

Equilibrium, kinetic and thermodynamic studies of mercury adsorption on almond shell

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ABSTRACT

The application of almond shell as a low cost natural adsorbent to remove Hg^{2+} from aqueous solution was investigated. Batch experiments were carried out to evaluate the adsorption capacity of the material. The chemical and physical parameters such as pH, sorbent amount, initial ion concentration, and contact time were optimized for the maximum uptake of mercury onto the solid surface. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models, and the experimental data were found to fit the Langmuir model rather than the Freundlich. The maximum adsorption capacity obtained from the Langmuir isotherm was 135.13 mg/g. A kinetic study was carried out with pseudo-first-order and pseudo-second-order reaction equations and it was found that the Hg^{2+} uptake process followed the pseudo-second-order rate expression. The thermodynamic values, ΔG^0 , ΔH^0 and ΔS^0 , indicated that adsorption was an endothermic and spontaneous process. The potential of this material for mercury elimination was demonstrated by efficient Hg^{2+} removal from a synthetic effluent.

Key words | adsorption isotherm, almond shell, kinetics, mercury removal, thermodynamic

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INTRODUCTION

The introduction of heavy metals into natural water from a variety of industrial wastewater has become a matter of concern over the last few decades. Mercury is one of the most toxic heavy metals in the environment. Mercury compounds are used as catalysts, fungicides, herbicides, disinfectants, pigments and for other purposes. Mercury is released into the environment by human activities such as the combustion of fossil fuels and waste disposal from different industries. Mercury and its compounds are considered health hazards, and there are numerous reports of Hg poisoning because of industrial, agricultural, and laboratory exposure as well as its suicidal use (Morita *et al.* 1998). Mercury is unique among metals in that it can evaporate when released to water or soil. Also, microbes can convert inorganic forms of mercury to organic forms which can be accumulated by aquatic life. Consequently, mercury pollution in water is a serious threat to natural ecosystems. Various methods and technologies such as phytoremediation, bioremediation, activated carbon adsorption, photocatalysis, ion exchange,

electrocoagulation, precipitation and polymer-based sorbents and membranes are in use to remove mercury from the environment (Endo *et al.* 2009; Ramadan *et al.* 2010; Shamsijazeyi & Kaghazchi 2010). All these techniques have advantages and disadvantages. In the past two decades application of biosorption to remove heavy metals has received considerable attention. The main advantages of these techniques are abundant materials, high yield of removal, low operation cost, rapid kinetics, and no production of secondary compounds which might be toxic (Melgar *et al.* 2007).

One of the richest sources for low-cost biosorbents is agricultural products and especially the waste resulting from crops. The use of agricultural products and by-products has been widely investigated as a replacement for current costly methods of removing heavy metals from water and wastewater (Kumar & Bandyopadhyay 2006). In recent years, a number of materials such as moss biomass (Sari & Tuzen 2009), *Ceiba pentandra* hulls (Rao *et al.* 2009),

walnut shell (Zabihi *et al.* 2009), chestnut shell (Yao *et al.* 2010), palm kernel fibre (Ofomaja 2010), the brown macroalga *Cystoseira myrica* (Naddafi & Saeedi 2009), hazelnut, walnut and almond shell (Pehlivan *et al.* 2009), green coconut shell (Sousa *et al.* 2010) and the green hulls of almond (Ahmadpour *et al.* 2009) were reported to be capable of removing mercury and other toxic heavy metals from aqueous solutions.

The functional groups associated with proteins, polysaccharides, lignin, and cellulose as major constituents of these materials make them good natural adsorbents for metal removal. Metal uptake is believed to occur through the sorption processes involving the functional groups mentioned above. Almond shell is generated as a residue of the food industry, and has no significant commercial and industrial uses. The cell walls of almond shell consist of silica, carbohydrate, lignin, cellulose and have many lots of hydroxyl groups in their structures (Bulut & Tez 2007; Pehlivan *et al.* 2009). Thus, these materials have the potential to adsorb metal ions from aqueous solutions (Pehlivan & Altun 2008).

