

Adsorptive removal studies of lead(II) ions using functionalized silica

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ABSTRACT

An adsorbent was prepared by the functionalization of 2-hydroxyacetophenone-3-thiosemicarbazone onto 3-aminopropyl silica by diazotation and characterized by Fourier transmission infra red spectrometry. The functionalized silica was evaluated for removal of lead(II) ions in aqueous solutions. The maximum adsorption capacity 385 $\mu\text{g/g}$ was obtained with an initial concentration of 1,000 $\mu\text{g/L}$ by the Langmuir isotherm. The results indicated that adsorption data could be fitted better by the Langmuir than the Freundlich isotherm. The adsorption kinetics followed pseudo-second-order reaction and the rate constants of kinetic model were calculated. The experimental results implied that functionalized silica has the potential to work as a good adsorbent for the removal of the heavy metals from contaminated water. This novel adsorbent was found to be easy to synthesize, simple, cost-effective and highly efficient and has potential application in the water purification field.

Key words | functionalized silica, heavy metal removal, 2-hydroxyacetophenone-3-thiosemicarbazone, isotherms, lead

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INTRODUCTION

Removal of trace amounts of heavy metal ions from wastewater is of great importance because of their high toxicity. Lead is classified as a hazardous substance because of its high toxicity and cumulative character in living organisms. Lead poisoning can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects and language difficulties (Liu *et al.* 2010). Major lead pollution occurs through various process such as in the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields and bearings (Ake *et al.* 2001; Tunali *et al.* 2006). Thus lead is an industrial pollutant, which enters the ecosystem through soil, air and water. According to the World Health Organization, the maximum permissible limit (MPL) of lead in drinking water is 0.05 mg/L (WHO 1984). Hence proper treatment of industrial wastewater

which is releasing lead into the aquatic and land systems is very important.

There are several methods, such as precipitation, oxidation, reduction, electrochemical treatment, reverse osmosis, solvent extraction, adsorption, ion-exchange and evaporation, available to treat the metal-bearing effluents; most of these methods are expensive and difficult to apply (Volesky 2001). Among these methods, adsorption has proved to be one of the most feasible; it is a simple, selective, cost-effective, easy to operate and highly efficient process for the removal of heavy metals from polluted sources. Various adsorbents have been reported, such as modified and unmodified kaolinite (Jiang *et al.* 2009), modified bentonite (He *et al.* 2010), acid-activated montmorillonite-illite (Oubagaranadin & Murthy 2010), zeolite (Ibrahim *et al.* 2010) and sepiolite (Bektas *et al.* 2004) for Pb(II) removal. A few biological-based materials such as *Saccharomyces cerevisiae* (Ghaedi *et al.* 2010),

Triticum aestivum (Farooq *et al.* 2010), *Aspergillus niger* (Amini & Younesi 2009), activated sludge biomass (Ahmad *et al.* 2010) and *Bacillus* sp. (Wierzbka & Latała 2010) have also been reported to remove Pb(II) ions from aqueous solutions by adsorption. Recently, scientists have reported carbon nanotubes as an adsorbent for the adsorption process of toxic metals (Lin *et al.* 2003; Peng *et al.* 2005). Carbon nanotubes have a high surface area, high adsorption capacity and high degree of surface reactivity, but are very expensive and there is a need for regeneration after each adsorption experiment (Ozcan & Ozcan 2004; Ozcan *et al.* 2004).

In order to reduce the cost of treatment, scientists have attempted to investigate inexpensive, efficient and easily available adsorbents. Among the different adsorbents, silica gel especially immobilized with various organic compounds with metal chelating functionality has received great attention (Zaporozhets *et al.* 1999; Anilan *et al.* 2010). Silica has various advantages over other organic/inorganic supports: easier immobilization on silica surfaces than on organic polymeric supports (Miyake *et al.* 2009), high specific surface area (Arakaki *et al.* 2000), high mass exchange characteristics and no swelling (Walcarius & Collinson 2009), great resistance to organic solvents (Chen *et al.* 2009) and very high thermal resistance (Fang *et al.* 2005). The adsorption approach involving use of functionalized silica in removal of lead from waste water can offer a complete solution (Misra *et al.* 2010). In this context, a detailed study on functionalized silica was carried out.

