Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21099

84 (2017) 292–298
July

Synthesis and application of functionalized nano silica for Ag(II) ions sequestration

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Received 30 January 2017; Accepted 1 July 2017

ABSTRACT

This paper communicates the synthesis of a new functionalized adsorbent and its applications as an efficient extractant for economically important Ag(II) metal. The functionalized adsorbent is synthesized through covalent attachment of a chelating compound thiosemicarbazide to the silica surface through modification route. Various characterization techniques such as Fourier transform infrared spectroscopy, Thermogravimetric analysis and Energy-dispersive X-ray spectroscopy confirmed that the ligand is successfully attached to the silica surface. The performance of the synthesized adsorbent is evaluated in batch adsorption experiments using radiotracer procedure. Rate transfer and thermodynamic factors are studied to ensure the practical use of the adsorbent for Ag(II) ions removal. The adsorption of Ag(II) followed first-order rate equation and is controlled by surface and intraparticle diffusions. Thermodynamic studies revealed that the Ag(II) adsorption is spontaneous (ΔG = –5,639.32 J/mol) and favorable (ΔS = 85.08 J/mol K). The equilibrium adsorption data followed Langmuir, Freundlich and D–R equations and from these models ion-exchange parameters are computed. The sorbent can be easily regenerated and used several times for Ag(II) ions adsorption.

Keywords: Thiosemicarbazide; Covalent modification; Nano silica; Radiotracer; Adsorption models

1. Introduction

Silver is a valuable noble metal and its compounds have a wide range of applications in photography, electroplating, alloys, jewelry, medicines, household utensils and ceramic materials [1,2]. Besides these important applications of silver, exposure to heavier dosage of silver can cause toxicity in living organism and leads to health and environmental problems. Exposure to high dosage of silver can decrease wound healing and discoloration of the skin (argyria) [3]. Therefore, cleaning and extraction of silver is of great environmental and economic significance. In general depending upon the nature of the species and their concentration, the literature reports a wide range of techniques for the removal of contaminants including precipitation [4], ion-exchange [5], solvent extractions [6], flotation [7], bioseparations [8] and reverse osmosis [9,10]. These methods suffered from some drawbacks and the researchers searched for some superior methods for the treatment of drinking/wastewater. In recent years, the idea of solid phase extraction gained wide spread attention and popularity [11,12] and a wide range of materials such as ion-exchangers [13], activated carbons [12], polymers/chitosan [14], etc., were employed for the selective removal of contaminants.

Nowadays organo-silica's are selectively used in solid phase extractions. Organo-silica with organic groups is employed in preconcentration procedure [12], ion-exchange [15], biotechnology [16], catalysis [17] and green chemistry [18]. The literature shows that various functionalized sorbents have been used for the extraction of metal ions from solutions. Thiol functionalized adsorbents were used for silver and mercury ions extraction [19–22]. Vieira et al. [23] studied the

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adsorption of mercury, silver and other cations on the surface of –SH groups modified silica gel. Kang et al. [24] confirmed selective adsorption of noble metal ions on functionalized mesoporous silica. These adsorbents displayed promising selectively that is of great help in many applications such as wastewater treatment that consists of mixture of heavy metals.

Although the literature reports a number of adsorbents for silver removal such as chelating resins [25], functionalized silica [26], clay [27], activated carbons [28], copolymers [29] and ion-exchanger [30] but a comprehensive report of silver adsorption on functionalized silica is lacking. Therefore, in this study a novel functionalized adsorbent was synthesized by covalent attachment of organic compound to the silica surface using sol–gel method. This adsorbent was employed for the extraction of silver ions in batch mode using radiotracer. The adsorbent showed great promise and effectively removed silver ions from aqueous solution.

2. Experimental setup

2.1. Chemicals/methods used

The silica precursor tetraethoxyorthosilicate (97%), templating agent *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide, chelating ligand thiosemicarbazide and 3-aminopropyltrimethoxysilane (3-APTMS, 98%) were all provided by Sigma-Aldrich (USA). All other analytical grade chemicals were used as supplied. Double distilled water distilled by Exelo ES-51 Still was used in the preparation of solutions, rinsing of glasswares and washing of sorbents. All pH measurements were made on a Metrohm-605 pH meter. The shaking was carried out in a 30 mL Pyrex glass vials lined with screw-type polythene cap. Gross gamma-ray detection was made on a Tennelec, USA, counting assembly equipped with a 25 cm^3 NaI (Tl) crystal.

