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ORIGINAL PAPER

Sol–gel derived ion imprinted thiocyanato-functionalized silica gel as selective adsorbent of cadmium(II)

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Abstract A Cd(II)-imprinted thiocyanato-functionalized silica gel adsorbent with high adsorption capacity was prepared by surface imprinting technique combined with sol–gel process for the selective adsorption of Cd(II) ion in aqueous solution, and was characterized by Fourier-transform infrared spectroscopy, nitrogen gas sorption and thermogravimetric analysis. The influences of different conditions (such as the pH of solutions, the contact time and the initial concentrations of Cd(II) ions) on the adsorption capacity of Cd(II) were investigated. The optimum pH of adsorption was in the range of 4–8.5. The adsorption equilibrium could be reached in 20 min. The relatively selectivity coefficients of the imprinted silica were higher than those of the non-imprinted adsorbents. Ho's pseudo-second-order model well described the kinetics of the adsorption reaction. The adsorption process of metals followed Redlich–Peterson isotherm model, and the experimental value of maximum adsorption capacity for Cd(II) was 72.8 mg·g^{-1}. The positive value of ΔH^o suggested endothermic nature of Cd(II) adsorption on the imprinted silica adsorbent. Increase in entropy of adsorption reaction was shown by the positive value of ΔS^o and the negative value of ΔG^o indicating that the adsorption was spontaneous in nature.

Keywords Ion imprinted · Sol–gel · Silica gel functionalization · Cd(II) Adsorption

1 Introduction

Cadmium is carcinogenic to human as well as it adversely affects animal tissues. Cadmium has an extremely long biological half-life that essentially makes it accumulative toxin [1, 2]. However, as the levels of cadmium in geological and environmental samples are low, the separation and removal of cadmium from the natural water is essential and needs much more attention [3–5].

Materials that specifically recognize cadmium may be created in synthetic polymers with a technique called ionic imprinting [6–10]. Ionic imprinted polymers (IIPs) are attractive materials that enable the selective extraction, separation and removal of cadmium from complex mixtures [6–10]. The preparation of IIPs based on the ion-imprinting concept was described: a matrix is synthesized in the presence of an ionic template and chelating ligands are then obtained by removal of the targeted ion [11, 12]. The cavities obtained in the polymer exhibit high selectivity towards specific metal ions [6–12]. The selectivity of the corresponding ion-adsorption process by a matrix relies on the specific interactions that the metal ion makes based on its size, charge, coordination number and coordination geometry in the binding site [11, 12]. Recently, surface ionic imprinted functionalized silica with outstanding advantages, such as being simple, convenient to prepare, high selectivity, fast mass transport rates, good mechanical and thermal stabilities, have been developed for the selective removal or separation of heavy metals from aqueous solution [13–15]. Two different routes to achieve the surface ionic imprinted functionalized silica are available. One is surface grafting

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imprinting method by surface functionalization of the silanol groups of already formed silica particles. Another is that silylation can be done at the monomer level, and then the functional monomers are co-condensed with silica precursors to form surface ionic imprinted functionalized silica particles. Compared to surface grafting imprinting method, the ionic imprinted functionalized silica which is prepared by surface imprinting technique combined with sol–gel processing has a higher adsorption capacity which is an important factor to evaluate the adsorbents and determines how much adsorbent is required to quantitatively concentrate the targeted ion from a given solution. However, the synthesis of surface ionic imprinted functionalized silica materials using a surface imprinting technique combined with sol–gel processing has been reported with only few articles [16–18].

Thiocyanato groups show strong affinity for cadmium ions and ideal functional sites on functionalized silica materials as an efficient adsorbent to remove heavy metal ions in waters [19–21]. In this paper, a Cd(II)-imprinted thiocyanato-functionalized silica gel adsorbent was synthesized via a surface imprinting technique combined with sol–gel process for the selective adsorption of Cd(II) ion from aqueous solutions. The materials were characterized using Fourier-transform infrared spectroscopy, nitrogen gas sorption and thermogravimetric analysis. Adsorption behaviors, adsorption isotherm, kinetics and thermodynamic of Cd(II) adsorption onto Cd(II)-imprinted thiocyanato-functionalized silica were studied.

2 Experimental

2.1 Materials

The tetraethoxysilane (TEOS), ethanol, $CdCl_2{\cdot}2.5H_2O$, $ZnCl_2$, $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Pb(NO_3)_2$, NaOH, HCl and $NH_3{\cdot}H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. 3-Thiocyanatopropyltriethoxysilane (TCPTS) was obtained from Jingzhou Jianghan Fine Chemical Co., Ltd., Hubei, China.

2.2 Apparatus

FT-IR spectra (4,000–450 cm^{-1}) with KBr pellets and a resolution of 1 cm^{-1} were recorded using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA). An ASAP-2010C surface analyser (Micromeritics, USA) was used for the study of surface area. An AA-6300c flame atomic absorption spectrometer (FAAS, Shimadzu Corporation, Japan) was used to measure the concentrations of Cd(II), Cu(II), Co(II), Zn(II) and Pb(II) in aqueous solutions after appropriate dilutions and acidification to pH $\sim$ 2 adjusted with HNO_3. Thermogravimetric analysis was performed on a TGA/DSC1 thermogravimetric analyzer (Mettler-Toledo Inc., Switzerland). The solution blanks were below the instrument detection limits of 15 $\mu g{\cdot}L^{-1}$ for Cd(II), 20 $\mu g{\cdot}L^{-1}$ for Cu(II), 20 $\mu g{\cdot}L^{-1}$ for Zn(II), 30 $\mu g{\cdot}L^{-1}$ for Ni(II), 30 $\mu g{\cdot}L^{-1}$ for Co(II) and 300 $\mu g{\cdot}L^{-1}$ for Pb(II). A PB-10 pH meter (Sartorius, German) was used for the pH measurement.