In this paper we discuss the preparation of a novel silica-based adsorbent which is capable of attaining equilibrium adsorption within very short time (10 min) compared to available adsorbents (Jiang *et al.* 2009; Ibrahim *et al.* 2010). We have functionalized silica by a condensation reaction with diazotized 3-aminopropyl silica and 2-hydroxyacetophenone-3-thiosemicarbazone. The adsorption studies of Pb(II) ions were carried out on functionalized silica in aqueous solution and adsorption kinetics constants were calculated. The possible adsorption interaction between functionalized silica and Pb(II) ions was also elucidated. To the best of our knowledge the use of such material for the water purification has not been reported before.

MATERIALS AND METHODS

Materials

All of the reagents used were of analytical grade. All laboratory wares used for analytical determination were cleaned first by trace metal grade nitric acid and hydrochloric acid, followed by repeated rinsing with deionized water. All the solutions were prepared with ultrapure water (resistivity: 18.2 MΩ cm.) from an Elix analytical reagent-grade water purification system. 3-Aminopropyl silica was purchased from Aldrich (characteristics: particle platform irregular, functionalized 9%, surface area 550 m²/g, mean pore size 60 Å).

Calibration standard solutions and internal standards were prepared from commercial metal standard solutions. Analytic grade nitric acid (Fisher) was used for the preparation of all the calibration standard solutions and analytical solutions.

Standard working solutions of lead were prepared from 1,000 mg/L standard solution (Merck, Germany) and solutions of varying initial concentrations were prepared from a 1,000 mg/L by serial dilution using distilled deionized water.

Methods

Synthesis of 2-hydroxyacetophenone-3-thiosemicarbazone

2-Hydroxyacetophenone (0.3 mol dissolved in 50 mL of methanol), thiosemicarbazide (0.3 mol dissolved in 200 mL of water) and potassium hydroxide (3 g dissolved in 25 mL of water) were mixed in a round bottomed flask and refluxed for 3 h and after cooling poured in to ice water. The yellow crystals obtained were washed two or three times with ethanol and then purified by recrystallization in ethanol (Figure 1).

Functionalization of 3-aminopropyl silica with 2-hydroxyacetophenone-3-thiosemicarbazone

3-Aminopropyl silica (10 g) and 20 mL HCl solution (conc. HCl : H₂O; 1:1 v/v) were stirred in a conical flask at 0–4 °C, then added drop wise to 10 mL NaNO₂ (5 M solution of

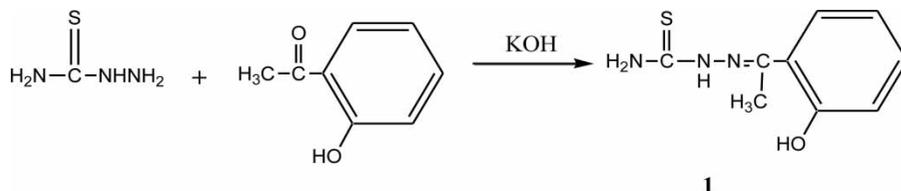


Figure 1 | Synthesis of 2-hydroxyacetophenone-3-thiosemicarbazone.

NaNO₂ in water) until the reaction mixture showed a permanent dark blue color with starch-iodine paper with continuous stirring. The diazotized silica was washed with ice cold water and reacted with 2-hydroxyacetophenone-3-thiosemicarbazone (2 g dissolved in 50 mL of 10% NaOH solution) at 0–4 °C for 10 h. The resulting brown silica was filtered, washed with water and air dried (Figure 2).

Experimental

Adsorption studies by batch method

Adsorption experiments were carried out in glass bottles (100 mL) containing functionalized silica (50 mg) with 20 mL of lead ions (concentration 1,000 µg/L) at pH 3 at 30 ± 1 °C. Five milliliters of the solution from each glass bottle was taken at different time interval (5, 10, 20, 30, 60 and 120 min) to determine the optimum contact time where the maximum adsorption was accomplished for lead(II) ions. The residual concentration of lead ions was determined using atomic absorption spectrometry (AAS).

