

Original Article

Removal of Hg (II) and Cd (II) Ions from Aqueous Solution Using Chitosan: Kinetics and Equilibrium Studies

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Abstract

Background and purpose: The discharge of toxic heavy metal ions into the environment is a serious pollution problem. Heavy metal ions pose adverse toxic risks to human health at very low concentrations. The aim of this paper is the adsorption potential of chitosan (CS) in the removal of Hg(II) and Cd(II) ions from aqueous solution.

Materials and Methods: This study was conducted in laboratory scale. In this research, CS was used as an adsorbent for the removal of Hg(II) and Cd(II) from aqueous solutions. In batch tests, the effects of various parameters such as metals concentration (40-350 mg/L), pH solution (2-8), contact time (5-120 min), and adsorbent dose (0.25-2 g) were investigated.

Results: The results showed that adsorption of Hg(II) and Cd(II) ions on CS strongly depends on pH. The experimental data were analyzed using the Langmuir and Freundlich isotherm models. Equilibrium data fitted well with the Langmuir model and the maximum adsorption capacity of the CS for Hg(II) and Cd(II) were 52.63 and 58.8 mg/g, respectively. Kinetic analysis showed that adsorption was most accurately represented by a pseudo-second-order model.

Conclusion: The obtained results showed that CS is a readily, available, economic adsorbent and was found suitable for removing Hg(II) and Cd(II) ions from aqueous solution.

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Key words: Adsorption, Chitosan, Mercury, Cadmium, Removal Efficiency

1. Introduction

Environmental contamination by heavy metals is of growing concern because of health risks on humans and animals (1). Heavy metals including mercury and cadmium are toxic for human health and other organisms. Metals are non-degradable and accumulation throughout the food chain and hence in the human body (2). Heavy metals are discharged into the aqueous environment through various sources including metal smelters, effluents from plastics, paper industries, microelectronics, mining operations, using of fertilizers and pesticides (3). The World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L for Cd in drinking water (4). Mercury has been reported to cause various diseases, for example, Amyotrophic lateral sclerosis, Alzheimer's diseases and Parkinson's disease (5). Also, cadmium can cause nausea, salivation, muscular cramps, anemia and cancer (6). So, the removal of metals in water samples is important. Many treatment processes, such as oxidation, reduction, precipitation, membrane filtration, ion exchange, and adsorption have been used to remove metal ions from aqueous solutions (7). Among the above methods, the adsorption is simple and cost-effective, thus has been widely used (8). One of the low-cost adsorbents is chitosan (CS). It is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin (9). CS (poly- β (1,4)-2-amino-2-deoxy-D-glucose) is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. CS can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites (10). From the literature it is clear that CS can be used to remove numerous trace metals (Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II),

Pt(IV), Ir(III), Pd(II), V(V) and V(IV)) from wastewater. In these studies CS has been used in a variety of forms, which include CS beads, flakes, and membranes (11-15).

In this study, CS was used for removal of Hg(II) and Cd(II) from aqueous solutions. The effect of pH, initial concentration, contact time and CS dose were investigated. Isotherm and kinetics of adsorption were evaluated.

2. Materials and Methods

CS (ash: 0.55%, moisture: 5.4%, deacetylation: 88%) was purchased from Sigma-Aldrich (South, Africa). Figure 1 show the structure of CS. Hg(NO₃)₂·6H₂O, Cd(NO₃)₂·6H₂O, hydrochloric acid (HCl) and sodium hydroxide (NaOH) with the highest purity available were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. Stock solution of Hg(II) and Cd(II) were prepared by dissolving Hg(NO₃)₂·6H₂O and Cd(NO₃)₂·6H₂O in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

