Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde

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Abstract

Magnetic chitosan resin was chemically modified by a Schiff's base cross-linker. The interaction of the resin obtained with Hg(II) was studied and uptake value of 2.8 mmol/g was reported. The kinetic and thermodynamic parameters of the adsorption process were estimated. These data indicated that the adsorption process is exothermic and follow the pseudo-second-order kinetics. The selectivity of Hg(II) from other different metal ions in solutions using the studied resin was also reported. Breakthrough curves for the recovery of Hg(II) were studied. The critical bed height was found to be 2.05 cm. The adsorbed Hg(II) was eluted from the resin effectively using 0.1 M potassium iodide.
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Keywords: Mercury; Resins: Chitosan; Recovery; Elution; Schiff's base

1. Introduction

Mercury contamination of the environment is caused by both natural and manmade sources. Natural sources include volcanic action and erosion of mercury-containing sediments. Some of the ways in which humans contaminate the environment with mercury include, mining, transportation and processing of mercury ores, dumping of industrial wastes into rivers and lakes, combustion of fossil fuels, pulp and paper industry, the use of mercury compounds as seed dressings in agriculture, and exhaust from smelters [1]. A broad spectrum of mercury treatment technologies has been described in the literature. These include precipitation, coagulation/co-precipitation, chemical reduction, membrane separation, biological treatment, and solid phase extraction (SPE) [2]. One of the promising methods is the use of chelating resins. Chelating resins are easily regenerated from metal ions and they differ from activated carbon and ion exchange resins in their high selectivity in sorption processes [3]. Many articles that cover a vast number of different chelating resins were reported [4–8]. Recently, we reported on the use of different chelating resins with various functionalities for the selective separation of mercury [9–12]. We also reported on the

use of magnetic resins in removal of some metals from aqueous solutions. These magnetic resins are easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free resin [13,14]. These methods are also cheap and often highly scalable. Moreover, techniques employing magnetism are more amenable to automation [15]. Attention has recently been focused on chitosan and its derivative as bioadsorbents. Chitosan is a major component of crustacean shells and one of the most abundant biopolymers in nature [16]. It is characterized by its ability to uptake several metal ions through different mechanisms, depending on the type of metal ion and the pH of the solution. The dissolution of chitosan was decreased through cross-linking treatments. The cross-linking procedure may be performed by reaction of chitosan with different cross-linking agents such as glutaraldehyde [17,18], 1,1,3,3-tetramethoxypropane [19], oxidized β-cyclodextrin (β-cyclodextrin polyaldehyde) [20], ethyleneglycol diglycidyl ether [21] or glycerolpolyglycidylether [22]. Tri-polyphosphate has also been selected as a possible cross-linking agent, which can be used for the preparation of chitosan gel beads by the coagulation/neutralization effect [23]. The cross-linking step may cause a significant decrease in metal uptake efficiency especially in the case of chemical reactions involving amine groups [24]. However, this limiting effect of chemical cross-linking significantly depends on the procedure used [12,18,25,26]. So the efforts have been

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directed towards modification by cross-linkers with chelating functionalities to improve the adsorption capacity. In the present work chemically modified magnetic chitosan with Schiff's base cross-linker will be prepared. The adsorption behaviour of the resin obtained towards Hg(II) will also be studied. Both kinetic and thermodynamic parameters of the adsorption process will also be calculated.

2. Experimental

2.1. Chemicals

Chitosan, glutaraldehyde, thiourea, ferric chloride, ferrous sulphate were Aldrich products. All other chemicals were Pro-labo products and were used as received. Mercuric chloride, cadmium nitrate, lead acetate, zinc chloride, copper acetate, calcium chloride and magnesium sulphate were used as a source for Hg(II), Cd(II), Pb(II), Zn(II), Cu(II), Ca(II) and Mg(II), respectively.

2.2. Preparation of magnetite

Magnetite was prepared using the modified Massart method [27]. A 250 mL (0.2 M) of $FeCl_3$ solution was mixed with 250 mL (1.2 M) of $FeSO_4$ solution. A 200 mL (1.5 M) of NH_4OH solution was added to the above solution of $FeCl_3/FeSO_4$ under vigorous stirring. A black precipitate was formed which was allowed to crystallize for another 30 min under magnetic stirring. The precipitate was filtered off and washed with deoxygenated water through magnetic decantation until the pH of the suspension became below 7.5.

