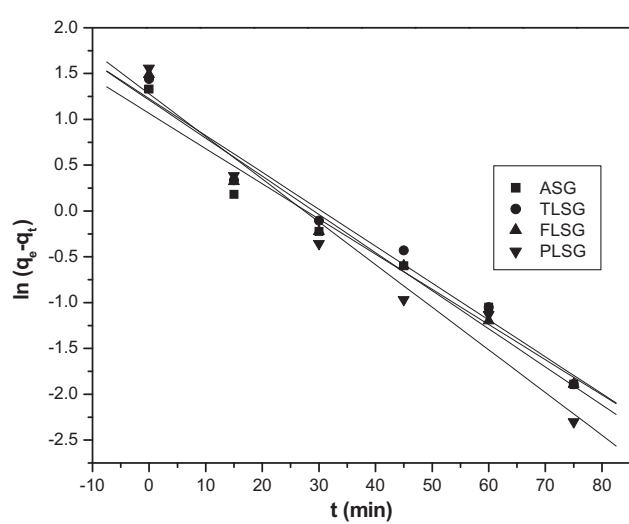


Figure 8 Pseudo-first order kinetics plots for adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; pH: 5.5; temperature: 303 K).

3.5. Adsorption kinetics

From Fig. 7, a two-stage kinetic behavior was evident: a very rapid initial adsorption over a few minutes, followed by a longer period of much slower uptake. The rate of adsorption of Pb(II) was very rapid in the first 15 min, thereafter it declined slowly with lapse of time. Maximum % adsorption was found at 90 min of contact time and thereafter no change was observed, this indicates that the adsorption process has reached the equilibrium point.

Several kinetic models have been proposed to clarify the mechanism of a solute adsorption from aqueous solution onto an adsorbent. The rate constant of adsorption was determined from the pseudo-first order rate expression (Eq. (3)) (Gupta et al., 2011) given by Lagergren:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e and q_t are the amounts of Pb(II) adsorbed at equilibrium and at time t (mg/g) respectively and k_1 (min^{-1}) is the rate constant of adsorption. The values of k_1 and q_e^{cal} were calculated from the slopes ($-k_1$) and intercepts ($\ln q_e$) of the plots of $\ln(q_e - q_t)$ vs. t (Fig. 8), respectively (Table 2).

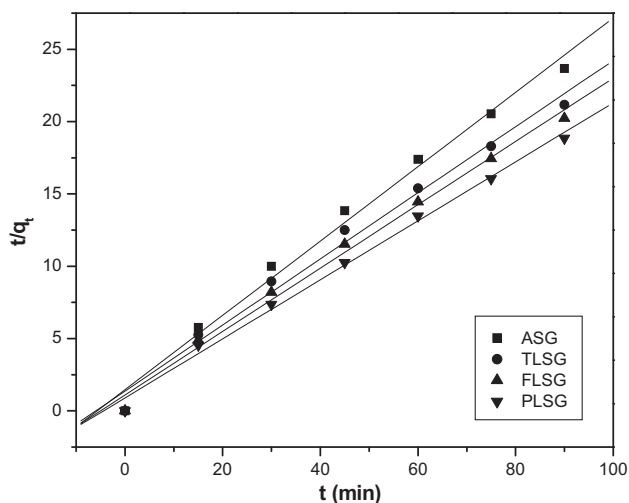
The pseudo-second order sorption kinetics (Gupta et al., 2011) may be written as follows:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{4}$$

where k_2 is the rate constant of adsorption (g/mg min), q_e and q_t are the amounts of Pb(II) adsorbed at equilibrium and at time t (mg/g) respectively. The values of k_2 and q_e^{cal} were calculated from the intercepts ($1/k_2 q_e^2$) and slopes ($1/q_e$) of the

Table 2 Kinetic parameters for adsorption of Pb(II) onto functionalized silica gel.