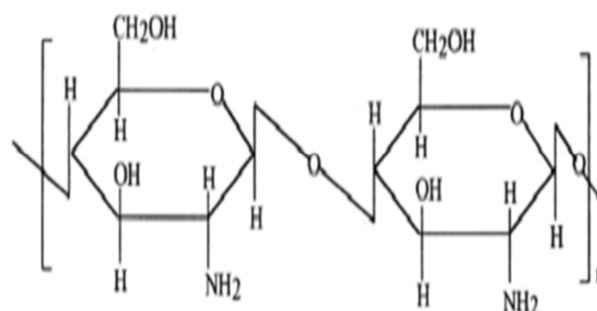


Figure 1. Chitosan structure

Cd(II) concentration was measured using an inductively coupled plasma spectrometry (Verian 710-Es Australia). All the operating parameters were those recommended by the manufacturer. The optimum operating conditions and measurement parameters for intracranial pressure are including RF power: 1.5 kW, carrier gas flow rate: 0.9 L/min,

makeup gas flow rate: 0.15 L/min, integration time: 0.1 s.

Hg(II) concentration was measured using cold vapor atomic absorption using direct mercury analyzer (DMA-80). All pH measurements were made with a 780 pH-meter (Metrohm Switzerland) with a combined glass-calomel electrode.

1 g of CS added to 40 ml of Hg(II) and Cd(II) solutions (40-350 mg/L), and the pH of the solution was adjusted at 6.0 with 0.1 mol/L HCl or/and 0.1 mol/L NaOH solutions and then the mixture was agitated using a magnetic stirrer with a the stirring speed 160 r.min⁻¹ for 60 min. Subsequently, the CS with adsorbed Hg(II) and Cd(II) were separated from the mixture using Whatman filter paper with a diameter of 42 μm. The concentration of the Hg(II) and Cd(II) ions that remained in the solution were determined by cold vapor atomic absorption using DMA-80 and inductively coupled plasma spectrometry (Verian710-Es Australia), respectively. Finally, the concentration of the Hg(II) and Cd(II) ions remained in the adsorbent phase (q_e , mg/g) were calculated using the Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where, C_0 and C_e are the initial and equilibrium Hg(II) and Cd(II) concentrations in solution, respectively (mg/L), V (L) is the volume of solution and W (g) is the weight of adsorbent.

For studying the effect of solution pH on Hg(II) and Cd(II) ions adsorption, experiments in different pH (varying from 2.0 to 8.0) were conducted. To observe the effect of adsorbent dose on Hg(II) and Cd(II) ions adsorption, different amounts of adsorbent (varying from 0.25 to 2 g) were used. In order to investigate the effect of contact time on adsorption Hg(II) and Cd(II) by CS used from contact times 5, 15, 30, 45, 60, 75, 90, 105 and 120 min.

Finally, the Hg(II) and Cd(II) removal percent (R%) was calculated by the Eq. (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where: C_0 and C_e (mg/L) were the initial and final Hg(II) and Cd(II) concentrations (16).

3. Results

Effect of solution pH

The primary study shows that the adsorption efficiency depends strongly on the solution pH, initial metal concentrations, CS dose and contact time. The influence of initial pH on adsorption amount was studied in the range of 2.0-8.0 for initial metals ion concentration of 40 mg.L. Also, the zero point charge (pH_{ZPC}) for the CS was determined around $pH = 5.1$ (Figure 2a). It was observed from figure 2b that the removal efficiency of Hg(II) and Cd(II) increased significantly with increasing pH from 1.0 to 6.0 and then remained nearly constant at higher pHs.

Effect of initial metal concentration

The effect of initial metals concentration on adsorption of Hg(II) and Cd(II) onto CS were investigated in the concentration range 40-350 mg/L at pH 6.0 and temperatures $25 \pm 1^\circ\text{C}$. The results are showed that the adsorption capacity decreases with the increase of initial Hg(II) and Cd(II) concentrations (Figure 3).

Effect of adsorbent dose

The dependence of the adsorption of Hg(II) and Cd(II) to the amount of CS were studied at temperature $25 \pm 1^\circ\text{C}$ and at pH 6.0 by varying the adsorbent amount from 0.25 to 2.0 g in contact with 40 mg/L of Hg(II) and Cd(II). The effect of adsorbent dose on Hg(II) and Cd(II) removal percentage is shown in figure 4.