2.3. Preparation of magnetic chitosan resin

One gram of chitosan was dissolved in 50 mL of 25% aqueous acetic acid solution. Three grams of thiourea (39.47 mmol) were dissolved in 100 mL distilled water. Twelve millilitres (25%) of glutaraldehyde solution (31.2 mmol) was added to thiourea solution in a round flask. The mixture was heated on a water bath for 2 h at 50 °C. Thereafter magnetite powder was added while stirring. The contents of the flask were then added to the chitosan solution and stirred until the solution become homogenous then heated up to 70 °C for 6 h. A large quantity of gel was formed, washed repeatedly with 0.5 NaOH solution then water and dried at 70 °C for 8 h. The dried gel was then grinded and sieved where the particle size fraction (−0.6/+0.5) mm was used in this study.

IR-spectra of the synthesized resin were performed using a Perkin-Elmer IR-spectrophotometer 550.

2.4. Preparation of solutions

A stock solution of Hg(II) (2×10^{-2} M) was prepared in distilled water. A stock solution of EDTA (5×10^{-3} M) was prepared and standardized against a solution of $MgSO_4 \cdot 7H_2O$ using Eriochrome Black-T (EBT). HCl and NaOH were used to change the acidity of the medium. Potassium iodide (0.1 M) was used as an eluent for stripping of Hg(II) from the resin.

2.5. Batch experiments

The effect of contact time on the uptake of Hg(II) by resin was studied by placing 0.1 g of dry resin that was swelled in a flask containing 50 mL of distilled water for 1 h. Fifty millilitres of metal ion solution (2×10^{-2} M) was added to the flask, where the concentration of the metal ion becomes (1×10^{-2} M) and pH 5. The contents of the flask were equilibrated for 3 h on a Vibromatic-384 shaker at 300 rpm and 28 ± 1 °C. Five millilitres of the solution was taken at different time intervals then filtered off, where the residual concentration of metal ion was determined via the titration against 5×10^{-3} M EDTA using PAR as indicator for Hg(II).

The selectivity studies of the investigated resin towards Hg(II) in the presence of binary mixtures of Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) or Mg(II) was carried at pH = 1. The estimation of these metal ions in the binary mixture was carried compleximetrically as above using murexide for Cu(II) and EBT for Ca(II), Mg(II), Cd(II), Zn(II) and Pb(II). KI was also used as a masking agent for Hg(II) [28].

Adsorption of Hg(II) on the resin obtained under controlled pH was carried out following the above procedures. The desired pH was controlled using HCl and NaOH while the equilibrium time was fixed at 3 h and 30 °C.
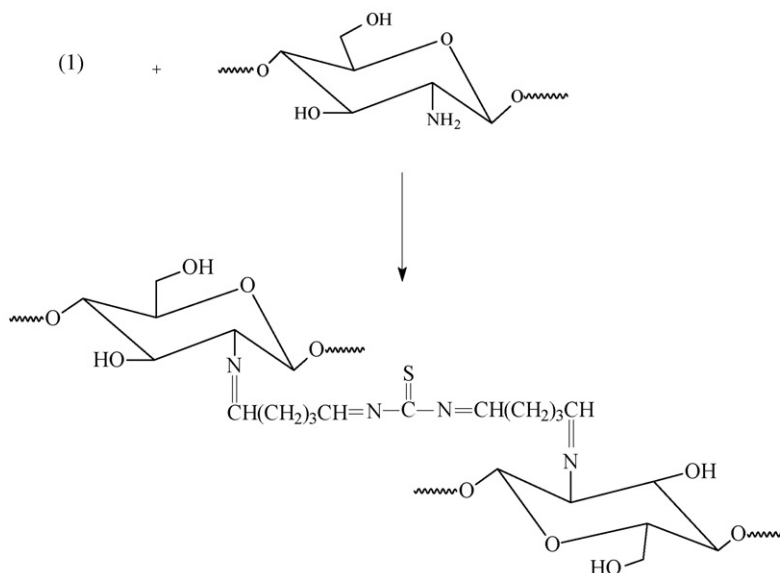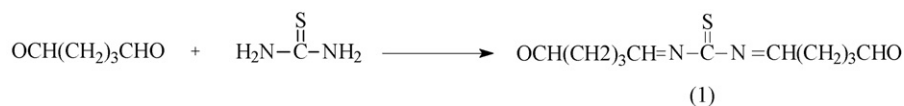
Complete adsorption isotherms were obtained by soaking 0.1 g of dry resin in a series of flasks containing 50 mL of distilled water for 1 h. Fifty millilitres of metal ions with different concentrations were added to each flask and pH 5 was recorded. The flasks were conditioned at 300 rpm while keeping the temperature at 30, 40, 50 or 60 °C for 3 h. Later on, the residual concentration was determined where the metal ion uptake was estimated.