^{110}Ag radiotracer was synthesized by the neutron activation of the pure metal in the research reactor (PINSTECH, Islamabad). 17.0 mg of metal oxide contained in polythene capsule was subjected to neutron irradiation (7×10^{13} n/cm^2 s) for 10 hrs. The treated metal oxide was dissolved in 5.0 cm^3 concentrated HNO_3 (65%) followed by 1 week cooling. The excessive acid was removed by continuous dilution with water and evaporation. Finally, a 5.0 cm^3 stock solution of the metal was prepared by diluting with deionized water. Further solutions were prepared by dilution method. The purity of the radiotracer was confirmed by Ge(Li) detector attached to a multichannel analyzer of 85 Canberra.

Buffer solutions of pH 1–8 were prepared by adding appropriate volumes of KCl and HCl (pH 1–2), sodium acetate and acetic acid (pH 3–6), pH 7–8 buffers were prepared by mixing boric acid and sodium hydroxide.

2.2. Synthesis of organo-silica

Organo-silica was synthesized by sol–gel route as reported earlier [31]. 3-APTMS modified silica is synthesized as described [32]. The amine functionalized silica was mixed with 5.0 g of chelating ligand thiosemicarbazide in deionized water (50.0 mL) on a hot plate in a three necked flask. 37% formaldehyde (30.0 mL) was introduced to this flask and refluxed (1 h). Excessive formaldehyde and water from the mixture was evaporated. Amine functionalized silica (10.0 g) and methanol (50.0 mL) were then added to the reaction mixture and refluxed again for 1 h. The resulting thiosemicarbazide functionalized silica was washed repeatedly with deionized water and organic solvents. The functionalized silica was kept in oven at 45°C for 10 hrs followed by drying in room temperature.

2.3. Procedure for Ag(II) ions adsorption

Ag(II) extraction was examined in batch mode using ^{110}Ag radiotracer. The adsorption experiments were performed at room temperature or as stated otherwise. 1.54×10^{-4} M of tracer solution was introduced to 5.0 mL glass culture tube having a solution of pH 5. This solution was equilibrated for 5.0 min to mix the activity uniformly and 1.0 mL was taken out for measuring gross gamma counts (A_0). Functionalized silica was introduced to this glass tube and shaken for 30 min on a mechanical shaker (wrist action, Griffin, UK). After equilibration and centrifugation for 5.0 min, 1.0 mL of the tracer solution was taken out for gamma counts (A_e). Percentage adsorption was measured as:

$$\% \text{ adsorption} = \frac{A_0 - A_e}{A_0} \times 100 \tag{1}$$

The distribution coefficient (K_d) is:

$$K_d = \frac{\text{Amount of metal ions adsorbed}}{\text{Amount of metal ions in solution}} \times \frac{\text{volume of solution (V)}}{\text{mass of the adsorbent (W)}} \left(\frac{\text{cm}^2}{\text{g}} \right) \tag{2}$$

3. Results and discussions

3.1. Structural characteristics of the adsorbent

Brunauer- Emmett- Teller surface area results were used to determine the textural characteristics of the as synthesized silica. The results showed that the product was porous with a high specific surface area of around 922 m^2/g, pore volume of 0.95 cm^3/g and pore diameter of around 4.18 nm. The scanning electron microscopy micrographs revealed the spherical morphologies of the silica and established that the original morphologies are retained after functionalization. The Energy-dispersive X-ray spectroscopy (EDX) results confirmed the existence of sulfur and oxygen along with carbon and silicon as a result of organic modification (Fig. 1).

The Fourier transform infrared spectroscopy (FTIR) analysis of the functionalized silica (Fig. 2(a)) showed adsorption peak at around 3,392.93 cm^{-1}, which was ascribed to the Si–OH stretching vibration and adsorbed water molecule. The asymmetric and bending vibration of siloxane network (Si–O–Si) was observed at 471.47 and 576.11 cm^{-1} [9]. The N–H bending vibration occurred at 1,569.57 and 1,659.57 cm^{-1}. The absorption peaks at 1,344.93 and 1,489.57 cm^{-1} are attributed to the functional group (–S=C–NH) vibration of organic ligand [33,34]. The –C=S group expected vibration peaks in the range from 730 to 1,089 cm^{-1} were not observed and these peaks may probably overlap with skeletal vibration of silica network.