The almond hulls are the outermost protective layer of the almond. Under the almond hulls there is a hard shell that further protects the almonds. The almond hulls are used as roughage feed for livestock but the majority of almond shells are used as a fuel source. Depending on the variety of almond, the hardness of the almond shell varies. In this work, hard almond shell was examined as a natural adsorbent material to remove Hg^{2+} from aqueous solution. To the best of our knowledge, this material, in its natural form, has never been applied for this task. Thus, the aim of this work was to evaluate the potential of almond shell as an adsorbent material through chemical and physical characterization, to establish the maximum adsorption capacities for mercury removal and to apply this material to treatment of industrial effluent. The influence of pH, mass to volume ratio, contact time and initial metal ion concentration on the maximum adsorption capacity were investigated over the range of 2 to 7, 0.4 to 10 g/L, 3 to 60 min, and 200 and 500 mg/L Hg^{2+} initial concentration, respectively. The thermodynamic parameters and the adsorption kinetics of Hg^{2+} were calculated and discussed. The application of the proposed method for effluent treatment was carried out in batch mode, and the efficiency was evaluated by taking into account the legislation for heavy metal removal before water disposal that was established by the US Environmental Agency Protection (EPA). The EPA has set a Land Disposal Restriction (LDR) standard of 0.15 mg/L (total mercury) for the treatment of wastewater.

METHODS

Reagents

Mercury chloride of analytical grade was obtained from Merck (Darmstadt, Germany). Stock solution of 0.01 mol/L of Hg^{2+} was prepared by dissolving 0.2740 g of HgCl_2 in double distilled water in a 100 mL volumetric flask. Other working solutions used for optimization and establishing the isotherms were prepared by successive dilution of stock solutions.

Preparation of biosorbent

Almond shell was obtained from farmers in Yazd (central province of Iran) and used for the preparation of biosorbent. It was washed with double distilled water several times to remove surface soluble impurities and then dried at 100 °C for 24 h. To prepare the powdered almond shell, it was ground using a blender (Pars Khazar, Tehran, Iran) for 5–8 min and particle size ≤ 260 microns (μm) was obtained by passing the milled material through a steel sieve. The ground shells were stored in polyethylene bottles and used without any other chemical treatment. The chemical and physical characteristics of almond shell are presented in Table 1. The surface functional groups containing oxygen were determined according to Boehm titration (Boehm 2002). The surface area was determined by a single-point N_2 gas adsorption method by using a Micromeritics Flow-Sorb III 2305 (Micromeritics Instrument Corporation, Georgia, USA). Values of the surface area of almond shell and other sorbents from the literature are given in Table 2 for comparison.

Table 1 | Physicochemical characterization of used almond shell

Parameter	Value
Particle size (μm)	≤ 260
Surface area (m^2/g)	21.11
Bulk density (g/cm^3)	1.06
pH (5 g/L solution)	5.30
Water soluble contents (%)	4.86
Moisture content (%)	5.15
Results of Boehm titration (mmol/g)	
Carboxylic groups	1.20
Lactonic groups	1.11
Phenolic groups	0.86
Surface basicity	0.00

Table 2 | Surface area for some adsorbents reported in the literature

Adsorbent	Surface area (m ² /g)	Reference
Almond green hull	186	Ahmadpour <i>et al.</i> (2009)
Lentil shell	0.19	Aydin <i>et al.</i> (2008)
Wheat shell	0.67	Aydin <i>et al.</i> (2008)
Rice shell	0.83	Aydin <i>et al.</i> (2008)
Grape bagass	0.4979	Farinella <i>et al.</i> (2008)
Chestnut shell	1.08	Yao <i>et al.</i> (2010)
Almond shell	21.11	Present study

Adsorption experiments

In the present investigation a batch mode operation at room temperature was selected in order to evaluate the adsorption process apart from an adsorption thermodynamic investigation which was performed at a temperature range 298–333 °K. The effect of pH (2–7), contact time (3–60 min), and adsorbent dose (0.4–10 g/L) were studied. In a typical experiment, the initial pH of the Hg²⁺ solution was adjusted by adding HNO₃ or NaOH solution, then 0.15 g of biosorbent was added to 30 mL of the 200 mg/L Hg²⁺ solution and mixed with a stirrer (500 rpm) for a predetermined time. After each run, the reaction mixture was filtered through Whatman filter paper (0.45 μm) to remove solid particles and the filtrate was analyzed by an inductively coupled plasma optical emission spectrometer (ICP OES, Varian 710 ES, Victoria, Australia) for Hg²⁺ determination. The satisfactory results for percentage recovery of 10 mg/L Hg²⁺ solution obtained after passing the solution through the membrane filter confirm non-interference of the membrane in mercury uptake.

After the optimization, adsorption isotherm studies were conducted at room temperature with constant amount of adsorbent (5 g/L) at pH 5.5 ± 0.1, to evaluate the efficiency of adsorbent for the removal of Hg²⁺. After the introduction of the initial concentration of Hg²⁺ in the range of 0.05 to 5 mM, samples were stirred for 15 min. Then, the reaction mixtures were filtered and the filtrates were analyzed by ICP OES.