Adsorbents	q_e^{exp}	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
		q_e^{cal}	k_1	R^2	q_e^{cal}	k_2	R^2	k_i	C	R^2
ASG	3.8	2.90	0.038	0.962	3.89	0.045	0.988	0.015	2.47	0.971
TLSG	4.25	3.40	0.040	0.970	4.38	0.038	0.987	0.018	2.72	0.962
FLSG	4.45	3.35	0.041	0.972	4.56	0.043	0.991	0.017	3.01	0.928
PLSG	4.77	3.58	0.046	0.960	4.90	0.046	0.994	0.017	3.35	0.842

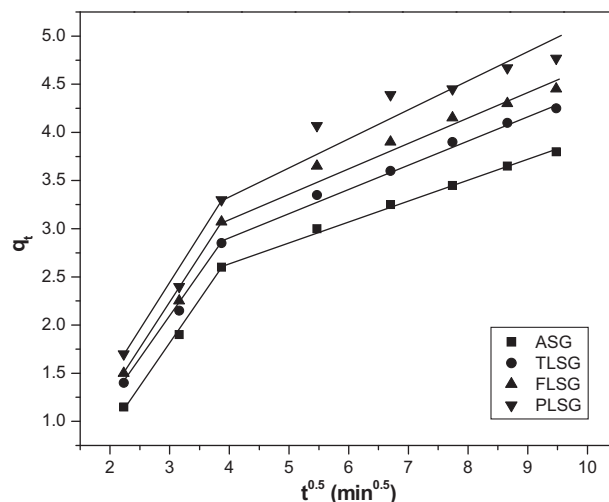
**Figure 9** Pseudo-second order kinetics plots for adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; pH: 5.5; temperature: 303 K).

plots of t/q_t vs. t . (Fig. 9) respectively (Table 2). Table 2 indicates that the values of regression correlation coefficient (R^2) are closer to unity and show a good agreement between experimental and calculated q_e values for pseudo-second order kinetic model. Therefore, it can be concluded that the adsorption of Pb(II) onto ASG, TLSG, FLSG and PLSG followed pseudo-second order kinetic model. A pseudo-second order fit indicates that the overall process was both dependent on the amount of Pb(II) present in solution and on the availability of adsorption sites on the adsorbents.

Intraparticle diffusion plays an important role in the adsorption process. It is a multi-step process, involving adsorption on the external surface and diffusion into interior. The intraparticle diffusion model (Kushwaha et al., 2010) can be expressed as follows:

$$q_t = k_i t^{0.5} + C \quad (5)$$

where k_i is the intraparticle diffusion constant ($\text{mg/g min}^{0.5}$) and the intercept (C) reflects the boundary layer effect. The values of k_i were calculated from slopes (k_i) of the plots of q_t vs. $t^{0.5}$ (Fig. 10) and are presented in Table 2. Fig. 10 shows two intersecting lines for each adsorbent, the first one representing adsorption of Pb(II) on the surface of adsorbent and the second one described diffusion of Pb(II) onto the adsorption site. Surface adsorption was more dominant in the first 15 min of contact time, thereafter diffusion became a rate-limiting process. This revealed the presence of both surface adsorption and intraparticle diffusion in the adsorption pro-

**Figure 10** Intraparticle diffusion plots for the adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; pH: 5.5; temperature: 303 K).

cess (Kumar and Porkodi, 2007). There was no significant change observed in the diffusion rate of Pb(II) after functionalization of silica gel and the values of C increased in the order ASG < TLSG < FLSG < PLSG. Larger the value of C , greater was the contribution of the surface adsorption.

3.6. Adsorption isotherm

Adsorption equilibrium describes the nature of adsorbate-adsorbent interaction. In the present study the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The analysis of the isotherm data by seeing how well they can be accommodated by different models is an important step in establishing a model that can be successfully used for design purposes.