The thermogram for functionalized silica is shown in Fig. 2(b). Three different mass losses were recorded for

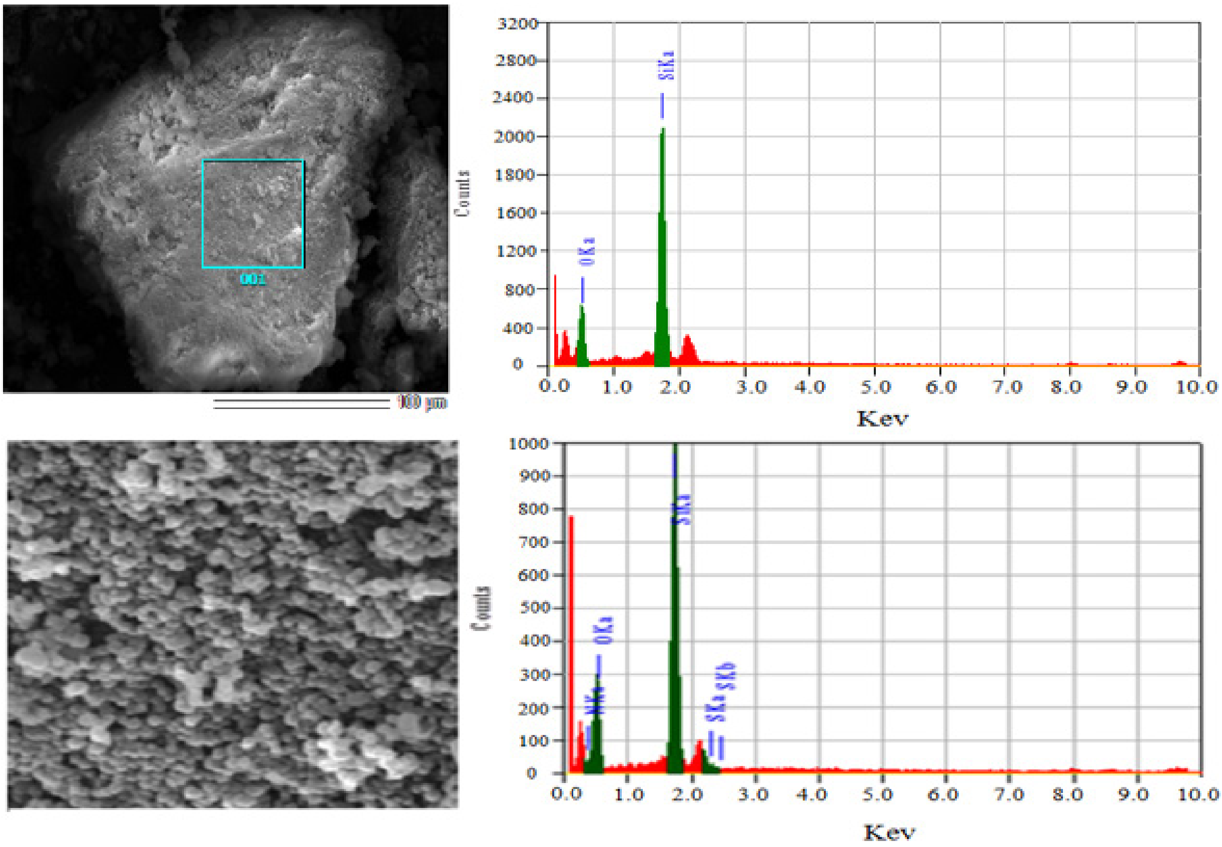

Fig. 1. EDX spectra of as synthesized (upper) and functionalized silica (lower).