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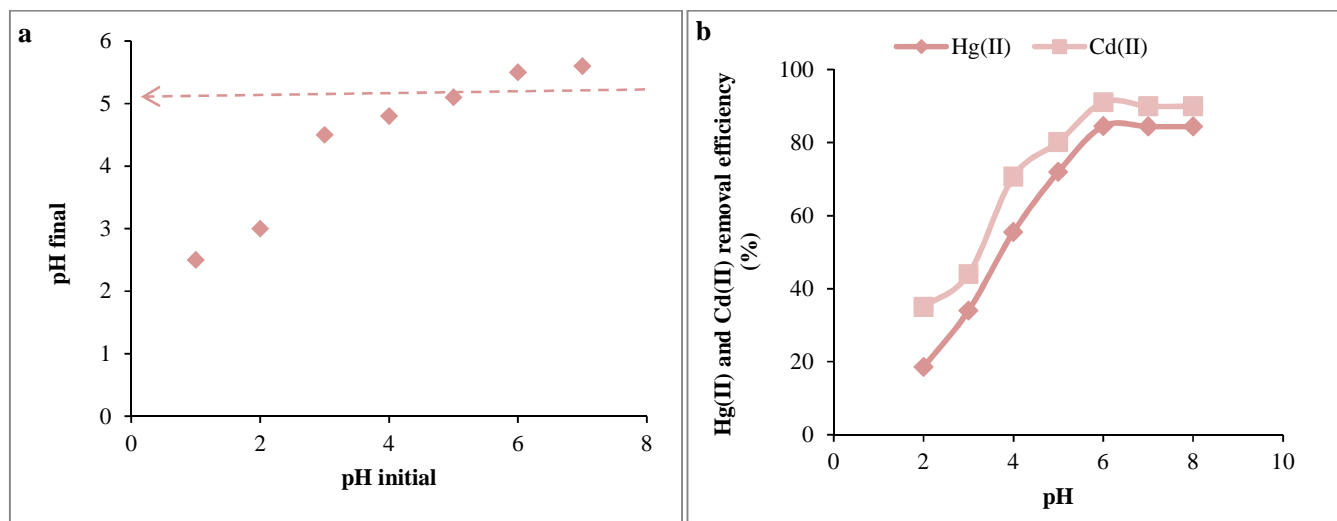


Figure 2. (a) The determination of the point of zero charge of the chitosan (CS), (b) effect of solution pH on the adsorption of Hg(II) and Cd(II) onto CS (initial concentration 40 mg/L, contact time 45 and 30 min for Hg(II) and Cd(II) respectively, adsorbent dose 1.0 g, temperature 25 ± 1°C)

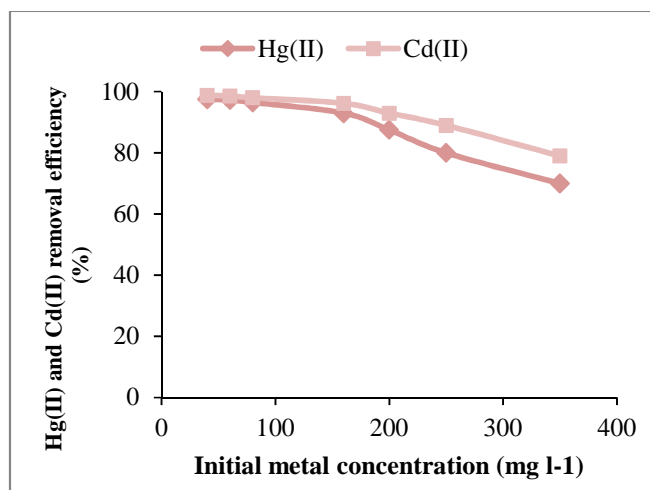


Figure 3. Effect of initial concentration on adsorption of Hg(II) and Cd(II) onto chitosan (pH = 6.0, contact time 45 and 30 min for Hg(II) and Cd(II) respectively, adsorbent dose 1.0 g, temperature 25±1°C)