3.6.1. Langmuir isotherm model

The saturated monolayer isotherm can be represented as:

$$q_e = Q_m b C_e / (1 + b C_e) \quad (6)$$

The linearized forms of Eq. (6) can be written as follows (Ghoul et al., 2003):

$$C_e/q_e = 1/bQ_m + C_e/Q_m \quad (7)$$

where q_e is the adsorption density (mg/g) at equilibrium of Pb(II), C_e is the equilibrium concentration (mg/L) of Pb(II)

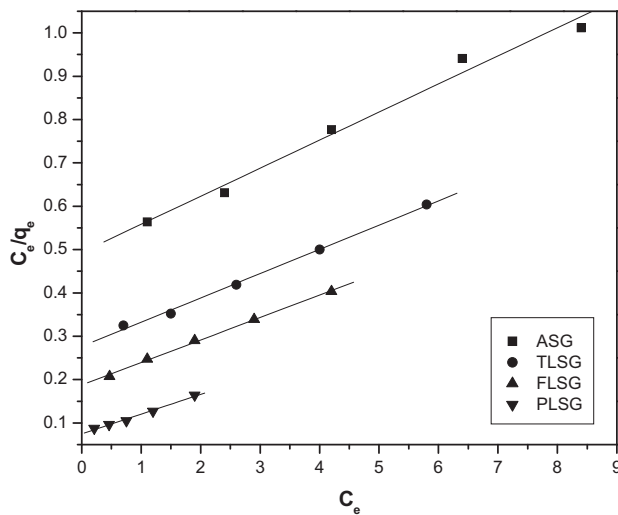


Figure 11 The Langmuir plots for the adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG.

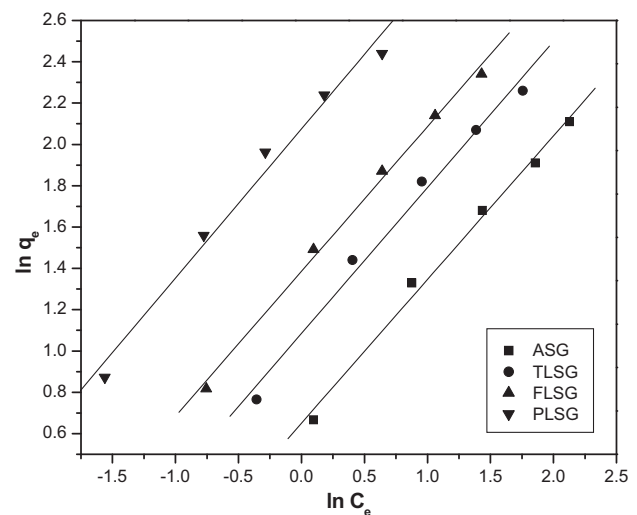


Figure 12 The Freundlich plots for the adsorption of Pb(II) on ASG, TLSG, FLSG and PLSG.

in solution, Q_m is the monolayer adsorption capacity (mg/g) and b is the Langmuir constant (L/mg) related to the free energy of adsorption. The values of Q_m and b were calculated from the slopes ($1/Q_m$) and intercepts ($1/bQ_m$) of the linear plots C_e/q_e vs. C_e (Fig. 11) and are given in Table 3. Linear plots of C_e/q_e vs. C_e show that the adsorption followed the Langmuir isotherm model for all the four adsorbents. Experimental results show that the monolayer adsorption capacity of adsorbents for Pb(II) was increased in the order $ASG < TLSG < FLSG < PLSG$.

3.6.2. Freundlich isotherm model

Freundlich isotherm can be expressed as follows (Aklil et al., 2004):

$$Q_e = K_f C_e^{1/n} \tag{8}$$

The logarithmic forms of Eq. (8) can be written as follows:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{9}$$

where K_f and n are Freundlich constants related to adsorption capacity [$\text{mg/g} (\text{mg/L})^{-1/n}$] and adsorption intensity of adsorbents. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of Pb(II) adsorbed onto the adsorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Hameed et al., 2007). The values of the K_f and n were calculated from the intercepts ($\ln K_f$) and slopes ($1/n$) of the plots $\ln q_e$ vs. $\ln C_e$ (Fig. 12) and are presented in Table 3. Linear plots of $\ln q_e$ vs. $\ln C_e$ show that the adsorption