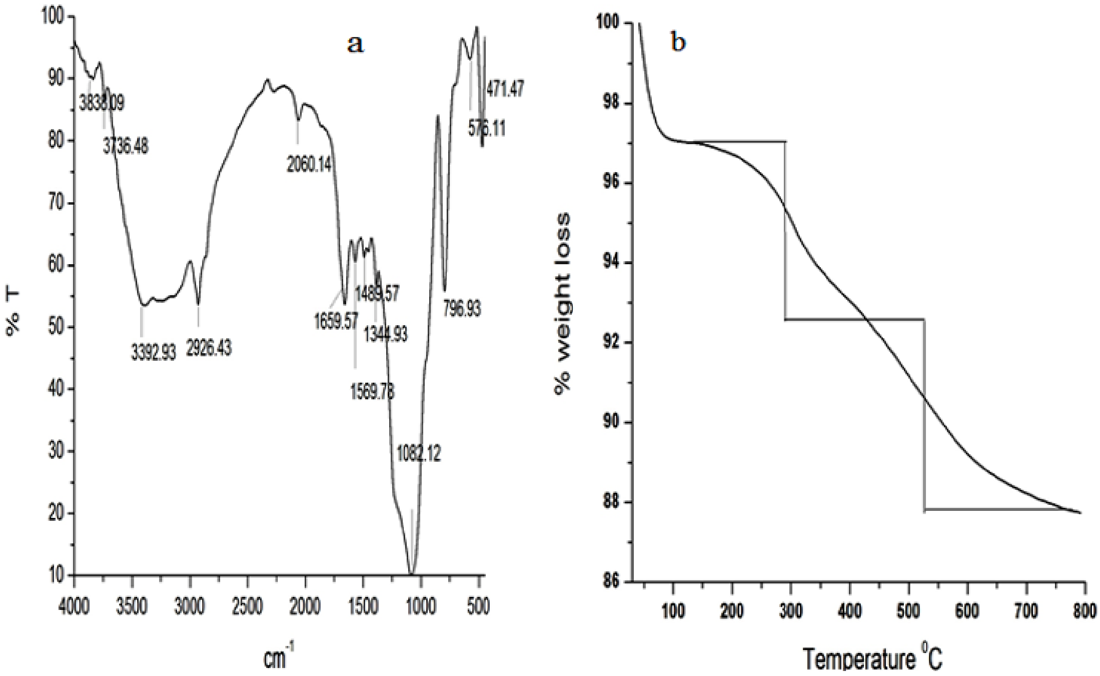

Fig. 2. FTIR (a) and Thermogravimetric analysis investigation (b) of functionalized silica.

functionalized silica. The mass loss from 30°C to 250°C (3%) is due to the evaporation of the water adsorbed and located in silica channels [35,36]. The mass loss in the region of 250°C–500°C is around 3% is due to the loss of organic groups. The mass loss from 500°C to 700°C is allocated to the condensation of surface silanol (Si–O–Si) to siloxane (Si–OH)

[37,38]. The overall mass loss of the adsorbent is around 12%, owing to the evaporation of adsorbed water or the decomposition of functionalized groups.

3.2. Adsorption studies of silver on nano silica

3.2.1. Effect of pH and mechanism of Ag(II) ions adsorption

pH is an important factor for metal ions speciation and sequestration. According to SHAB concept of soft and hard acids and bases [39], with the changes in solution pH, the functional groups (–NH_2 and –S=C–NH) of the adsorbent may become soft or hard for the metal ions and thus affect the extraction efficiency of the adsorbent. The effect of varying solution pH 1–8 on adsorption is presented in Fig. 3. The results showed that the percentage adsorption of Ag(II) increased as pH of the solution increased and approached maximum at pH 5, signifying that the acidic media helps the Ag(II) adsorption. At this pH, the nitrogen (–NH_2) and sulfur (–C=S) containing donor groups become available for coordination with Ag(II) ions. In acidic medium ($pH < 5$), H^+ is in abundance and compete with metal ions for available adsorption sites [40] and makes it difficult for metal cation to adsorb on the surface and hence the result is lower adsorption [41]. At $pH > 5$, the OH^- is a competing counter ion for the metal ion which results in lower adsorption. At pH 5, the two phenomenon's are counter balanced ideally and the Ag(II) adsorption is maximum. pH 5 was chosen as an optimal pH for further experiments. These result are in agreement with previous reports [29,42].