2.3 Preparation of Cd(II)-imprinted thiocyanato-functionalized silica

The Cd(II)-imprinted thiocyanato-functionalized silica adsorbent was prepared by base–catalyzed sol–gel process with 0.1 $mol{\cdot}L^{-1}$ of ammonium hydroxide solution [16–18]. Solution (a) was prepared by mixing 20 mL of TEOS and 10 mL of H_2O and the pH was adjusted at 2.0 with the addition of 1 $mol{\cdot}L^{-1}$ HCl for stirring 30 min. Solution (b) was prepared by mixing 1.92 g of $CdCl_2$ 2.5 H_2O which was dissolved in 40 mL of methanol and 40 mL of H_2O, and 4 mL of TCPTS under stirring for 1 h. Solution (a) and (b) were mixed and added dropwise 0.1 $mol{\cdot}L^{-1}$ of ammonium hydroxide solution (pH $\approx$ 5) under stirring at 333 K for 30 min. Gel formed was aged for 48 h at room temperature. Then, the white solid was filtered and washed by 1 $mol{\cdot}L^{-1}$ HCl solution until the cadmium concentration in the filtrated solution is undetectable by FASS. The resulting gels were neutralized with 0.1 $mol{\cdot}L^{-1}$ $NaHCO_3$ to pH 7.5, filtered, washed with deionized water, and dried under vacuum at 60 °C for 12 h. Furthermore, the Cd(II)-imprinted thiocyanato-functionalized silica gel was sieved to obtain the particle size between 100 and 200 mesh. For comparison, the non-imprinted silica adsorbents was also prepared using an identical procedure, but without the addition of $CdCl_2{\cdot}2.5\ H_2O$.

2.4 Characterization of Cd(II)-imprinted thiocyanato-functionalized silica

The Cd(II)-imprinted thiocyanato-functionalized silica were characterized by IR and thermogravimetric analysis spectra. The surface areas of Cd(II)-imprinted silica and non-imprinted silica were determined from adsorption–desorption isotherms of nitrogen at 77 K. Specific surface areas were estimated using BET equation. Meanwhile, the pore volume and pore diameter were evaluated using Barrett-Joyer-Halendal (BJH) model.

2.5 Cadmium adsorption studies

Adsorption of Cd(II) from aqueous solutions was investigated in a batch experiments. The stock solution of Cd(II) (1,000 $mg{\cdot}L^{-1}$) was prepared by dissolving a known amount of $CdCl_2$ $2.5H_2O$ in distilled water and batch process for the adsorption was carried out. 0.2 g of dry adsorbent was placed in 50 mL of solution with different Cd(II) concentrations in a conical flask. This was then placed in a shaker incubator at 100 rpm for desired time interval. The concentration of Cd(II) in the supernatant solution was determined by FAAS to estimate the adsorbed amount of Cd(II). The adsorption capacity of metal ions was determined from equilibrium binding data by following equation:

$$Q = \frac{(Ci - Cf)V}{1000\ W} \tag{1}$$

where C_i and C_f are the initial and final concentration of Cd(II) (mg·L^{-1}) before and after the adsorption, V is the volume of Cd(II) solution (mL), and W is the mass used of adsorbents (g).

Adsorption studies were carried out at varied adsorption concentrations (50–900 mg·L^{-1}), the varied pH values (2–10.5), and adsorption time (5–50 min). The selective adsorption experiments of Cu(II), Co(II), Pb(II), Ni(II) and Zn(II) ions with respect to Cd(II) ions were conducted using the Cd(II)-imprinted silica or non-imprinted silica adsorbents. The Cd(II)-imprinted silica or non-imprinted silica adsorbents (0.1 g) were added to 25 mL of binary metal mixed aqueous solution containing 50 mg·L^{-1} Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Co(II) and Cd(II)/Pb(II) at a pH of 5 in the flasks with stirring. After adsorption equilibrium, the concentration of each ion in the remaining solution was measured by FAAS. The distribution and selectivity coefficients of Cu(II), Co(II), Pb(II) and Zn(II) with respect to Cd(II) can be obtained from equilibrium binding data according to Eqs. 2 and 3 [22].

$$K_d = [(C_i - C_f)/C_f](V/m) \tag{2}$$

In Eq. 2, K_d represents the distribution coefficient; C_i and C_f are the initial and final concentrations of metal ions (mg·L^{-1}), respectively. V is the volume of the solution (mL); m is the mass of Cd(II)-imprinted silica used (g).

$$k = K_d(Cd(II)) / K_d(X(II)) \tag{3}$$

In Eq. 3, k is the selectivity coefficient, and X(II) represents Cu(II), Co(II), Pb(II) and Zn(II) ions. A comparison of the k values of The Cd(II)-imprinted silica or non-imprinted silica adsorbents with those metal ions allows an estimation of the effect of imprinting on selectivity.

A relative selectivity coefficient $k^{'}$ (Eq. 4) can be defined as

$$k' = k_{\text{imprinted}}/k_{\text{non-imprinted}} \tag{4}$$

Results from the comparison of the $k^{'}$ values of Cd(II)-imprinted silica with non-imprinted silica adsorbents allow an estimation of the effect of imprinting on selectivity.