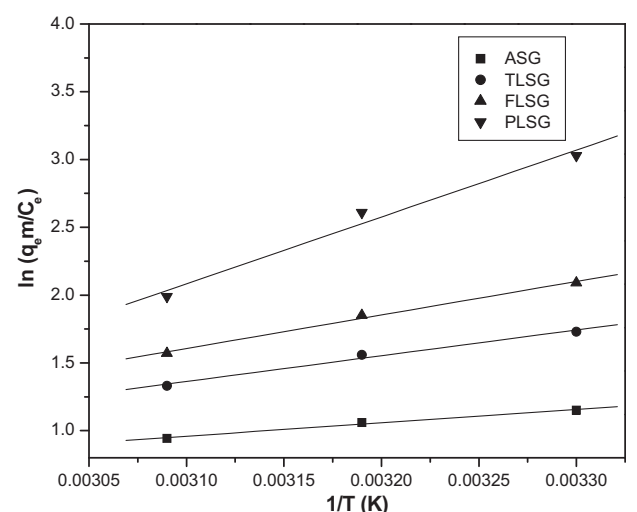


Figure 13 The plots of $\ln (q_e m / C_e)$ vs. $1/T$ for the adsorption Pb(II) on ASG, TLSG, FLSG and PLSG (adsorbent dose: 2 g/L; initial Pb(II) concentration: 10 mg/L; pH: 5.5; contact time: 90 min).

isotherm of Pb(II) on all the four adsorbents was also fitted well in the Freundlich isotherm model and the adsorption capacity (K_f) of adsorbents for Pb(II) was increased in the order $ASG < TLSG < FLSG < PLSG$. The values of $n > 1$ indicate favorable adsorption conditions (Hameed, 2009; Hameed et al., 2008).

Table 3 Isotherm parameters for adsorption of Pb(II) onto functionalized silica gel.

Adsorbents	Langmuir isotherm parameters			Freundlich isotherm parameters		
	Q_{max}	b	R^2	K_f	n	R^2
ASG	15.62	0.129	0.985	1.91	1.43	0.992
TLSG	17.85	0.202	0.996	2.95	1.41	0.987
FLSG	19.60	0.272	0.997	3.99	1.42	0.995
PLSG	22.22	0.608	0.989	7.96	1.38	0.982

Table 4 Thermodynamic parameters for adsorption of Pb(II) onto functionalized silica gel.

Adsorbents	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)		
			303 K	313 K	323 K
ASG	-8.164	-17.35	-2.907	-2.734	-2.560
TLSG	-15.779	-37.60	-4.387	-4.011	-3.635
FLSG	-20.543	-50.34	-5.290	-4.787	-4.284
PLSG	-41.012	-109.8	-7.743	-6.645	-5.547

3.7. Thermodynamic study

To observe the effect of temperature on adsorption of Pb(II) onto ASG, TLSG, FLSG and PLSG experiments were conducted at three different temperatures 303, 313 and 323 K. It was observed that the adsorption decreased as the temperature increased, which indicates a low temperature favors Pb(II) adsorption for all the four adsorbents. This may be due to the tendency of Pb(II) molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution. A similar observation was also reported in the study on the sorption of Pb onto modified and unmodified kaolinite clay (Jiang et al., 2009).

Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and Gibb's free energy (ΔG°) are important for a better understanding of the effect of temperature on adsorption, were determined by Eq. (10) (Nandi et al., 2009) and (11).

$$\ln(q_e m / C_e) = \Delta S^\circ / R - \Delta H^\circ / RT \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

where m is the adsorbent dose (mg/L), C_e is the equilibrium concentration (mg/L) of Pb(II) in the solution and $q_e m$ is the solid-phase concentration (mg/L) at equilibrium. R is the gas constant (8.314 J/mol/K) and T is the temperature (K). ΔH° , ΔS° and ΔG° are changes in enthalpy (J/mol), entropy (J/mol/K) and Gibb's free energy (J/mol), respectively.