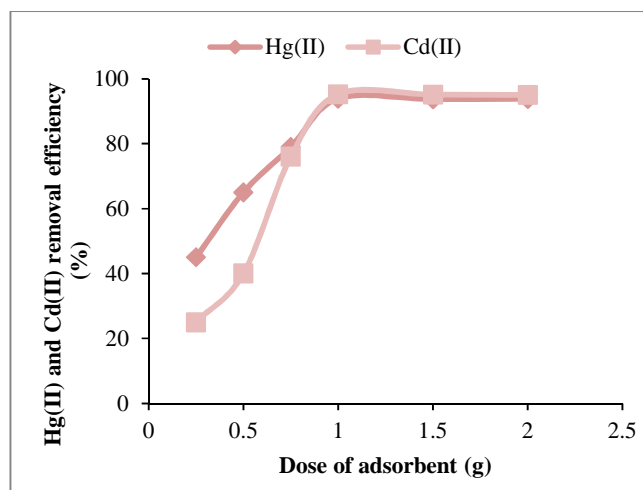


Figure 4. Effect of adsorbent dose on the adsorption of Hg(II) and Cd(II) onto CS (pH = 6.0, Initial concentration 40 mg/L, contact time 45 and 30 min for Hg(II) and Cd(II) respectively, temperature 25 ± 1°C)

Effect of contact time

The effect of contact time on the adsorption of Hg(II) and Cd(II) were studied to determine the time taken by CS to remove 40 mg/L Hg(II) and Cd(II) solutions at temperatures 25 ± 1°C. Figure 5, shows the removal percentage of Hg(II) and Cd(II) ions at various time intervals onto CS from aqueous solution. The uptake-percent of metals by CS increased with increasing contact time and then became constant.

Adsorption isotherm

Two different isotherms such as Langmuir and Freundlich models are applied in this study for analyzing experimental adsorption equilibrium parameters to obtain some important information on the surface properties of the adsorbent and its affinity to the metals molecules. Figure 6 and table 1 show the results of linear fitting in Langmuir and Freundlich isotherm for CS.

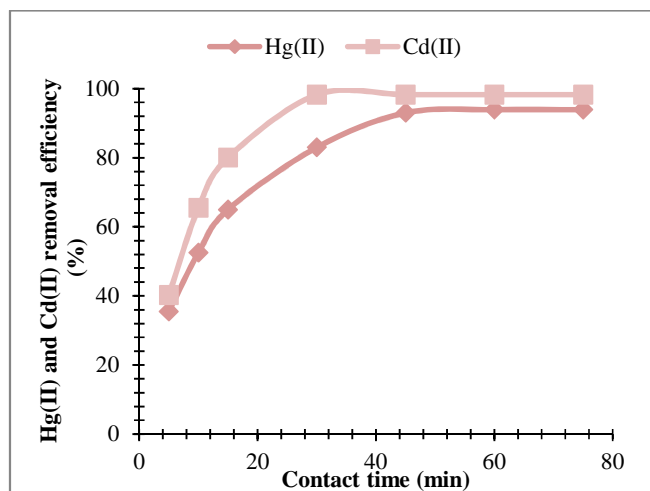


Figure 5. Effect of contact time on adsorption of Hg(II) and Cd(II) onto CS (pH = 6.0, initial concentration 40 mg/L, adsorbent dose 1 g, temperature 25 ± 1°C)

Adsorption kinetics

In order to analyze the adsorption kinetics of Hg(II) and Cd(II) by adsorbent the pseudo-first-order and pseudo-second-order models,

were tested. The result of fitting are listed in figure 7 and table 2.

Effect of initial metal concentration

The effect of initial metals concentration on adsorption of Hg(II) and Cd(II) onto CS were investigated in the concentration range 40-350 mg/L at pH 6.0 and temperatures 25 ± 1°C. The results are showed that the adsorption capacity decreases with the increase of initial Hg(II) and Cd(II) concentrations (Figure 3).

Effect of adsorbent dose

The dependence of the adsorption of Hg(II) and Cd(II) to the amount of CS were studied at temperature 25 ± 1°C and at pH 6.0 by varying the adsorbent amount from 0.25 to 2.0 g in contact with 40 mg/L of Hg(II) and Cd(II). The effect of adsorbent dose on Hg(II) and Cd(II) removal percentage is shown in figure 4.