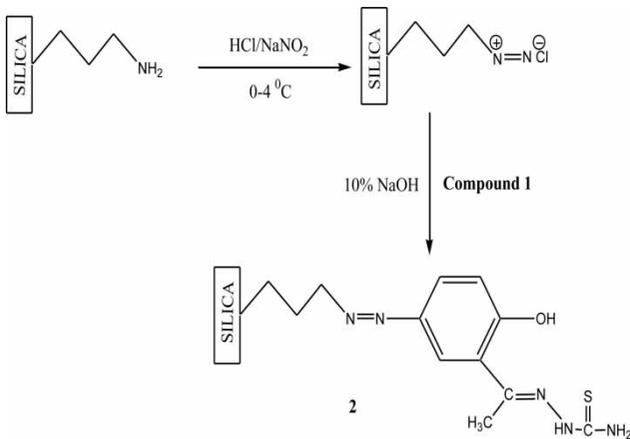


Figure 2 | Functionalization of 3-aminopropyl silica with 2-hydroxyacetophenone-3-thiosemicarbazone.

The quantity of metal ion adsorbed by silica (q_e mmol/g) was calculated according to the following equation:

$$Q_e = (C_i - C_e) \times V/m \quad (1)$$

where C_i and C_e are initial and equilibrium concentration (µg/L), respectively. V (L) and m (g) are volume of the sample solution and mass of the functionalized silica, respectively.

The optimum contact time was determined as 10 min and used throughout all adsorption experiments. Uptake experiments of metal ions at different pH (3, 7 and 10) were carried out in glass bottles (100 mL) containing functionalized silica (50 mg) with 20 mL of lead ions at an initial concentration of 1,000 µg/L. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl. The residual concentration of lead ions was determined using AAS. The quantity of metal ion adsorbed by silica (q_e mmol/g) was calculated according to Equation (1). The results showed that q_e maximum observed at pH 3 (solution pH).

Solutions were prepared with lead ions concentrations of 500, 600, 900, 1,000, 1,100 and 1,200 µg/L and used to obtain the adsorption isotherm data on the adsorption process. Fifty milligrams of silica was placed in a series of glass bottles containing 20 mL of lead ions solution with above mentioned concentrations at pH 3 for 10 min. After equilibration, 5 mL of the solution was taken for the determination of residual concentration of metal ions by AAS. The amount of metal ion adsorbed by silica (q_e mmol/g) was calculated according to Equation (1). To check the adsorption capacity of 3-aminopropyl silica, the starting material, the experiment was repeated. It was found there is no significant removal.

Kinetic adsorption experiment

The kinetic study was carried out at two concentrations (500 and 1,000 µg/L) at pH 3 keeping the pH of solution

at 3. The data acquisition protocol includes the treatment of a series of 50 mg of functionalized silica with 20 mL of lead solution. This series of samples was quenched at time intervals by filtration. The concentrations of the filtrate were analyzed by AAS. These results were also used to obtain the adsorption kinetics.

Instrumentation

Atomic absorption spectrometry

An atomic absorption spectrometer (Analytik-Jena-Nova-400) equipped with 100 mm burner, a cross flow nebulizer 5.0 mL/min and 1.2 mm slit were used throughout the experiments. All AAS measurements were carried out on flame mode with single beam. Each experiment was duplicated under identical conditions using this instrument for concentration determination.

Fourier transmission infra red spectrometry

The functionalized silica was characterized using Fourier transmission infra red spectrometry (FT-IR) (Jasco FT-IR spectrometer model 610). The spectra were recorded by using KBr pellets.

pH measurements

The pH measurements were made on a digital pH meter (HACH, sension 1, model 51935-00) equipped with a gel-filled pH electrode. The meter was calibrated with the buffers of 4, 7 and 10.

RESULTS AND DISCUSSION

Characterization of material

A schematic representation of synthesis of 2-hydroxyacetophenone-3-thiosemicarbazone (1) is shown in Figure 1. The FT-IR spectrum of 2-hydroxyacetophenone-3-thiosemicarbazone (Figure 3) showed absorption bands at 3,420, 3,250, 1,623, 1,376, 1,240 and 1,106 cm^{-1} due to NH_2 stretching, O-H stretching, C=N stretching,

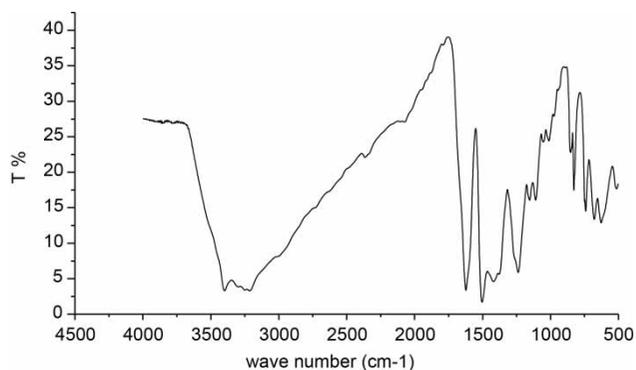


Figure 3 | FT-IR spectra of 2-hydroxyacetophenone-3-thiosemicarbazone.