The values of ΔH° and ΔS° were determined from the slope ($-\Delta H^\circ/R$) and the intercept ($\Delta S^\circ/R$) of the plots of $\ln(q_e m / C_e)$ vs. $1/T$ (Fig. 13). The ΔG° values were calculated by using Eq. (11). The values of thermodynamic parameters are presented in Table 4. Negative values of ΔG° indicate that the adsorption process was feasible and spontaneous in nature. The negative values of ΔG° increased in the order ASG < TLSG < FLSG < PLSG indicate that the adsorption was more spontaneous on PLSG. Negative value of ΔS° described the decrease in randomness at the adsorbent-solution interface during the adsorption and was more negative for PLSG indicating Pb(II) ion is more stable on PLSG. Negative values of ΔH° suggest the exothermic nature of adsorption and are in the range of -8 to -41 kJ/mol, which indicate that both the physical and chemical adsorption mechanisms were present in the adsorption process.

3.8. Adsorption mechanism

At optimum condition % removal of Pb(II) by adsorption was observed as 76%, 85%, 89% and 95% by ASG, TLSG, FLSG and PLSG respectively. All the three functionalized adsorbents having an adsorption capacity greater than ASG and PLSG were found to be best among the four adsorbents. The % re-

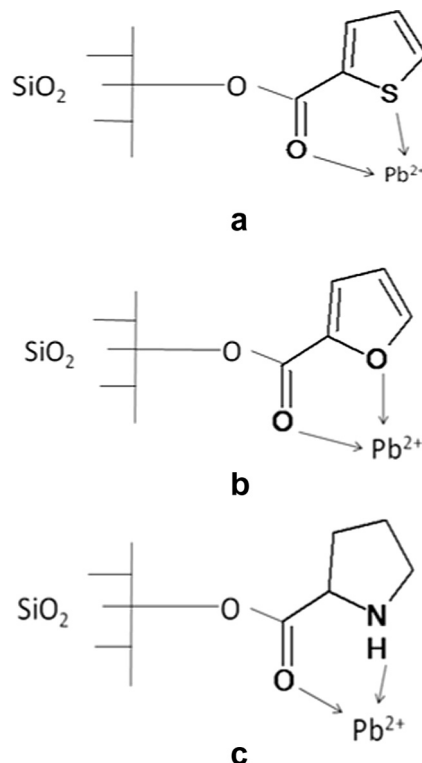


Figure 14 Scheme of adsorption mechanism of Pb(II) on TLSG (a), FLSG (b) and PLSG (c).

moval of Pb(II) was increased by 9%, 13% and 19% after the modification of ASG to TLSG, FLSG and PLSG respectively. The highest % removal shown by PLSG was due to the presence of nitrogen as a donor atom having a lone pair of electrons, which was freely available for chelation with Pb(II), but in the case of TLSG and FLSG a lone pair of sulfur and oxygen was conjugated with double bonds and used to stabilize the aromatic ring, which reduced its availability for chelation and adsorption capacity. The proposed scheme for the adsorption mechanism is given in Fig. 14.

4. Conclusions

The % removal of Pb(II) increased after loading SG with organic functional groups and the highest adsorption was observed on PLSG (95%). The optimum condition for the adsorption was found to be pH 5.5 and temperature 303 K. Adsorption processes followed pseudo-second order kinetics, surface adsorption and intraparticle diffusion mechanism. Equilibrium studies showed that the adsorption of Pb(II) onto

ASG, TLGS, FLSG and PLSG followed the Langmuir and Freundlich isotherm models. Negative values of ΔH° and ΔG° indicate that the adsorption of Pb(II) onto ASG, TLGS, FLSG and PLSG was thermodynamically feasible, spontaneous and exothermic.

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