2.6. Column experiments

Column experiments were performed in a plastic column with a length of 10 cm and a diameter of 1.0 cm. A small amount of glass wool was placed at the bottom of the column to keep the contents. A known quantity of the resin under investigation was placed in the column to yield the desired bed height. Hg(II) solution having an initial concentration of 1×10^{-2} M was flowed downward through the column at a desired flow rate. Samples were collected from the outlet of the column at different time intervals and analyzed for metal ion concentration. The operation of the column was stopped when the outlet metal ion concentration matches its initial concentration. The outlet metal ion concentrations were plotted versus time at different flow rates and bed heights to give the breakthrough curves.

2.7. Elution

One gram of the studied resin was placed in a plastic column (10 cm length and 1.0 cm diameter). A solution of the studied Hg(II) with the desired initial concentration of (1×10^{-2} M) was allowed to flow gradually through the column under the force of gravity at flow rate of 1 mL/min. Five millilitres of the underflow solution was removed every 10 min where the resid-

$$OCH(CH_2)_3CHO \quad + \quad H_2N-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2 \quad \longrightarrow \quad OCH(CH2)_3CH=N-\overset{\overset{\displaystyle S}{\|}}{C}-N=CH(CH_2)_3CHO$$

$$(1)$$

Scheme 1. The suggested structure of the modified magnetic chitosan resin.

ual concentration of Hg(II) was determined. The experiment was terminated when the concentration of the underflow matches its initial concentration. Thereafter the column was washed carefully by flowing distilled water through it. The resin loaded by Hg(II) was then subjected for elution using 100 mL of potassium iodide (0.1 M) at flow rate of 1 mL/min. After elution the resin was carefully washed with water, dilute alkali and finally with distilled water to become ready for reuse. This process was repeated for three cycles.

3. Results and discussions

The suggested structure of resin shown in Scheme 1 was confirmed from IR spectral measurements. The spectrum of modified chitosan displays new bands near 1651 and 1548 cm^{-1}. These bands are assigned to υ C=N of Schiff's base moiety [18], and υ C–N of thiourea moiety [29,30], respectively. On the other hand the spectrum shows no characteristic band related to free aldehydic group near 1720 cm^{-1} for glutaradehyde. These information indicate the success of modification process of chitosan through Schiff's base cross-linker obtained from condensation between glutaraldehyde and thiourea. The resin was formed as a thin film over the magnetite particles as shown in Scheme 2.