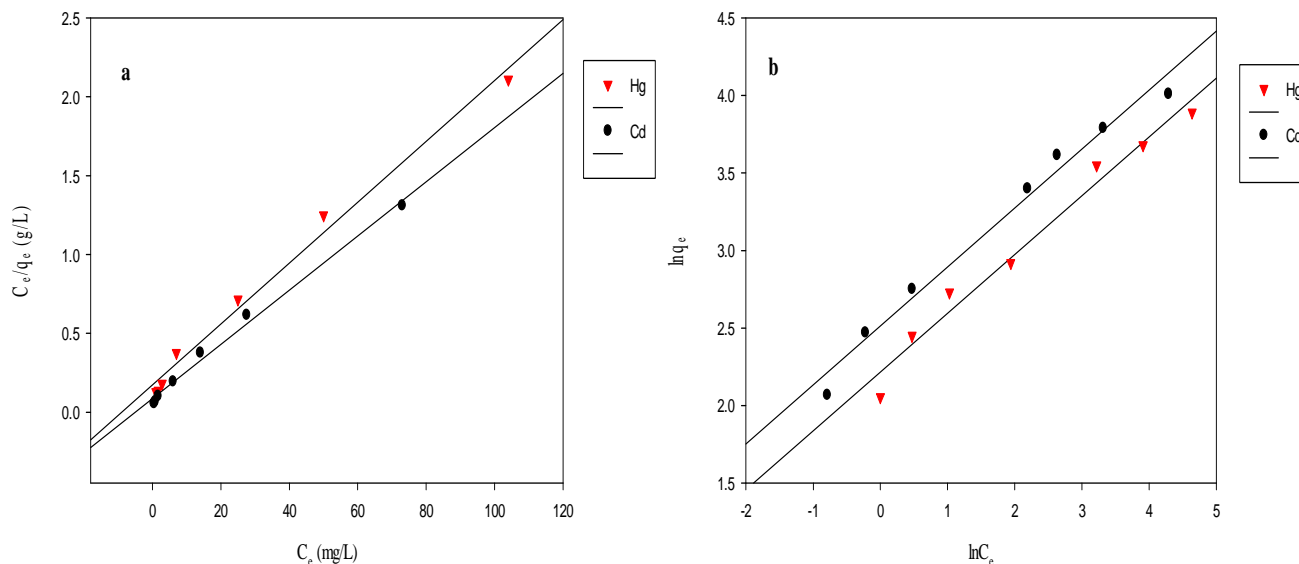


Figure 6. (a) Langmuir and (b) Freundlich isotherms for Hg(II) and Cd(II) adsorption onto Chitosan at 25 ± 1°C

Table 1. Isotherm parameters of adsorption of Hg(II) and Cd(II) onto CS

Parameters	Langmuir			Freundlich		
	b (L/mg)	q _m (mg/g)	R ²	K _f (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	n	R ²
Hg(II)	0.111	52.63	0.989	164.05	2.638	0.976
Cd(II)	0.197	5558.80	0.992	325.08	2.630	0.981

CS: Chitosan

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Effect of contact time

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Adsorption isotherm

Two different isotherms such as Langmuir and Freundlich models are applied in this study for analyzing experimental adsorption equilibrium parameters to obtain some important information on the surface properties of the adsorbent and its affinity to the metals molecules. Figure 6 and table 1 show the results of linear fitting in Langmuir and Freundlich isotherm for CS.

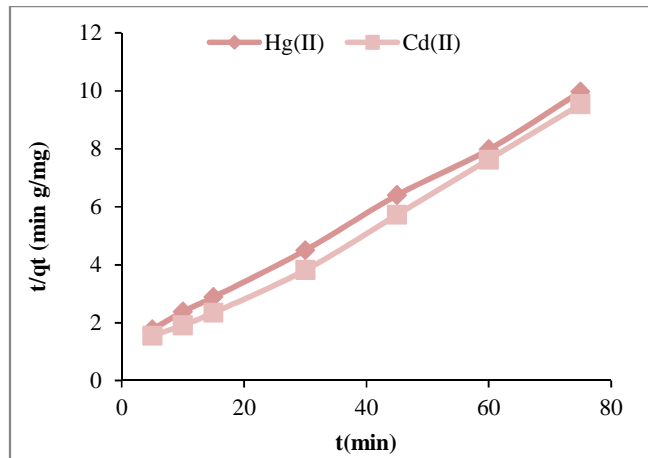


Figure 7. Pseudo-second-order kinetic plot for the adsorption of Hg(II) and Cd(II) onto chitosan at $25 \pm 1^\circ\text{C}$

Adsorption kinetics

In order to analyze the adsorption kinetics of Hg(II) and Cd(II) by adsorbent the pseudo-first-order and pseudo-second-order models, were tested. The result of fitting are listed in figure 7 and table 2.