3.2.2. Adsorption kinetics of Ag(II)

Ag(II) ions adsorption kinetics was examined by equilibrating an optimum quantity of 30 mg of the adsorbent with 1.55 × 10^{-5} M Ag(II) ions at pH = 5. The adsorbent was recovered from absorption media by centrifugation after agitation at different intervals of time and analyzed. The Ag(II) ions adsorption kinetics was examined within a time range of 5–60 min (Fig. 4). The data showed that there was an increase in silver adsorption up to 30 min and then it became steady. These results showed that the adsorption equilibrium between silver ions and the adsorbent is quick and around 96% silver is removed within 30 min. Similar observations are also reported in literature [29]. These investigations suggested that the functionalized adsorbent has a good affinity for silver. The steady silver extraction after the equilibrium is owing to the saturation of the adsorbent.

The kinetic details of mass transfer were examined by using Morris–Webber and Lagergren equations [25]. The results of Morris–Webber plot suggested that the intraparticle diffusion predominantly controlled the adsorption with a diffusion rate, R_D of 0.863 μmol/g/min. The Lagergren plot showed that the Ag(II) adsorption is kinetically first-order process with $K = 0.1020$ min^{-1}. Such kinetic observations are also reported earlier [43].

3.2.3. Effect of quantity of adsorbent on silver removal

The adsorbent quantity was varied from 10 to 60 mg under optimized conditions, using 1.55 × 10^{-5} M Ag(II) at pH 5 (Fig. 5). The adsorption of silver increased directly with increasing adsorbent quantity up to 30 mg and then it became steady. 30 mg of adsorbent extracted around 96% of Ag(II) and was chosen as optimum amount for further experiments.

3.2.4. Adsorption isotherms

The quantity adsorbed under optimized condition is known as adsorption isotherm. It is an essential requirement for large scale application of adsorption process [44]. It provides information about the quantity of adsorbent needed for the removal of a given amount of metal ions under optimized conditions at constant temperature. The effect of initail concentration of Ag(II) on its adsorption was studied under optimimal conditions and presented in Fig. 6. Initially with increasing concentration, the adsorption increased and attained maximum of 97% up to eightfolds increase in concentration and then declined upon the saturation of the adsorbent. At this point 1,319.20 μg/g of Ag(II) is adsorbed, which is the maximum adsorption capacity of the functionlized nano silica.

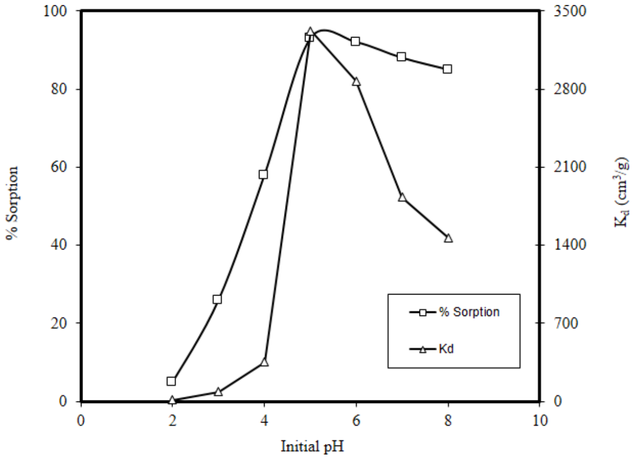

Fig. 3. The effect of initial pH on Ag(II) adsorption onto nano silica.

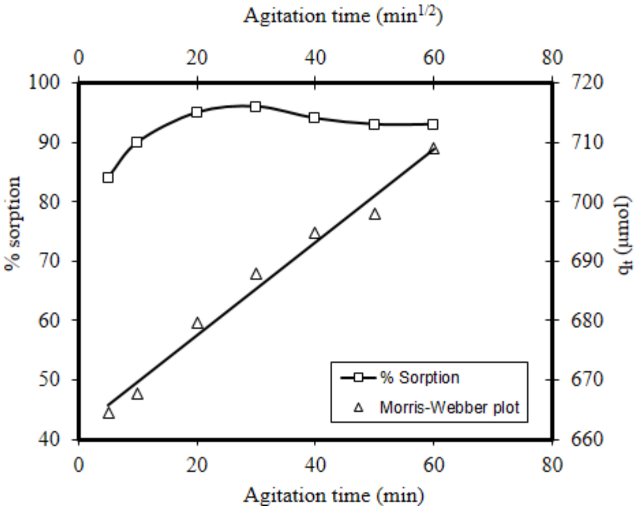

Fig. 4. Kinetics of silver adsorption onto organo-silica.