### 3.1. Uptake studies using batch method

The effect of the acidity of the medium on the uptake of Hg(II) was studied and the results were presented in Fig. 1. It is seen that the uptake of Hg(II) slightly increases as the pH increases in the range of pH 1–5, at pH > 5, the metal ions get out of the solution due to formation of colloidal precipitate of Hg(OH)$_2$
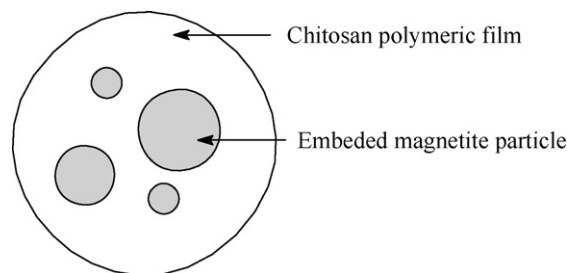
Scheme 2. Schematic representation of chitosan resin with embedded magnetite particles.
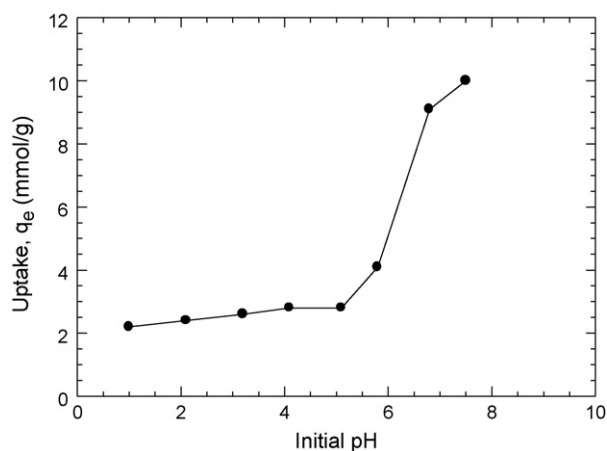
Fig. 1. Effect of pH on the adsorption of Hg(II) on the modified chitosan resin at initial concentration of 1×10^{-2} M.

and not due to the adsorption of free Hg(II) ions. This conclusion was taken from the studying the precipitation of Hg(II) as a function of pH [11]. The highest uptake value was recorded at the pH 5 (natural). This may be attributed to the presence of free lone pair of electrons on nitrogen and sulphur atoms suitable for coordination with the metal ion to give the corresponding resin–metal complex. The higher affinity of Hg(II) towards the resin active sites may be attributed to the soft base nature of (S) atom which capable for interaction with Hg(II) [31]. The slight decrease of the uptake in the acidic media may be attributed to the protonation of the lone pair of nitrogen and sulphur that hinder the complex formation. These findings are in agreement with that early reported by us [11]. The uptake of Hg(II) beyond the natural pH (pH > 5) is attributed to the formation of metal hydroxide species such as soluble $Hg(OH)^+$ and/or insoluble precipitate of $Hg(OH)_2$. The relatively higher uptake of Hg(II) at lower pH values may be due to the presence of HCl in the medium which result in the formation anion complex such as $HgCl_3^-$. This anion could be able to exchange through the Cl^-, which is electrostatically attached to the resin, according to the following reaction

Polymeric matrix-NH^+Cl^- + $HgCl_3^-$

$\rightleftharpoons$ Polymeric matrix-$NH^+HgCl_3^-$ + Cl^-
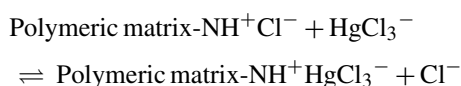
This adsorption behaviour of the resin is appreciated in the selective separation of Hg(II) from other metal ions.

3.1.1. Selectivity studies

Selective separation of Hg(II) from binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) or Mg(II) was studied at pH 1 and initial concentration of 1×10^{-2} M. The uptake values were found to be 0.01, 0.02, 0.2, 0.1, 0.0 or 0.0 mmol/g for Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) and Mg(II), respectively, whilst that of Hg(II) was 2.1 mmol/g. The relative higher uptake of Hg(II) at lower pH values was taken as indication for its selective separation from other metal ions.

3.1.2. Kinetic studies

Fig. 2 shows the change in the uptake of Hg(II) by the given resin as a function of time at initial concentration of 1×10^{-2} M and pH 5. It could be seen that about 90% of the maximum uptake of Hg(II) could be achieved within 70 min and maximum uptake capacity of 2.8 mmol/g. This value of uptake by the modified magnetic chitosan resin is relatively higher than the value reported earlier by us [12] (2.0 mmol/g). This increase in Hg(II) uptake was attributed to inserting of thiourea groups in the structure of the resin.