2.6 Repeated reuse

The adsorption/desorption cycle was performed up to nine times to evaluate the possibility of repeated reuse of the Cd(II)-imprinted silica adsorbent. The metal ions were removed from the adsorbents by washing with 3 mol·L^{-1} HCl for 2 h [19]. The adsorbents were rinsed several times with deionized water and then neutralized to pH 7.5 using 0.1 mol·L^{-1} $NaHCO_3$ solution to ensure complete H^+ neutralization. The adsorbents were washed again with deionized water and dried under vacuum at 60 °C overnight before another extraction cycle. The sorption capacity of each cycle was calculated as a percentage of the uptake at the first sorption.

The experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95 % were calculated for each set of samples in order to determine the margin error.

3 Results and discussion

3.1 Characterization

The FT-IR spectrum of Cd(II)-imprinted thiocyanato-functionalized silica adsorbent is shown in Fig. 1. The absorption bands at 3,419 and 1,635 cm^{-1} are assigned to OH groups due to the surface silanol groups with hydrogen bond and the remaining adsorbed water molecules. The absorption band at 2,937 cm^{-1} is assigned to CH_2 groups. The absorption band at 2,158 cm^{-1} is assigned to C = N vibrations of thiocyanato groups [23]. A broad peak is noted at 1,101 cm^{-1}, due to thesiloxane vibrations of $(SiO)_n$ groups. The band at 957 cm^{-1} is assigned to Si–OH stretching. The bands at 802 and 467 cm^{-1} are assigned to Si–O-Si stretching and Si–O-Si bending vibrations, respectively. The bands at 1,414 cm^{-1} corresponds to δ(N-CH_2) [24]. The results of FT-IR showed that TCPTS had been successfully immobilized on the surface of silica gel.

The specific surface area of the Cd(II)-imprinted silica and non-imprinted silica adsorbents was found to be 187 and 121 m^2·g^{-1}, respectively. The high surface area could reduce diffusion resistance and facilitate mass transfer. B J H desorption cumulative volumes of pores between 17,000 and 3,000,000 diameter of Cd(II)-imprinted silica and non-imprinted silica were 0.0228 and 0.0198 cm^3·g^{-1}, respectively. BJH desorption average pore diameter of Cd(II)-imprinted silica was 19.3 Å. The Cd(II)-imprinted silica mainly consisted of micropores with the size higher than 10 Å.

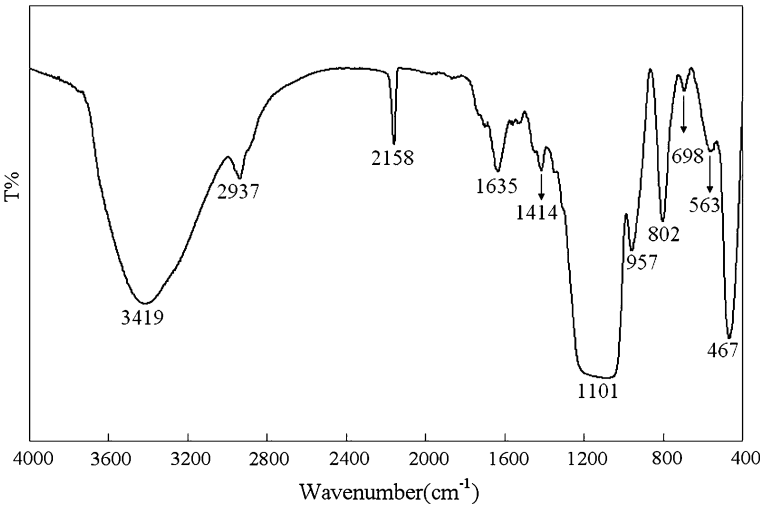

Fig. 1 IR spectra of Cd(II)-imprinted thiocyanato-functionalized silica gel

The TGA and DTA curves of Cd(II)-imprinted silica are presented in Fig. 2. DTA curves showed the presence of one exothermic peak at 353 °C attributed to the oxidative decomposition or combustion of the thiocyanato groups. A 9 wt% loss at temperature below 200 °C was due to a loss of residual water. The second 27 % step within the 200–530 °C interval, corresponded to the decomposition of the organic groups covalently bonded on the silica surface, together the condensation of the remaining silanol groups to produce siloxane groups. At continuous and small weight loss (2 %) was observed above 530 °C, which could be attributed to the combustion of residual organic material and/or to the desorption of water resulting from silanol condensation. The TGA and DTA results confirmed the successful incorporation of thiocyanato groups on the surface of silica.