C=S stretching, O-H bending and C-N stretching, respectively. The presence of the characteristic IR absorption bands confirmed that compound 1 was successfully prepared. The synthesized compound was further functionalized with 3-aminopropyl silica as shown in Figure 2.

The FT-IR spectrum of 3-aminopropyl silica showed absorption bands (Figure 4(a)) at 1,150 cm^{-1} for the Si-O-Si group and O-H stretching of silanol group at 3,450 cm^{-1} . The 3-aminopropyl silica was diazotized followed by reaction with compound 1 shows new absorption bands (Figure 4(b)) appear at 3,436, 1,670, 1,525, 1,390, 1,230 and 1,105 cm^{-1} which may be assigned to NH_2 stretching, C=N stretching, N=N stretching, O-H bending, C=S stretching and C-N stretching, respectively, and the presence of Si-O-Si group absorption band at 1,150 cm^{-1} . The

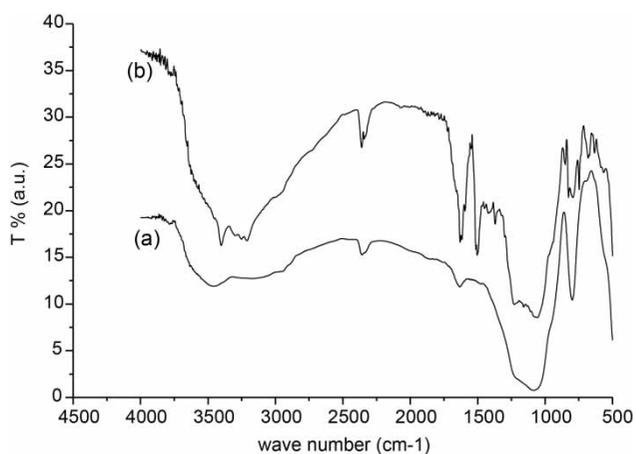


Figure 4 | Comparative FT-IR spectra of (a) 3-aminopropyl silica (b) functionalized silica with 2-hydroxyacetophenone-3-thiosemicarbazone.

presence of absorption band of these groups confirmed that 3-aminopropyl silica was functionalized successfully with 2-hydroxyacetophenone-3-thiosemicarbazone.

Adsorption isotherms

The initial lead(II) concentrations (500, 600, 900, 1,000, 1,100 and 1,200 $\mu\text{g/L}$) were used for investigation of the adsorption isotherm. The equilibrium concentrations were obtained after 10 min of contact time. The amount of lead(II) adsorbed on the functionalized silica was found to increase as the initial metal ion concentration increased and continued up to 1,000 $\mu\text{g/L}$ and leveled off thereafter (C_e in Figure 5). The Langmuir and Freundlich models were employed to describe the adsorption process.

The Langmuir model (Langmuir 1916) is given as:

$$C_e/Q_e = 1/(Q_m b) + C_e/Q_m \quad (2)$$

where C_e is the equilibrium concentration obtained from the initial concentration upon a certain period of contact time with the chelating silica, Q_e is the amount of lead(II) ions adsorbed by functionalized silica ($\mu\text{g/g}$) at equilibrium, and Q_m is the maximum adsorption capacity ($\mu\text{g/g}$); b is the Langmuir parameter related to energy of adsorption. A straight line obtained in the plot of C_e/Q_e vs C_e (Figure 6) indicated that adsorption data obeyed the Langmuir equation (Gupta & Babu 2009). The linear plot of C_e/Q_e vs C_e gives the intercept and slope

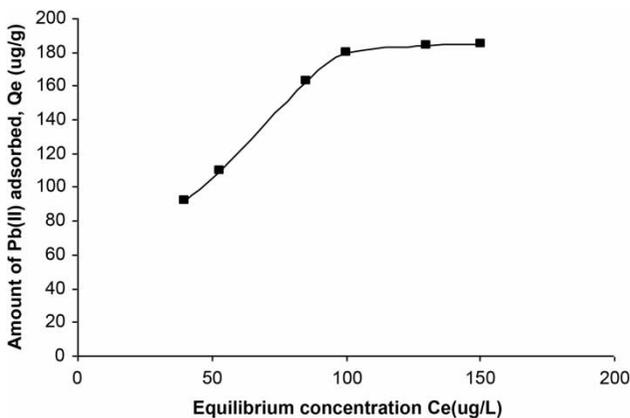


Figure 5 | Effect of the initial concentration on lead(II) adsorption determined through equilibrium concentration and adsorption capacity.