The uptake time data obtained was treated in the form of two simplified kinetic models including pseudo-first and pseudo-second-order. The pseudo-first-order model is expressed as [32]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{1}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mmol/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. The value
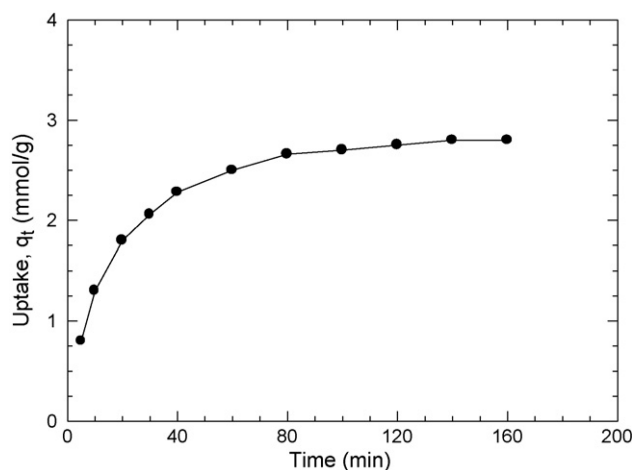

Fig. 2. Effect of time on the adsorption of Hg(II) on the modified magnetic chitosan resin.

of $\log(q_e - q_t)$ was calculated from the experimental results and plotted against t (min). On the other hand, the pseudo-second-order model is expressed as [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{2}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g/(mmol min)). The aforementioned two models basically considering external film diffusion, intraparticle diffusion and interaction step for adsorption process. The rate determining step of adsorption reaction may be one of the above three steps. The external film diffusion is eliminated by stirring. So, the adsorption rate may be controlled by intraparticle diffusion or interaction step. The kinetic parameters for pseudo-first and pseudo-second-order models are determined from the linear plots of $\log(q_e - q_t)$ versus t or (t/q_t) versus t, respectively, Fig. 3. The validity of each model is checked by comparing the R^2 values. Accordingly as shown in Table 1, the adsorption of Hg(II) on the resin is perfectly fit pseudo-second-order model rather than pseudo-first-order one. It is also seen that, the experimental and theoretical values of q_e (obtained from pseudo-second-order model) are much closed, confirming the validity of that model. This behaviour implies that the dependence of the reaction rate on the textural properties of the resin.

Table 1
Parameters of the pseudo-first-order and pseudo-second-order for the adsorption of Hg(II) on the studied resin

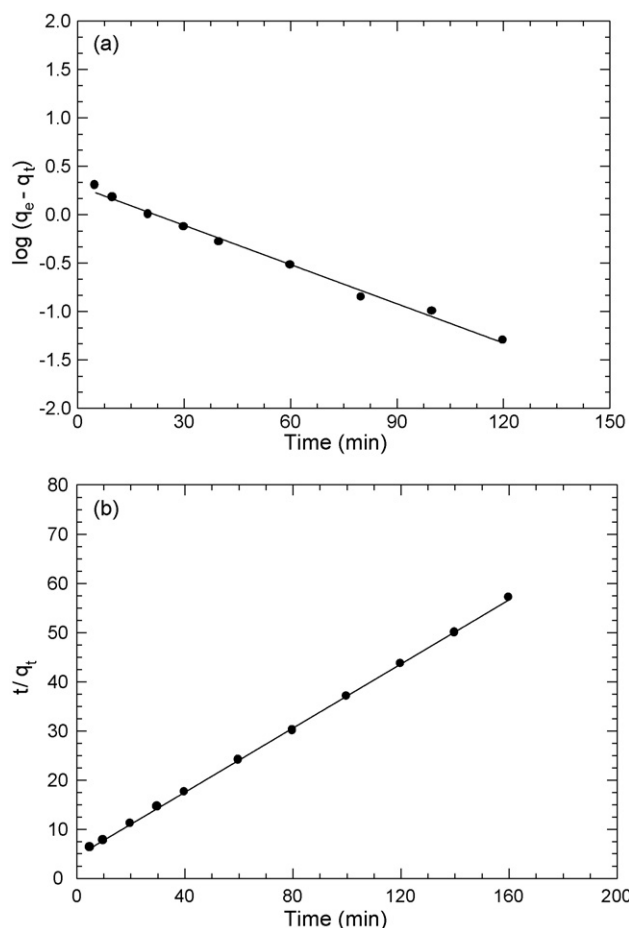|	
$q_{e,exp}$ (mmol/g)	2.805
Pseudo-first-order	
k_1 (min^{-1})	0.031
$q_{e,cal}$ (mmol/g)	1.977
R^2	0.993
Pseudo-second-order	
k_2 (g/(mmol min))	0.0237
$q_{e,cal}$ (mmol/g)	3.064
R^2	0.999

Fig. 3. Pseudo-first and pseudo-second kinetics of the uptake of Hg(II) by the studied resin at 30 °C.