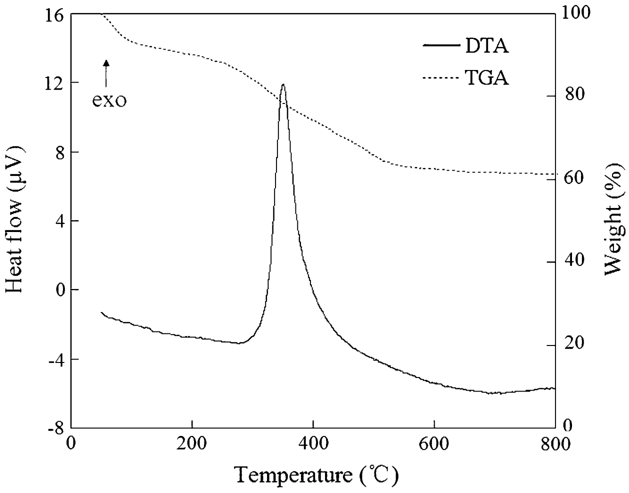

Fig. 2 TGA-DTA of Cd(II)-imprinted thiocyanato-functionalized silica gel

3.2 Effects of pH

Metal ion adsorption onto specific adsorbents is pH dependent. Figure 3 presents the effect of pH (2–10.5) on the Cd(II) adsorption. It could be seen that the adsorption of metals were found to be pH dependent and the uptakes were less at low pH and high pH. The adsorption capacity reached a plateau in range of pH from 4 to 8.5. In highly acidic medium ($pH < 4$), the active sites of the Cd(II)-imprinted silica adsorbent were protonated and the adsorption capacity of Cd(II) ion was reduced [25]. Small amount of Cd(II) were bound at $pH > 8.5$ due to the formation of insoluble hydroxide forms of metals. The optimum pH for metals uptake was recorded at pH range of 4–8.5. Thus, all the adsorption studies were carried out in low acidic medium ($pH = 5$) to avoid the formation of Cd(II) hydroxide.

3.3 Effects of the contact time

Figure 4 shows the time dependence of the adsorption capacity of Cd(II) ion on the Cd(II)-imprinted silica. It could be seen from Fig. 4 that the Cd(II) ions was adsorbed quickly within the first few minutes, and a complete equilibrium between the two phases was established in 20 min. This fast adsorption equilibrium was most probably due to high complexation and geometric shape affinity (or memory) between Cd(II) ions and the cavities of the Cd(II)-imprinted silica structure.

3.4 Effects of the initial metals concentrations

Figure 5 shows the initial concentrations of Cd(II) ion dependence of the adsorbed amount of the Cd(II) ions onto the Cd(II)-imprinted silica. The adsorption capacities increased with increasing concentrations of Cd(II) ions, and a saturation

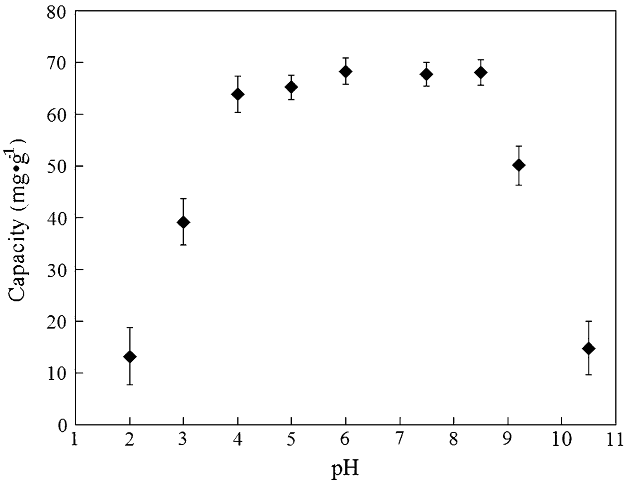

Fig. 3 Effect of pH on the adsorption capacity

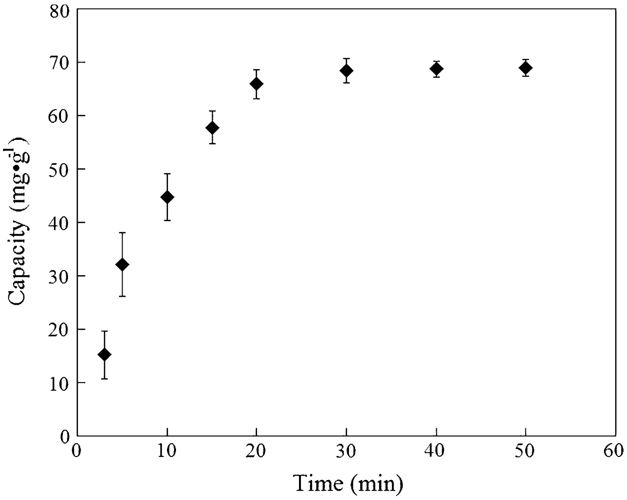

Fig. 4 Effect of the contact time on the adsorption capacity

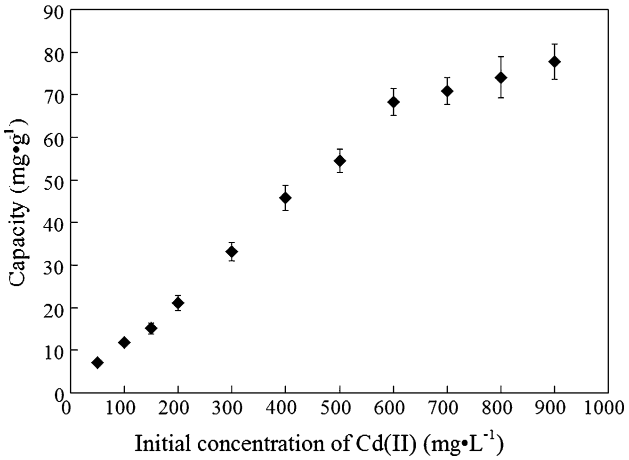

Fig. 5 Effect of initial concentrations on the adsorption capacity

value was achieved at ion concentration of 600 mg·L^{-1}, which represented the saturation of the active binding cavities on the Cd(II)-imprinted silica. The experimental value of maximum adsorption capacity was 72.8 mg·g^{-1}.

3.5 Adsorption isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. Three equilibrium models, including Langmuir isotherms, Freundlich isotherms, and Redlich–Peterson isotherm, were chosen to describe the adsorption process. The isotherm parameters were estimated by linear regression analysis.