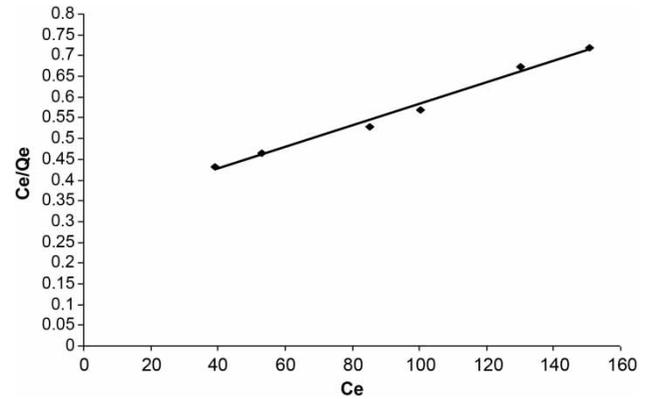


Figure 6 | Langmuir isotherm for the removal of Pb(II) ions at pH 3, contact time 10 min and different initial concentrations (500–1,200 $\mu\text{g/L}$).

corresponding to $1/(Q_m b)$ and $1/Q_m$, respectively, from which both Q_m and b are derived.

The Freundlich model (Freundlich 1906) can be expressed as:

$$\log Q_e = 1/n \log C_e + \log K \quad (3)$$

where K and $1/n$ are Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. The plot of $\log Q_e$ against $\log C_e$ gives the intercept and slope corresponding to $\log K$ and $1/n$, respectively, from which both K and n are obtained (Figure 7).

Results from analysis of both models are listed in Table 1. The Langmuir model is more likely applicable because of the higher correlation coefficient, indicating possible monolayer coverage of lead(II) on the surface of the functionalized silica.

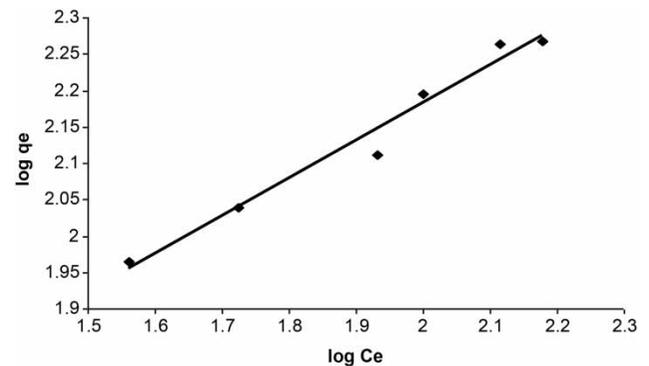


Figure 7 | Freundlich isotherm for the removal of Pb(II) ions at pH 3, contact time 10 min and different initial concentrations (500–1,200 $\mu\text{g/L}$).

Table 1 | Langmuir and Freundlich parameters of Pb(II) adsorption on functionalized silica

Langmuir model			Freundlich model		
Q_m ($\mu\text{g/g}$)	b ($\text{L}/\mu\text{g}$)	R^2	K	$1/n$	R^2
385	0.0080	0.9903	14.09	0.517	0.9338

Effect of pH

The pH of aqueous solution has an important role in heavy metal adsorption. This is partly because hydrogen ions themselves are strongly competing with metals (Forstner & Wittman 1981) at lower pH. Moreover, at lower pH, protonation of chelating groups also takes place, so complexation with available ligands is reduced and hence the percentage removal decreases. But at higher pH, salt formation occurs and percentage uptake decreases. The removal of Pb(II) ions were carried out at pH 3, 7 and 10; the best result was obtained at pH 3 whereas removal decreased at pH 7 and 10 due to salt formation (Table 2).