The equilibrium data were feed to several adsorption models such as Langmuir, Freundlich and D–R [32]. This treatment of data is necessary for the designing of future industrial operations. The isotherms were applied to the equilibrium adsorption data and various constants computed are reported in Table 1.

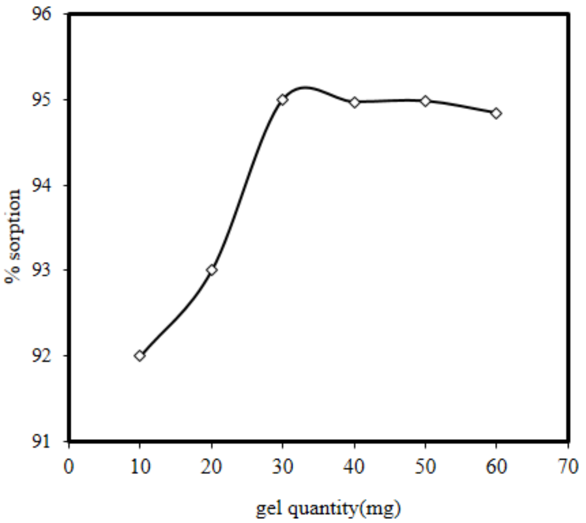

Fig. 5. Adsorbent dosage effect on Ag(II) adsorption onto nano silica.

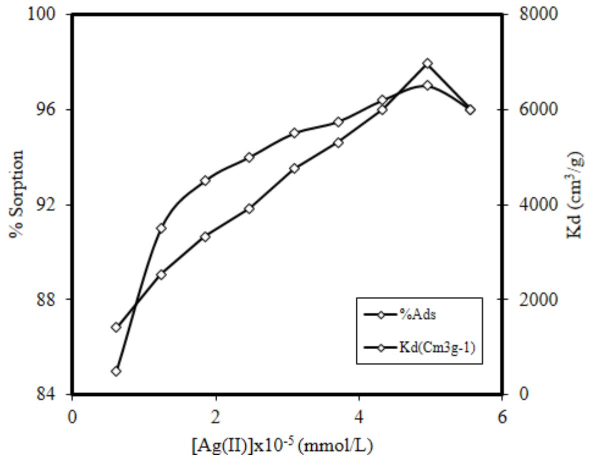

Fig. 6. Isotherm of Ag(II) ions adsorption onto functionalized nano silica.

3.2.5. *Effect of temperature on Ag(II) removal*

According to the law of conservation of energy, energy can neither be created nor destroyed in an isolated system and the change in entropy is the only driving force [45]. The energy and change in entropy both should be taken into account to predict the spontaneity of the adsorption process. To explain whether the adsorption of silver is spontaneous or not, the temperature of the system was varied over 283–323 K using optimal conditions and the corresponding thermodynamic parameters were determined [46].

$$\log K_c = \frac{-\Delta H}{2.303\,RT} + \frac{\Delta S}{2.303\,R} \tag{3}$$

$$\Delta G = -RT\,\text{In}K_c \tag{4}$$

where $K_c = F/1-F$ and 'F' is the fraction of silver adsorbed at equilibrium, T is the temperature (K) and R is the universal gas constant in units of J/mol/K. The quantity $1/T$ was plotted vs. $\log K_c$ and is depicted in Fig. 7. The differential enthalpy $\Delta H = -18.54$ J/mol/K and entropy $\Delta S = 85.09$ J/K/mol are computed from the slope and intercept of the figure. The change in entropy suggested the stability of Ag-ligand complexes. The negative ΔH value showed that silver adsorption is exothermic process and the change in Gibb's free energy (ΔG = –5,639.30 J/K/mol at 293.16 K) revealed the spontaneous adsorption. Similar thermodynamic findings regarding silver adsorption are also reported earlier [43,47].