The Langmuir sorption isotherm is often used to describe adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm can be represented in a linear expression as Eq. (5) [26]:

$$C_{eq}/q_{eq} = 1/(q_{max}b) + C_{eq}/q_{max} \tag{5}$$

where q_{eq} is the amount of adsorbed metals in the adsorbent (mg·g^{-1}), C_{eq} is the equilibrium ion concentration in solution (mg·L^{-1}), b (L·mg^{-1}) is the equilibrium constant related to the adsorption energy, and q_{max} is the maximum adsorption capacity (mg·g^{-1}).

The Freundlich expression is an exponential equation that describes reversible adsorption and is not restricted to the formation of the monolayer [27]. The linear form equation of Freundlich adsorption isotherm can be represented by Eq.(6)

$$\lg q_{eq} = \lg k_F + (1/n)\lg C_{eq} \tag{6}$$

where K_F and n are the Freundlich constants; C_{eq} is the equilibrium ion concentration in solution (mg·L^{-1}).

Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms [28], which incorporates three parameters into an empirical equation and can be applied either in homogeneous or heterogeneous systems due to its versatility [29].

$$q_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{g}} \tag{7}$$

where, q_{eq} amount of adsorbate in the adsorbent at equilibrium (mg·g^{-1}); C_{eq} equilibrium concentration (mg·L^{-1}); K_R Redlich–Peterson isotherm constant (L·g^{-1}); a_R Redlich–Peterson isotherm constant (L·mg^{-1});g Redlich–Peterson isotherm exponent which lies between 0 and 1, has two limiting behaviors: Langmuir form for $\beta = 1$ and Henry's law form for $\beta = 0$. This equation can be converted to a linear form by taking logarithms in Eq. (8)

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_R} + \frac{a_R}{K_R} C_{eq}^g \tag{8}$$

Plotting the left-hand side of Eq. (8) against $C_{\mathrm{eq}}^{\mathrm{g}}$ to obtain the isotherm constants is not applicable because of the three unknowns, a_{R}, K_R and g. Therefore, a minimization procedure is adopted to solve Eq. (8) by maximizing the correlation coefficient between the theoretical data for q_{eq} predicted from Eq. (8) and experimental data.

The relative parameters of Langmuir, Freundlich, and Redlich-Peterson isotherms by linear regression analysis were obtained from the plots of $C_{\mathrm{eq}}/q_{\mathrm{eq}}$ *versus* C_{eq}, $\lg q_{\mathrm{eq}}$ *versus* $\lg C_{\mathrm{eq}}$, and $C_{\mathrm{eq}}/q_{\mathrm{eq}}$ *versus* $C_{\mathrm{eq}}^{\mathrm{g}}$, respectively. The isotherm parameters are presented in Table 1. According to the correlation coefficients of isotherms (r^2), in the order of: Redlich-Peterson > Langmuir > Freundlich isotherm. Consequently, the Redlich-Peterson isotherm was found to be the most-suitable model for this adsorption system with a high coefficient of determination.

3.6 Adsorption dynamics

Parameters from four kinetic models, pseudo-first-order [30], pseudo-second-order [31], Elovich model [32, 33] and intraparticle diffusion model [34, 35] were fit to the experimental data to examine the adsorption kinetics of metals uptakes the Cd(II)-imprinted silica adsorbent.

The pseudo-first-order equation (Lagergren's equation) describes adsorption in solid–liquid systems based on the adsorption capacity of solids [30]. The linear form of pseudo first-order-model can be expressed as:

$$\lg(q_e - q_t) = \lg q_e - k_1 t/2.303 \tag{9}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first adsorption. q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (min), respectively. The rate constants k_1, q_e and correlation coefficients r^2 were calculated using the slope and intercept of plots of $\lg(q_{\mathrm{e}} - q_{\mathrm{t}})$ versus t (as shown in Table 2).

The pseudo-second-order rate expression, which has been applied for analyzing chemisorption kinetics from liquid solutions [31], is linearly expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{10}$$

where q_{e} and q_{t} are the adsorption capacity at equilibrium and time t ($\mathrm{mg \cdot g^{-1}}$), k_2 ($\mathrm{g \cdot mg^{-1} \cdot min^{-1}}$) is the rate constant of the pseudo-second-order adsorption. The rate constants k_2, q_{e} and correlation coefficients r^2 were calculated from the linear plots of t/q_{t} versus t (as shown in Table 2).

The Elovich equation is another rate equation in which the absorbing surface is heterogeneous [32, 33]. It is generally expressed as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{11}$$

Where α is the initial adsorption rate ($\mathrm{mg \cdot g^{-1} \cdot min^{-1}}$) and β is the desorption constant ($\mathrm{g \cdot mg^{-1}}$) during any one experiment. Integrating this equation for the boundary conditions, Eq. (11) becomes

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \tag{12}$$

A plot of q_{t} *vs* $\ln t$ gives a linear trace with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$. The results of Elovich plot for the adsorption of Cd(II) were given in Table 2.

Another simplified model, the intraparticle diffusion model, has been tested to better identify the diffusion mechanism involved [34, 35]. The intraparticle diffusion model is expressed as

$$q_t = k_i t^{0.5} \tag{13}$$

Where, k_{i} is the intraparticle diffusion rate constant ($\mathrm{mg \cdot g^{-1} \cdot min^{-0.5}}$) and is calculated by the slope of straight-line portion of plotting q_{t} *vs* $t^{0.5}$. The results were given in Table 2.