4. Discussion

The aqueous solution pH is an important controlling parameter in the heavy metals adsorption processes. The increase in the adsorption of Hg(II) and Cd(II) on CS with increase in the solution pH can be explained based on the surface charge of CS and the metal molecule (Figure 2b). At lower pH ($< \text{pH}_{zpc}$), the CS surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the CS and the Hg(II), and Cd(II) ions. At higher pH ($> \text{pH}_{zpc}$), the number of positively charged sites is reduced and raised the number of negatively charged sites, which increases the electrostatic attractions between metals ions and CS surface. The increase in the adsorption of Hg(II) and Cd(II) on CS with increase in the solution pH is also explicable on the basis of increased dissociation of surface hydroxyl groups from the surface of CS and the subsequent formation of metal ions species such as HgOH^+ , $\text{Hg}(\text{OH})_2$, CdOH^+ and $\text{Cd}(\text{OH})_2$ of low solubility may contribute in part to maximum percentage removal of metal ions. At a lower pH, the oxide surface will have a positive character and there exists a competition between H^+ ions and $\text{M}(\text{II})$ ions for the active surface sites and hence, lesser adsorption was observed.

Table 2. Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption of Hg(II) and Cd(II) onto CS

Parameters	C_0 (mg/L)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
		$q_e \text{ exp}(\text{mg/g})$	$q_{e1}(\text{mg/g})$	$k_1 (\text{min}^{-1})$	R^2	$q_{e2} (\text{mg/g})$	$k_2 (\text{g/mg/min})$	R^2
Hg(II)	40	7.52	1.010	0.170	0.842	8.62	0.011	0.999
Cd(II)	40	7.86	0.828	0.138	0.855	8.69	0.019	0.995

CS: Chitosan

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At higher pHs, metals were precipitated in the form of hydroxides. Therefore, the effects of pHs higher than 8.0 were not investigated. A similar phenomenon has also been shown in the adsorption of Ni(II) ion from water with oxidized multi-walled carbon nanotubes (17).

The adsorption capacity is dependent on the initial metal ion concentration. As in figure 3 was seen, by increasing the initial metals concentration from 40 to 350 mg/L, the removal efficiency (%) decreased from 97% to 70% for Hg(II) and from 98 to 76% for Cd(II). At a constant CS dose, the decrease in the adsorption efficiency is probably due to the saturation of the active binding sites on the CS surface at higher Hg(II) and Cd(II) concentrations. On the other hand, by increasing the initial Hg(II) and Cd(II) concentrations the actual amount of metals adsorbed per unit mass of the CS increased. The higher initial Hg(II) and Cd(II) concentrations provides an important driving force to overcome the mass transfer resistance for Hg(II) and Cd(II) transfer between the solution and the surface of the CS. Similar results were observed by Ruis (2005) who investigated the effect of initial concentration of metal ions on removal of mercury (II) from aqueous solution by clay mineral montmorillonite and indicated that adsorption decreases with increasing initial concentration of metals (18).

One of the parameters that strongly affect the adsorption capacity is the adsorbent dose. As it is clear from figure 4, the removal efficiency increased with the increase in dose of the CS and the maximum adsorption was observed at 1.0 g for Hg(II) and Cd(II). This phenomenon was also observed by Madrakian et al. who studied the adsorption efficiency of U(VI) on modified maghemite nanoparticles and indicated that adsorption percentage increases with increasing adsorbent dose (19).