3.2.6. *Regeneration of the adsorbent and recovery of Ag(II)*

The silver adsorbed on the adsorbent was recovered completely by agitating the adsorbent with HCl (1.0 M). The functionalized adsorbent was reconditioned with distilled water and pH solution. The regenerated adsorbent was again recycled for the removal of silver and used in three sorption desorption cycles for silver extraction. The adsorbent remained stable and did not deteriorated. The adsorption capacity of the regenerated adsorbent (96.5%, 94.7% and 94%) was very close to that of the freshly prepared adsorbent (97%).

Table 1
Isotherms constants of adsorption models

Freundlich isotherm			Langmuir isotherm			D–R isotherm			
$\log C_{\text{ads}} = \log C_m + \frac{1}{n}\log C_e$			$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Q_b} + \frac{C_e}{Q}$			$\ln C_{\text{ads}} = \ln X_m - \beta\varepsilon^2$ $\varepsilon = RT\left(1+\frac{1}{C_e}\right)$			
C_m (mmol/g)	$1/n$	R^2	Q (μmol/g)	$b \times 10^3$ (L/mol)	R^2	X_m (mmol/g)	β (kJ²/mol²)	E_s (kJ²/mol)	R^2
1.18	0.70	0.99	2,000	555.55	0.99	321.37	–0.0168	8.0	0.99

Note: C_e, equilibrium Ag(II) concentration (mol/L); b, Langmuir constant; C_m, Freundlich sorption capacity; $1/n$, sorption intensity, equilibrium Ag(II) concentration (mol/dm³); Q, maximum adsorption capacity; R, gas constant (8.314 J/mol K); R^2, regression coefficient; T, Kelvin temperature, β, D–R constant in units of kJ²/mol²; ε, Polanyi potential (J/mol) and E_s, mean sorption energy.

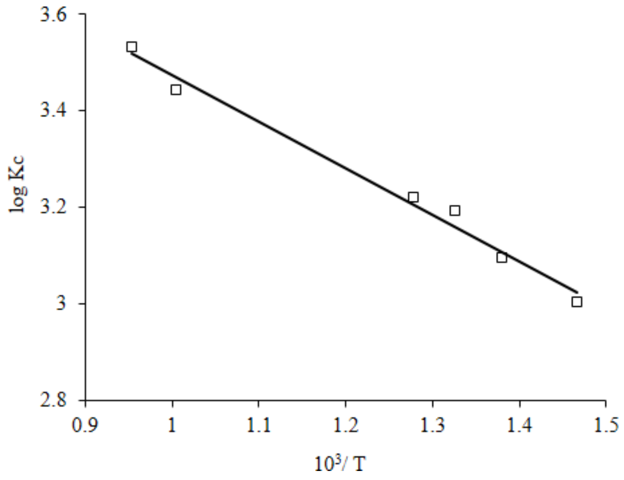

Fig. 7. Thermodynamics of Ag(II) adsorption onto nano silica.

4. Conclusions

Nitrogen and sulfur donor atoms containing organo-silica was synthesized by covalent grafting of chelating ligand. The adsorbent was applied for Ag(II) ions extraction in batch experiments. The adsorbent can extract 97% of silver at optimal conditions of pH 5 and 30 min equilibration. The Ag(II) ions equilibrium adsorption data followed Freundlich, Langmuir and D–R isotherms and Langmuir model predicted a maximum sorption capacity of 2,000 μmol/g under optimized conditions. The kinetic details established that silver adsorption follows first-order (with $K = 0.1020\ \text{min}^{-1}$) and the mass transfer models examined suggested that the intraparticle and surface diffusion predominantly controlled the Ag(II) adsorption with a diffusion rate, R_D of 0.863 μmol/g/min. The differential entropy (ΔS = 85.09 J/mol K) showed that the adsorption is favorable and Ag(II) complexes are stable. The free energy (ΔG = –5639.30 J/mol) and enthalpy (ΔH = 18.54 J/mol K) reflected spontaneous and endothermic adsorption of Ag(II). The mean adsorption energy (E_s = 8.0 kJ/mol) established the chemisorption nature of adsorption. The adsorbent can be regenerated by agitation with 1.0 M HCl and used for several times.

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