The R^2 values for pseudo-second-order kinetic model were higher than the pseudo-first-order kinetic model, Elovich model and intraparticle diffusion model. Results indicated better obeyed pseudo-second-order kinetic as compared to pseudo-first-order kinetic model, Elovich model and intraparticle diffusion model under the studied concentration range. The theoretical value of maximum adsorption capacity estimated from the pseudo-second-order kinetic model was very close to the experimental value. These results suggested that the pseudo-second-order mechanism was predominant, and that chemisorption might be the rate-limiting step that controls the adsorption process.

Table 1 Isotherms parameters for the adsorption of Cd(II) onto Cd(II)-imprinted thiocyanato-functionalized silica gel sorbent

Langmuir isotherm	Freundlich isotherm	Redlich–Peterson isotherm
$q_{\max} = 87.7\ \mathrm{mg \cdot g^{-1}}$	$K_{\mathrm{F}} = 0.42$	$K_{\mathrm{R}} = 0.0826\ \mathrm{L \cdot g^{-1}}$
$b = 0.16\ \mathrm{L \cdot mg^{-1}}$	$n = 1.17$	$a_{\mathrm{R}} = 0.311\ \mathrm{L \cdot mg^{-1}}$
		$g = 0.259$
$R^2 = 0.9899$	$R^2 = 0.9637$	$R^2 = 0.9999$

3.7 Selectivity experiment

Adsorption and competitive ion recognition studies were performed with the double mixture solutions of Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Co(II), Cd(II)/Ni(II) and Cd(II)/Pb(II) ions in order to measure the selectivity of the Cd(II)-imprinted silica adsorbent. The Cu(II), Zn(II), Co(II), Ni(II) and Pb(II) ions were chosen as the competitor species

Table 2 Calculated kinetic parameters for the adsorption of Cd(II) onto Cd(II)-imprinted thiocyanato-functionalized silica gel sorbent

Pseudo-first-order model	Pseudo-second-order model	Elovich model	Intraparticle diffusion model
$k_1 = 0.054\ \mathrm{min}^{-1}$	$k_2 = 2.03 \times 10^{-3}\cdot\mathrm{mg}^{-1}\cdot\mathrm{min}^{-1}$	$\alpha = 19.1\ \mathrm{mg}\cdot\mathrm{g}^{-1}\cdot\mathrm{min}^{-1}$	$k_i = 9.55\ \mathrm{mg}\cdot\mathrm{g}^{-1}\cdot\mathrm{min}^{-1}$
$q_{eq}(\mathrm{cal}) = 35.8\ \mathrm{mg}\cdot\mathrm{g}^{-1}$	$q_{eq}(\mathrm{cal}) = 79.4\ \mathrm{mg}\cdot\mathrm{g}^{-1}$	$\beta = 0.051\ \mathrm{g}^{-1}\cdot\mathrm{mg}$	
$r^2 = 0.8189$	$r^2 = 0.9924$	$r^2 = 0.9339$	$r^2 = 0.8139$

because they had the same charge and also binded well with the ligand. Table 3 summarizes the data for distribution coefficient (K_d), selectivity coefficient of the Cd(II)-imprinted silica adsorbent toward Cd(II) (k), and the relative selectivity coefficient (k') obtained in these competitive ion-binding experiments between Cd(II) and interfering ions.

Comparison of the K_d and k values for the Cd(II)-imprinted adsorbents with the non-imprinted adsorbent revealed a significant increase for Cd(II). The relative selectivity coefficients of the Cd(II)-imprinted adsorbents for Cd(II)/Cu(II), Cd(II)/Zn(II), Cd(II)/Co(II), Cd(II)/Ni(II) and Cd(II)/Pb(II) were 8.6, 10.1, 7.9, 9.9 and 12.8, respectively. Therefore, competitive adsorption between Cd(II) and interfering ions was apparent for the binary mixture and the Cd(II)-imprinted adsorbents showed the superiority of adsorption for Cd(II). Formation of the Cd(II)–SCN complex ultimately built template-selective recognition sites with functional ligands in a orderly stereochemical arrangement. However, the functional ligands of the non-imprinted adsorbent arranged randomly and disorderly, resulted in unremarkable selectivity performance.

3.8 Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative value. The thermodynamic parameters can be determined from the thermodynamic equilibrium constant, K_0. The standard Gibbs free energy ΔG^o ($\mathrm{kJ}\cdot\mathrm{mol}^{-1}$), standard enthalpy change ΔH^o ($\mathrm{kJ}\cdot\mathrm{mol}^{-1}$), and standard entropy change ΔS^o ($\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$) are calculated using the following equations:

$$\Delta G^o = -\mathrm{RT}\ \ln K_0 \tag{14}$$

$$\ln K_0 = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{15}$$

R, the universal gas constant, 8.314 $\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$, and T is the solute temperature (K). K_0 can be defined as [36–38]:

$$K_0 = \frac{a_s}{a_e} = \frac{\gamma_s}{\gamma_e}\frac{C_s}{C_e} \tag{16}$$

where a_s is the activity of adsorbed metals, a_e is the activity of metals in solution at equilibrium, γ_s is the activity coefficient of adsorbed metals, γ_e is the activity coefficient of metals in equilibrium solution, C_s is the metals adsorbed on Cd(II)-imprinted silica adsorbents ($\mathrm{mmol}\cdot\mathrm{g}^{-1}$), and C_e is the metals concentration in equilibrium solution ($\mathrm{mmol}\cdot\mathrm{mL}^{-1}$). The expression of K_0 can be simplified by assuming that the concentration in the solution approaches zero resulting in $C_s \to 0$ and $C_e \to 0$ and the activity coefficients approach unity at the every low concentration [36–38]. Equation (16) can be written as:

$$C_s \xrightarrow{\lim} 0 \frac{C_s}{C_e} = \frac{a_s}{a_e} = K_0 \tag{17}$$

K_0 at different temperatures was determined by plotting $\ln(C_s/C_e)$ versus C_s and extrapolating C_s to zero [36–38].The thermodynamic parameters, K_0, ΔG°, ΔH° and ΔS°, are shown in Table 4. The values of ΔH° and ΔS° for the adsorption process were calculated to be 9.16 $\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ and 45.80 $\mathrm{J}\cdot\mathrm{mol}^{-1}\mathrm{K}^{-1}$, respectively. The negative value of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption with a high preference for Cd(II) onto Cd(II)-imprinted silica. The value of ΔH° was positive, indicating that the adsorption reaction was endothermic. The positive value of ΔS° showed the increasing randomness at the solid/liquid interface during the adsorption of Cd(II) ions onto Cd(II)-imprinted silica.

Table 3 The selectivity parameters of Cd(II)-imprinted thiocyanato-functionalized silica gel sorbent

Metals	Sorbents	K_d		k	k'
		K_d (Cd)	K_d (X)		
Cd(II)/Co(II)	IIP	6,110	2,094	2.918	7.9
	NIP	1,148	3,114	0.369	
Cd(II)/Cu(II)	IIP	6,292	1,596	3.942	8.6
	NIP	1,104	2,406	0.459	
Cd(II)/Pb(II)	IIP	7,028	1,045	6.725	12.8
	NIP	1,064	2,022	0.526	
Cd(II)/Zn(II)	IIP	6,367	1,649	3.861	10.1
	NIP	1,018	2,648	0.384	
Cd(II)/Ni(II)	IIP	6,854	1,547	4.431	9.9
	NIP	1,231	2,756	0.447	

Table 4 The various thermodynamic parameters for the adsorption of Cd(II) on Cd(II)-imprinted thiocyanato-functionalized silica gel sorbent

Thermodynamic constants	Temperature (K)		
	298.15	308.15	318.15
K_0	6.17	6.82	7.79
ΔG^{o} (kJ mol^{-1})	−4.51	−4.92	−5.43
ΔH^{o} (kJ mol^{-1})	9.16	9.16	9.16
ΔS^{o} (J mol^{-1} K^{-1})	45.8	45.8	45.8

3.9 Regeneration

Regeneration of any exhausted adsorbent is an important factor in the adsorption process for improving the process economics. Regeneration allows for the repeated use of the adsorbent material and decreasing costs. After the nine adsorption/desorption cycle, the adsorption capacity of Cd(II) was found to about 80 % of the fresh adsorbent. The data showed that Cd(II)-imprinted silica had good regeneration ability.

4 Conclusion

In this work, the Cd(II)-imprinted thiocyanato-functionalized silica adsorbent which was prepared by surface imprinting technique combined with sol–gel processing exhibited high adsorption capacity of Cd(II), a stable uptake of metals at pH in the range of 4–8.5, fast adsorption kinetics, high selectivity for Cd(II), and facile regeneration property. The kinetic data showed well fitted pseudo-second-order kinetic model in compared to pseudo-first-order kinetic model, Elovich model and intraparticle diffusion model. The adsorption of Cd(II) on Cd(II)-imprinted thiocyanato-functionalized silica followed the Redlich–Peterson isotherm with the better correlation coefficients. Thermodynamic analysis showed that the adsorption process was endothermic and spontaneous in nature. It was concluded that the combination surface imprinting technique with sol–gel processing could be a promising technique for the preparation of the imprinted adsorbents with high adsorption capacity.