3.1.3. Adsorption isotherms

Fig. 4 shows the adsorption isotherms of Hg(II) on resin at different temperatures. The adsorption curves indicate that the maximum uptake of Hg(II) is 2.8 mmol/g at 30 °C and decreases as the temperature increases. The adsorption data were plotted
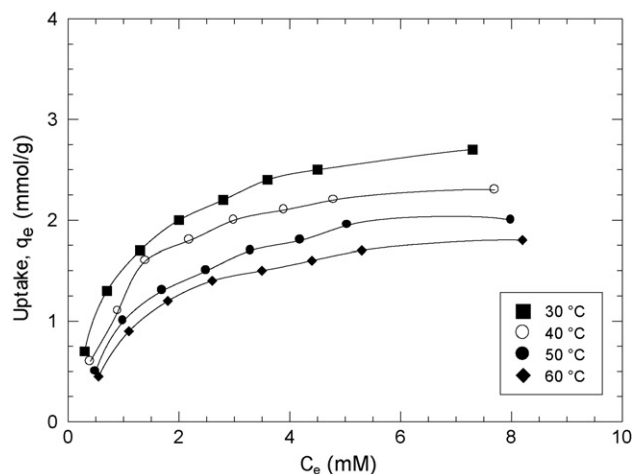

Fig. 4. Adsorption isotherms of the adsorption of Hg(II) on the modified chitosan resin at equilibrium time and at different temperatures.

Table 2
Langmuir constants for adsorption of Hg(II) on the studied resin

Temperature (°C)	Q_{max} (mmol/g)	K_L (L/mmol)	R^2
30	3.060	0.998	0.999
40	2.688	0.884	0.996
50	2.520	0.592	0.994
60	2.214	0.589	0.992

according to Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \tag{3}$$

where C_e is the equilibrium concentration of metal ions in solution (mmol/L), q_e the adsorbed value of metal ions at equilibrium concentration (mmol/g), Q_{max} the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives a straight line with slope and intercept equal to $1/Q_{max}$ and $1/K_L Q_{max}$, respectively. The values of K_L and Q_{max} at different temperatures for adsorption of Hg(II) were reported in Table 2. The value of Q_{max} (obtained from Langmuir plots) at 30 °C is consistent with that experimentally obtained.

The degree of suitability of resin towards metal ions was estimated from the values of the separation factor constant (R_L), in the following relation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where K_L is the Langmuir equilibrium constant and C_0 is the initial concentration of metal ion. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible [34]. The values of R_L at 30 °C lies between 0.091 and 0.5 indicating the suitability of the resin for the recovery of Hg(II).

The observed decrease in both values of Q_{max} and K_L with elevated temperature indicates the exothermic nature of the adsorption process. The values of K_L at different temperatures were treated according to van't Hoff equation [35]:

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

where ΔH° and ΔS° are enthalpy and entropy changes, respectively, R the universal gas constant (8.314 J/(mol K)) and T is the absolute temperature (in K). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° were calculated and reported in Table 3. The negative values of ΔH° confirm the

Table 3
Thermodynamic parameters for adsorption of Hg(II) on the resin at different temperatures

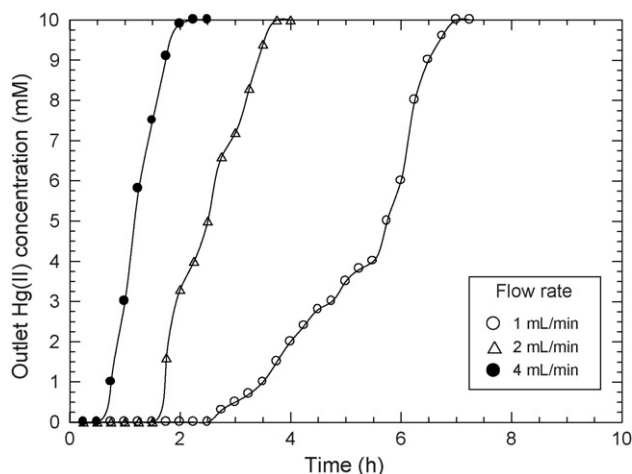| Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol K))	$T\Delta S^\circ$ (kJ/mol)
303	−17.02	−16.39	2.11	0.63
313	−17.05			0.66
323	−17.07			0.68
333	−17.09			0.70