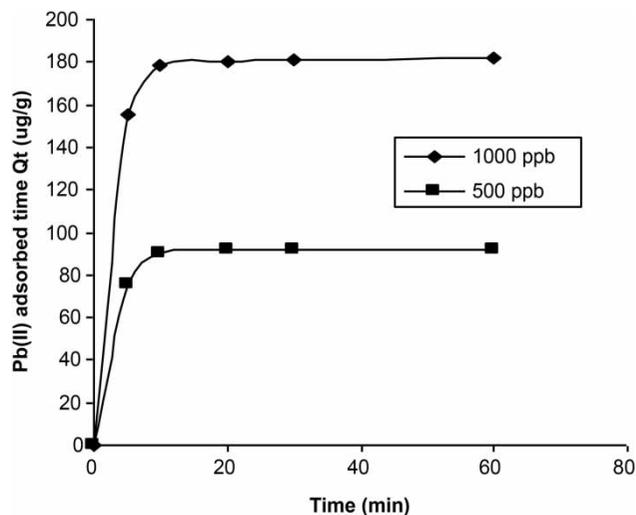
Adsorption kinetics

The kinetic property of lead(II) adsorption on the functionalized silica was assessed (Figure 8). The adsorption rates were determined at pH 3 in the range of lead(II) concentrations 500 and 1,000 $\mu\text{g/L}$ in aqueous media. The adsorption kinetics exhibits the following characteristics: the adsorption is rapid and increases with increasing concentration of the metal ion. The adsorption reached equilibrium capacity within 10 min; this equilibrium time is very short compared to already reported adsorbents for Pb(II) from aqueous solutions (Jiang *et al.* 2009; Ibrahim *et al.* 2010). The fast kinetics may be attributed to the high complexation process rate between the metal and the chelating units.

Table 2 | Effect of pH on adsorption of Pb(II) onto the functionalized silica

pH	Removal (%)
3	92.5
7	69.8
10	57.3

Note: Optimum condition: initial concentration 1,000 $\mu\text{g/L}$, contact time 10 min.

**Figure 8** | The adsorbed amounts of Pb(II) at initial concentration (500 and 1,000 $\mu\text{g/L}$) with different exposure times (5–60 min).

The adsorption kinetic mechanism was evaluated using one conventional model, namely pseudo-second-order equations (Ho & McKay 2000).

A pseudo-second-order reaction is guided by the expression:

$$t/Q_t = 1/(k_2 Q_e)^2 + t/Q_e \quad (4)$$

where Q_e ($\mu\text{g/g}$) is the amount of metal ion sorbed at equilibrium, Q_t ($\mu\text{g/g}$) is the amount of metal ion on the surface of the sorbent at time t and k_2 [$\text{g}/(\mu\text{g min})$] is the rate constant of pseudo-second-order adsorption (Allen & Brown 1995; Ho & McKay 1999). The values of $1/(k_2 Q_e)^2$ and $1/Q_e$ were derived experimentally from the intercept and slope of the linear plot of t/Q_t versus t , which eventually leads to values of k_2 and Q_e (Figure 9).

It is found that pseudo-second-order reaction gives high correlation coefficient values, indicating that it is the model applicable to the present adsorption kinetics. The kinetic data for second-order assessment are listed in Table 3.

It is apparent that the high adsorption rate corresponds to the fast equilibrium. This coupled with the Langmuir monolayer adsorption coverage suggests that the chelating silica has most of their chelating groups on or near the surface for easy access.

Lead(II) ions and functionalized silica interaction take place with different types of coordination

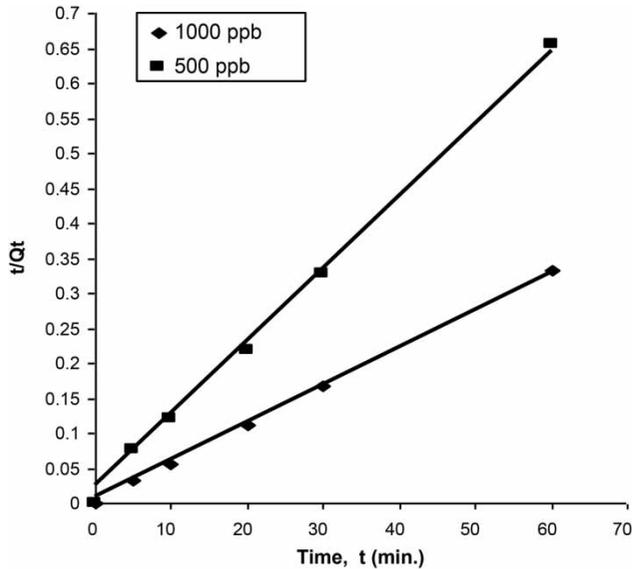


Figure 9 | Pseudo-second-order reaction kinetic plot for the adsorption of Pb(II) at initial concentration (500 and 1,000 µg/L).