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References

1. Waalkes MP, Rehm S (1992) Carcinogenicity of oral cadmium in the male *Wistar* (WF/NCr) rat: effect of chronic dietary zinc deficiency. Fundam Appl Toxicol 19:512–520
2. Hydari S, Sharififard H, Nabavinia M, Parvizi M (2012) A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium. Chem Eng J 193–194:276–282
3. Elkady MF, Abu-Saied MA, Rahman AMA, Soliman EA, Elzatahry AA, Yossef ME, Eldin MSM (2011) Nano-sulphonated poly (glycidyl methacrylate) cations exchanger for cadmium ions removal: effects of operating parameters. Desalination 279: 152–162
4. Bhatnagar A, Minocha AK (2009) Utilization of industrial waste for cadmium removal from water and immobilization in cement. Chem Eng J 150:145–151
5. Mahmoud ME, Haggag SMS (2011) Static removal of cadmium from aqueous and nonaqueous matrices by application of layer-by-layer chemical deposition technique. Chem Eng J 166: 916–922
6. Fang G-Z, Tan J, Yan X-P (2005) An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol–gel process for selective solid-phase extraction of cadmium(II). Anal Chem 77:1734–1739
7. Segatelli MG, Santos VS, Presotto ABT, Yoshida IVP, Tarley CRT (2010) Cadmium ion-selective sorbent preconcentration method using ion imprinted poly(ethylene glycol dimethacrylate-co-vinylimidazole). React Funct Polym 70:325–333
8. Gawin M, Konefał J, Trzewik B, Walas S, Tobiasz A, Mrowiec H, Witek E (2010) Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium(II) via flow-injection-flame atomic absorption spectrometry. Talanta 80: 1305–1310
9. Fan H-T, Li J, Li Z-C, Sun T (2012) An ion-imprinted amino-functionalized silica gel sorbent prepared by hydrothermal assisted surface imprinting technique for selective removal of cadmium (II) from aqueous solution. Appl Surf Sci 258: 3815–3822
10. Mahmoud ME, Osman MM, Ahmed SB, Abdel-Fattah TM (2011) Improved adsorptive removal of cadmium from water by hybrid chemically and biologically carbonaceous sorbents. Chem Eng J 175:84–94
11. Rao TP, Kala R, Daniel S (2006) Metal ion-imprinted polymers—novel materials for selective recognition of inorganics. Anal Chim Acta 578:105–116
12. Rao TP, Daniel S, Gladis JM (2004) Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE), TrAC. Trends Anal Chem 23:28–35
13. Fan H-T, Sun T (2012) Selective removal of iron from aqueous solution using ion imprinted cyanato-functionalized silica gel sorbents. Sep Sci Technol 47:507–512
14. Chang X, Jiang N, Zheng H, He Q, Hu Z, Zhai Y, Cui Y (2007) Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique. Talanta 71:38–43
15. Fan H-T, Fan X, Li J, Guo M, Zhang D, Yan F, Sun T (2012) Selective removal of arsenic(V) from aqueous solution using a surface-ion-imprinted amine-functionalized silica gel sorbent. Ind Eng Chem Res 51:5216–5223
16. Buhani Narsito, Nuryono Kunarti E S (2010) Production of metal ion imprinted polymer from mercapto–silica through sol–gel process as selective adsorbent of cadmium. Desalination 251: 83–89
17. Lu Y-K, Yan X-P (2004) An imprinted organic-inorganic hybrid sorbent for selective separation of cadmium from aqueous solution. Anal Chem 76:453–457
18. Quirarte-Escalante CA, Soto V, de la Cruz W, Porras GR, Manríquez R, Gomez-Salazar S (2009) Synthesis of hybrid adsorbents combining sol-gel processing and molecular

imprinting applied to lead removal from aqueous streams. Chem Mater 21:1439–1450

19. Li Z-C, Fan H-T, Zhang Y, Chen M-X, Yu Z-Y, Cao X-Q, Sun T (2011) Cd(II)-imprinted polymer sorbents prepared by combination of surface imprinting technique with hydrothermal assisted sol–gel process for selective removal of cadmium(II) from aqueous solution. Chem Eng J 171:703–710
20. Blitz IP, Blitz JP, Guńko VM, Sheeran DJ (2007) Functionalized silicas: structural characteristics and adsorption of Cu(II) and Pb(II). Colloids Surf A 307:83–92
21. Fan H-T, Sun T (2012) Selective removal of iron from aqueous solution using ion imprinted thiocyanato-functionalized silica gel sorbents. Korean J Chem Eng 29:798–803
22. Andac M, Özyap E, Şenel S, Say R, Denizli A (2006) Ion-selective imprinted beads for aluminum removal from aqueous solutions. Ind Eng Chem Res 45:1780–1786
23. Grishchuk BD, Prodanchuk NG, Sinchenko VG, Gorbovoi PM, Kudrik EY (1994) Synthesis of thiocyanato-, isothiocyanato-, and halo derivatives of 1-arylpropanes and their antimicrobial properties. Pharm Chem J 28:657–659
24. Bois L, Bonhommé A, Ribes A, Pais B, Raffin G, Tessier F (2003) Functionalized silica for heavy metal ions adsorption. Colloids Surf A 221:221–230
25. Prakash S, Kumar M, Tripathi BP, Shahi VK (2010) Sol–gel derived poly(vinyl alcohol)-3-(2-aminoethylamino) propyltrimethoxysilane: cross-linked organic–inorganic hybrid beads for the removal of Pb(II) from aqueous solution. Chem Eng J 162:28–36
26. Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1403
27. Freundlich HMF (1906) Über die adsorption in lösungen. Z Phys Chem 57:385–470
28. Redlich O, Peterson DL (1959) A useful adsorption isotherm. J Phys Chem 63:1024–1026
29. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156:2–10
30. Lagergren S (1898) About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetensk Handl 24:1–39
31. Ho YS, McKay G (1999) Pseudo-second-order model for sorption processes. Process Biochem 34:451–465
32. Chien SH, Clayton WR (1980) Application of Elovich equation to the kinetics of phosphate release and sorption on soils. Soil Sci Soc Am J 44:265–268
33. Low MJD (1960) Kinetics of chemisorption of gases on solids. Chem Rev 60:267–312
34. Weber WJ, Morris JC (1963) Kinetics of adsorption of carbon from solutions. J Sanit Eng Div Am Soc Civ Eng 89:31–63
35. Allen SJ, McKay G, Khader KYH (1989) Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. Environ Pollut 56:39–50
36. Fan H-T, Wu J-B, Fan X-L, Zhang D-S, Su Z-J, Yan F, Sun T (2012) Removal of cadmium(II) and lead(II) from aqueous solution using sulfur-functionalized silica prepared by hydrothermal-assisted grafting method. Chem Eng J 198–199:355–363
37. Huang Y-H, Hsueh C-L, Cheng H-P, Su L-C, Chen C-Y (2007) Thermodynamics and kinetics of adsorption of Cu(II) onto waste iron oxide. J Hazard Mater 144:406–411
38. Fan H-T, Su Z-J, Fan X-L, Guo M–M, Wang J, Gao S, Sun T (2012) Sol–gel derived organic–inorganic hybrid sorbent for removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solution. J Sol-Gel Sci Technol 64:418–426