Fig. 5. Effect of flow rate on breakthrough curves for the uptake of Hg(II) by the studied resin from initial metal ion concentration of 10 mM.
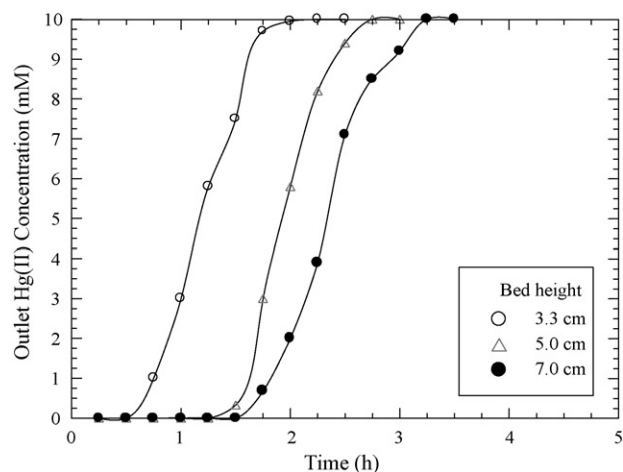

Fig. 6. Effect of bed height on breakthrough curves for the uptake of Hg(II) by the studied resin from initial metal ion concentration of 10 mM.

exothermic nature of adsorption process. Gibbs free energy of adsorption (ΔG°) was calculated from the relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

The negative values of ΔG° (Table 3) indicate that the adsorption reaction is spontaneous.

3.2. Column studies

3.2.1. Effect of flow rate

The breakthrough curves of the studied resin towards adsorption of Hg(II) at different flow rates (1, 2 and 4 mL/min) and a fixed bed height of 3.3 cm are shown in Fig. 5. Breakthrough and exhaustion occurred faster at higher flow rates. Also as the flow rate increases, the metal concentration in the effluent increases rapidly resulting in much sharper breakthrough curves. This behaviour may be attributed to the insufficient residence time of the metal ions on the column, which negatively affects the interaction process as well as the diffusion of metal ions through the pores of resin. At lower flow rates, the breakthrough curve becomes less sharp. This implies that the diffusion of Hg(II) through the resin pores is more pronounced at low flow rates. This may assist the conclusion that the adsorption of Hg(II) on chitosan resin follows pseudo-second-order kinetics and diffusion controlled process.

3.2.2. Effect of bed height

As shown in Fig. 6, the bed height was varied from 3.3 to 7.0 cm while the flow rate was held constant at 4 mL/min. The influence of bed height was well checked in terms of breakthrough time (t_b) and service time (t_s), as both were increased by increasing the bed height. Generally, the removal efficiency of resin was significantly affected by bed height and found to be directly proportional to it. Bed depth service time model (BDST) is a simple model, which states that bed height (Z) and service time (t_s) of the column shows a linear relationship according to

the relation [36]:

$$t_s = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_t} - 1 \right) \tag{7}$$

where C_t is the concentration (mM) at the service time just before reaching to the initial concentration (C_0), here is 99/100 of it, N_0 the total adsorption capacity (mmol solute/L of sorbent bed), v the linear velocity (cm/h) and K_a characterizes the rate constant of transfer (L/(mmol h)). The values of N_0 and K_a were calculated from the slope and intercept of the BDST plots (not shown), respectively. The value obtained of 0.62 (L/(mmol h)) for K_a means a short bed height is efficient to delay the breakthrough. The critical bed height (Z_0) can be calculated by setting $t_s = 0$ in Eq. (7) and rearranging to get [36]:

$$Z_0 = \frac{v}{K_a N_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \tag{8}$$

where C_b is the breakthrough metal ion concentration (mmol/L). The above equation implies that Z_0 depends on the kinetics of the sorption process, the residence time of the solute and the sorption capacity of the resin. The critical bed height of the resin's column towards Hg(II) is 2.05 cm.