The contact time between the adsorbate and the adsorbent is important in the metals removal from the solution by the adsorption

process. As was seen in the figure 5, the removal efficiency of Hg(II) and Cd(II) by CS increased with increasing contact time and then became constant. An equilibrium adsorption is observed within 45 and 30 min for Hg(II) and Cd(II), respectively, that due to the availability of large number of vacant sites. Subsequently, the less availability of the remained active sites and the decrease in the driving force lead to the slow adsorption process. Similar results have been found by Sobhanardakani et al. (20).

The analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required for the design of an adsorption system. In this study, the Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherms are using to describe the adsorption behaviors of Hg(II) and Cd(II) onto CS. The linear equations are as follows (21,22):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f \quad (4)$$

Where, C_e (mg/L) is the equilibrium concentration of Hg(II) and Cd(II) ions in solution, q_e (mg/g) is the equilibrium adsorption capacity of CS, q_m (mg/g) is the maximum adsorption capacity of CS for monolayer coverage, b (L/mg) is a constant related to the adsorption free energy, K_f ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) is a constant related to adsorption capacity, and n is an empirical parameter related to adsorption. Figure 6a and b shows the equilibrium isotherms for the adsorption of Hg(II) and Cd(II) onto CS, and the parameters of adsorption isotherms are summarized in table 1. The results indicate that Langmuir isotherm fit better with experimental data than Freundlich isotherm. This also suggests that Hg(II) and Cd(II) adsorption on CS maybe monolayer coverage.

Table 3. Comparison of maximum adsorption capacity (qm) of different adsorbents for Hg(II) and Cd(II)

Adsorbent	Maximum adsorption capacity (mg/g)		Ref.
	Hg(II)	Cd(II)	
ZnO nanoparticles	714	384	(3)
Thiol modified Fe ₃ O ₄ @SiO ₂	148.8	-	(5)
Graphenes magnetic material	23.03	27.83	(23)
Magnetite nanorods	-	88.39	(2)
Clay mineral montmorillonite	0.86	-	(18)
Multi-carboxylic-functionalized silica gel	-	41.4	(24)
CS	52.63	58.8	This work

CS: Chitosan

The maximum adsorption capacity of CS for Hg(II) and Cd(II) were 52.63 and 58.8 mg/g. In table 3, we compared the ability of the proposed adsorbent in the removal of Hg(II) and Cd(II) ions from water with some other works.

In order to explain the adsorption mechanism particularly the potential rate-controlling step, two adsorption kinetics models, pseudo-first-order model and pseudo-second-order model were used to analyze the adsorption kinetic data. The linear forms of pseudo-first-order and pseudo-second-order models are expressed as follows (25,26):

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e and q_t are the amount of Hg(II) and Cd(II) ions adsorbed (mg/g) at equilibrium and time t (min); k_1 is the rate constant of pseudo-first-order (min^{-1}); k_2 is the rate constant of pseudo-second-order (g/mg/min) for adsorption. As shown in table 2, higher values of R^2 were obtained for pseudo-second-order than for pseudo-first-order adsorption rate models, indicating that the adsorption rates of Hg(II) and Cd(II) onto the CS can be more appropriately described using the pseudo-second-order rate rather than pseudo-first-order rate (Figure 7).

This study shows that the CS is an effective adsorbent for removal of Hg(II) and Cd(II) ions from aqueous solution. Results of

adsorption experiments revealed that the removal efficiency of the CS is strongly affected by the initial solution pH. The optimum pH for the maximum adsorption by CS were found at pH 6.0 for Hg(II) and Cd(II). The adsorption efficiency of Hg(II) and Cd(II) on CS decreased with the increase initial Hg(II) and Cd(II) concentrations from 40 to 350 mg/L. Adsorption equilibrium were attained after 45 and 30 min for Hg(II) and Cd(II) respectively. Moreover, the adsorption efficiency of Hg(II) and Cd(II) on CS increases with increasing adsorbent dose. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of Hg(II) and Cd(II) onto the CS as compared to Freundlich model. The kinetic study of Hg(II) and Cd(II) on CS were performed based on pseudo-first-order and pseudo-second-order. The data indicate that the adsorption kinetics follows the pseudo-second-order rate.

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