Table 3 | Kinetic parameters for Pb(II) adsorption onto the functionalized silica at concentration 500 and 1,000 µg/L.

Pseudo-second-order concentration (µg/L)	K_2 [g/(min µg)]	Q_e (µg/g)	R^2
500	0.2561	38.463	0.993
1,000	0.0748	181.815	0.999

mode. They are based on the number of chelating units involved in complexation (Figure 10) to cover two scenarios: (i) when only one unit is available, an anion has to participate either in the inner or outer coordination sphere to balance the charge (Figure 10(a)–(c)); (ii) if two chelating units in close proximity from the same chain and adjacent chains are available, they would complete six coordination spheres (Figure 10(d)).

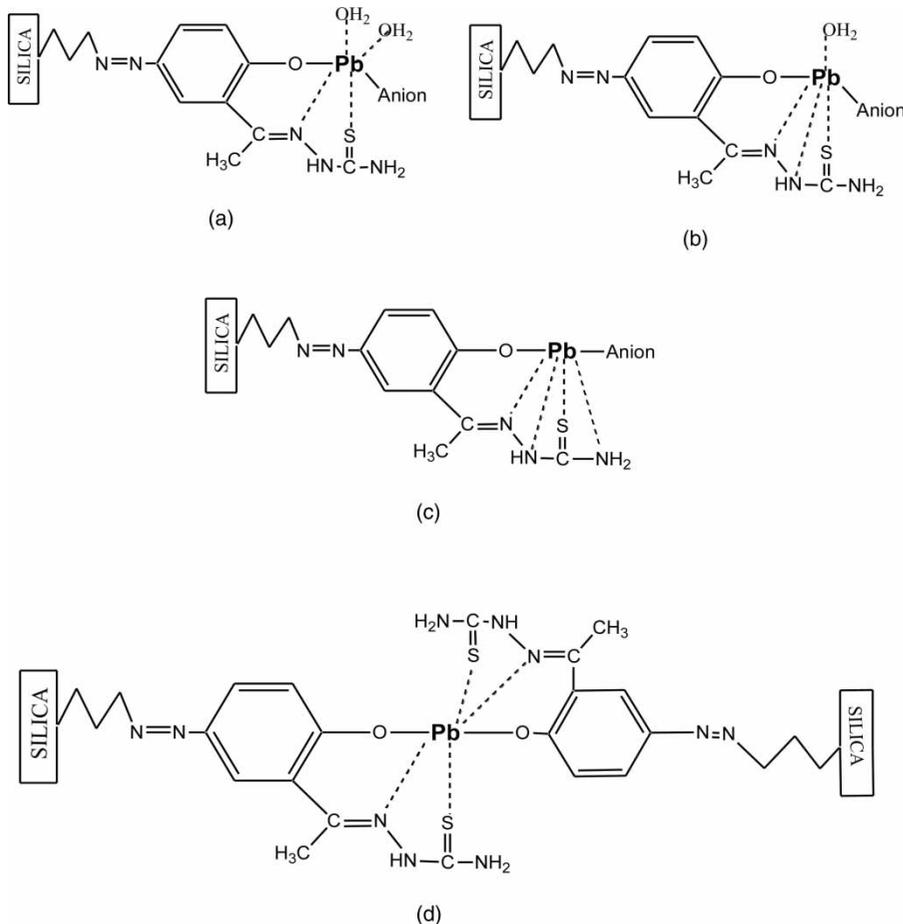


Figure 10 | Plausible coordination modes of Pb(II) ions and chelating units of functionalized silica.

CONCLUSION

2-Hydroxyacetophenone-3-thiosemicarbazone was successfully immobilized onto silica through a diazotization reaction. Functionalized silica showed excellent adsorption affinity towards Pb(II) ions even at low concentration ($\mu\text{g/L}$) with maximum adsorption capacity of $385 \mu\text{g/g}$ at initial concentration of $1,000 \mu\text{g/L}$. The adsorption data fitted well with the Langmuir model, indicating monolayer coverage of the metal ion on the surface of functionalized silica. Detailed kinetic studies of the fast adsorption process revealed that the equilibrium adsorption is attained within a short time of 10 min. The adsorption rate follows the pseudo-second-order according to reaction constants (k_2) 0.2561 and 0.0748 for 500 and $1,000 \mu\text{g/L}$ respectively.

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