3.2.3. Comparison of the modified chitosan resin with a commercial resin

Fig. 7 shows the breakthrough curves for the recovery of Hg(II) from a synthetic solution with the concentration of (1×10^{-2} M) using the investigated chitosan resin and Dowex-D3303, as a weakly basic anion exchanger, particle size 350–450 μm. The column was packed with the 1 g of investigated resin or Dowex-D3303. The pregnant liquor containing Hg(II) (10 mM) was allowed to pass through the column at flow rate of 1 mL/min. The investigated resin showed a relatively efficiency in the recovery of Hg(II) than that of Dowex-D3303. Thus breakthrough and exhaustion occurred earlier in case of Dowex-D3303.
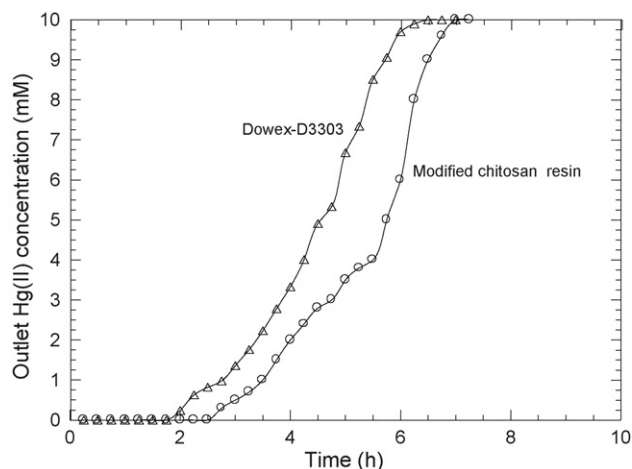
Fig. 7. Comparison of the breakthrough curves for the uptake of Hg(II) by the modified chitosan resin and Dowex-D3303.
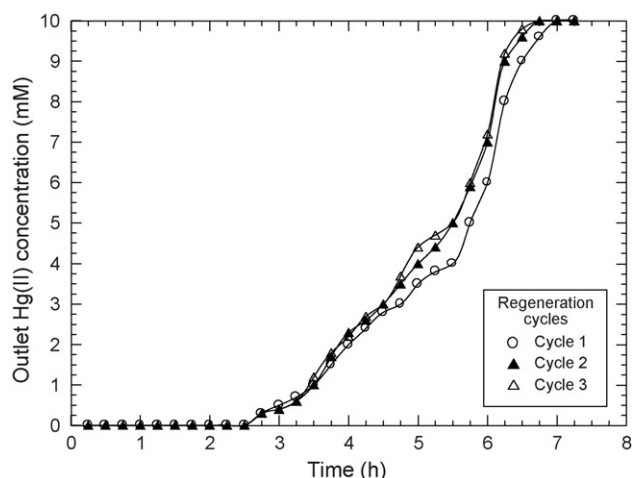

Fig. 8. Effect of successive desorption cycles on the breakthrough curves for the recovery of Hg(II) at flow rate of 1 mL/min.

3.3. Elution and regeneration cycles

Sorption/desorption cycles up to three runs were carried out for Hg(II) columns using 100 mL of 0.1 M potassium iodide as eluent. As shown in Fig. 8, the breakthrough curves for recovery of Hg(II) showed no appreciable changes during successive cycles. This indicates that the resin has good durability as well as good efficiency for repeated use.

4. Conclusions

Magnetic chitosan resin modified by Schiff's base derived from thiourea and glutaraldehyde was prepared. The resin obtained was applied for separation of Hg(II) from aqueous solution. The nature of interaction between the metal ion and the resin was found to be dependent upon the acidity of the medium. At pH 1, Hg(II) could be selectively separated from Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) and Mg(II). The recovery process was carried out through batch and column methods. Kinetic and thermodynamic studies indicated

that the adsorption process is pseudo-second-order exothermic spontaneous reaction and proceeds according to Langmuir isotherm. The resin was regenerated effectively using 0.1 M potassium iodide. The studied resin showed an efficient uptake behaviour towards Hg(II) relative to the commercial resin Dowex-D3303.

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