For modeling of the adsorption process two adsorption models were used: Langmuir and Freundlich models. The mathematical expression of the Langmuir isotherm is as below:

$$\text{Original form: } q_e = \frac{bq_m C_e}{1 + bC_e} \quad (1)$$

$$\text{Linearized form: } \frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bq_m} \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate in solution (mg/L), q_e is the equilibrium loading of sorbate on sorbent (mg/g), q_m and b are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (L/mg), respectively.

The sorption capacity, q_e , the amount of ions adsorbed per mass unit of adsorbent, (in milligram of Hg²⁺ per gram of sorbent) was calculated using the following equation:

$$q_e = [(C_0 - C_e)m/V] \quad (3)$$

where C_0 and C_e are the initial and equilibrium Hg²⁺ concentration (mg/L), m is the weight of sorbent (g), V is volume of the metal solution (L).

The logarithmic form of the Freundlich model is given by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where q_e is the sorption capacity (mg/g), C_e is the equilibrium concentration of the sorbate (mg/L) and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

RESULTS AND DISCUSSION

Effect of pH on removal of Hg²⁺

The pH of the aqueous solution is an important variable in the heavy metal adsorption process. As shown in Figure 1, the

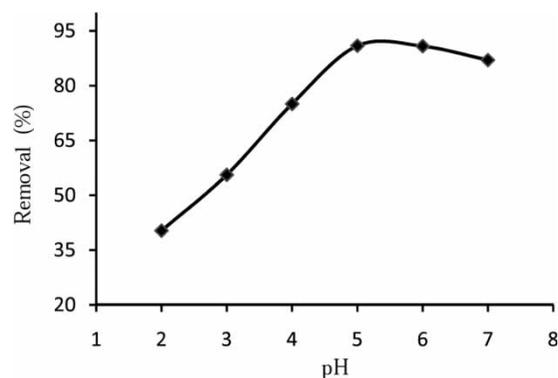
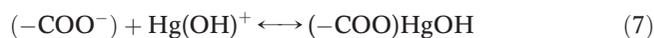


Figure 1 | Effect of initial pH on the adsorption of Hg²⁺ by almond shell (initial concentration of Hg²⁺: 200 mg/L, 5 g/L sorbent).

removal percent of Hg^{2+} was affected by initial pH, and strongly increased by increasing pH from 2 to 5. At pH higher than 6 only slight decreases in Hg^{2+} removal was observed.

Different mechanisms, such as electrostatic forces, ion exchange, and chemical complexation, have been taken into account when examining the effect of pH on metal ion adsorption on biosorbent. The adsorption profile as a function of pH can be explained on the basis of the degree of ionization of functional groups, the surface charge of the adsorbent and speciation of adsorbate. It is reported that the most dominant mercury species at $\text{pH} < 3$ and $\text{pH} > 5$ are Hg^{2+} and $\text{Hg}(\text{OH})_2$, respectively. Besides, both Hg^{2+} and $\text{Hg}(\text{OH})_2$ are present at $3 < \text{pH} < 5$ (Shin & Bae 2009). Considering that the adsorbent consists of carboxylic acid groups, which act as anionic chelating agents, the adsorption process may be attributed to the electrostatic attraction between positively charged metal ions (Hg^{2+} , $\text{Hg}(\text{OH})^+$) and negatively charged sorbent (R-COO^-). At lower pH values (< 3.0), the active sites of the adsorbent are less available for Hg^{2+} ions due to protonation of the above sites. As pH increased the degree of dissociation of carboxylic acid groups (Equation (5)) increased too, resulting in an increase in the adsorption of mercury ions. At the pH range 3.0–6.0, it is believed that ion exchange and complexation process (Equations (6) and (7)) are major mechanisms for removal of mercury ions. It is observed that as Hg^{2+} is adsorbed on the adsorbent from solution there is a decrease in pH of the solution. At the initial pH (pH_{ini}) 2.0–3.0 the final pH (pH_{Fin}) didn't change. However, when pH_{ini} of the reaction mixture varied between 3.0 and 7.0, pH_{Fin} of the reaction mixture remained between 3.0 and 5.0 and 2.8 and 4.5 for an initial concentration of 100 and 200 mg/L Hg^{2+} , respectively (Figure 2). Mercury may most likely be bound on the surface of almond shell via

the following equations:



Interaction between functional groups in the carbohydrate backbone and metal ions has been confirmed using X-ray photoelectron spectroscopy and FT-IR by Chen (Chen et al. 2002) and our results are in good agreement with results of this reference.

Given the above description and results from Figure 1 initial pH 5.5 was selected as the optimum value.

Effect of contact time on removal of Hg^{2+}

With the initial pH now fixed at 5.5 ± 0.1 the effect of contact time on the adsorption of Hg^{2+} for a fixed biosorbent dose of 0.15 g was evaluated. The initial concentration was 200 mg/L. Figure 3 illustrates the effect of adsorption time on removal efficiencies. The results show that the removal rate of metal ions increases with the increase of the contact time. The majority of metal ions removal was achieved in the first 10 min and the sorption tended toward saturation at 15 min. That situation is probably due to the large surface area ($22.11 \text{ m}^2/\text{g}$) of almond shell for the adsorption of metal ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Dorrls et al. 2000). Therefore a time of 15 min was considered in each sorption experiment. Values of the

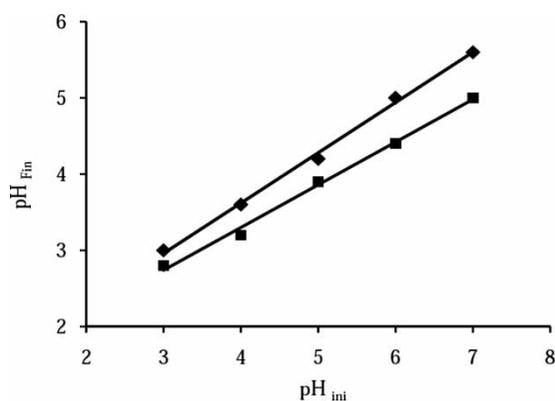


Figure 2 | The relationship between final pH and initial pH (initial concentration of Hg^{2+} : (◆) 100 mg/L and (■) 200 mg/L, pH: 5.5 ± 0.1 ; contact time: 20 min).

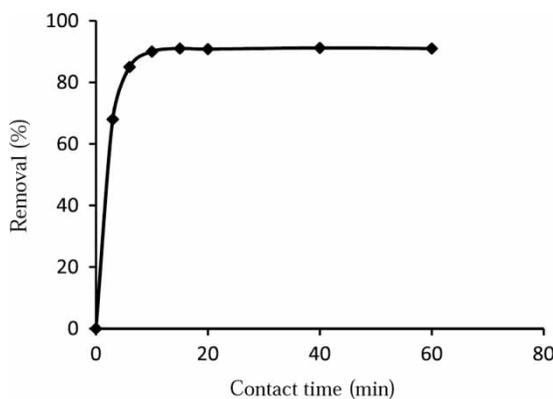


Figure 3 | Effect of contact time on the Hg^{2+} removal (Hg^{2+} initial concentration: 200 mg/L, 5 g/L sorbent; pH: 5.5 ± 0.1).

surface area of other sorbents from the literature are given in Table 2 for comparison.

Effect of amount of sorbent

The effect of variation of sorbent amount from 0.012 to 0.30 g (from 0.4 to 10 g/L) on the removal of metal ion was investigated in two solutions with different Hg^{2+} initial concentration, 200 and 500 mg/L. The results are shown in Figure 4. As shown, the Hg^{2+} concentration in solution decreases with increasing sorbent amount up to 0.15 g (5 g/L) for an initial Hg^{2+} concentration of 200 mg/L and 0.25 g (7 g/L) for an initial Hg^{2+} concentration of 500 mg/L. These results can be explained on the basis of a higher amount of adsorbent provides greater surface area for a fixed initial solute concentration. Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. Lignocellulosic materials are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicelluloses and lignin. Thus, the aqueous metal solution is exposed to a very large surface area of different cell wall components (Pehlivan *et al.* 2009).

Adsorption isotherms

The adsorption isotherms are shown in Figure 5(a–c). The Hg^{2+} initial concentration is in the range of 10–1,035 mg/L. As shown, adsorption of Hg^{2+} is higher for greater values of initial concentration of metal ions. This increase is probably due to a high driving force for mass transfer. When the metal ion concentration was higher, the adsorption capacity increased (Aydin *et al.* 2008).

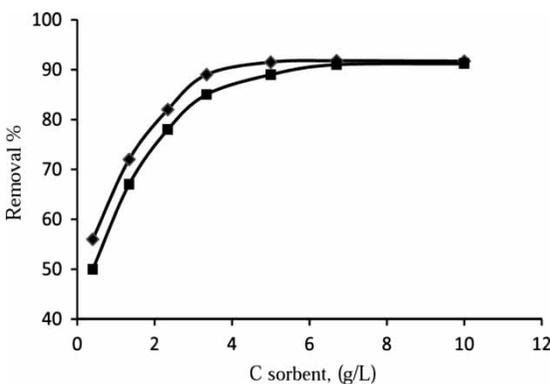


Figure 4 | Effect of sorbent dosage on the adsorption of Hg^{2+} (initial concentration of Hg^{2+} : (◆) 200 mg/L and (■) 500 mg/L, pH: 5.5 ± 0.1 ; contact time: 20 min).

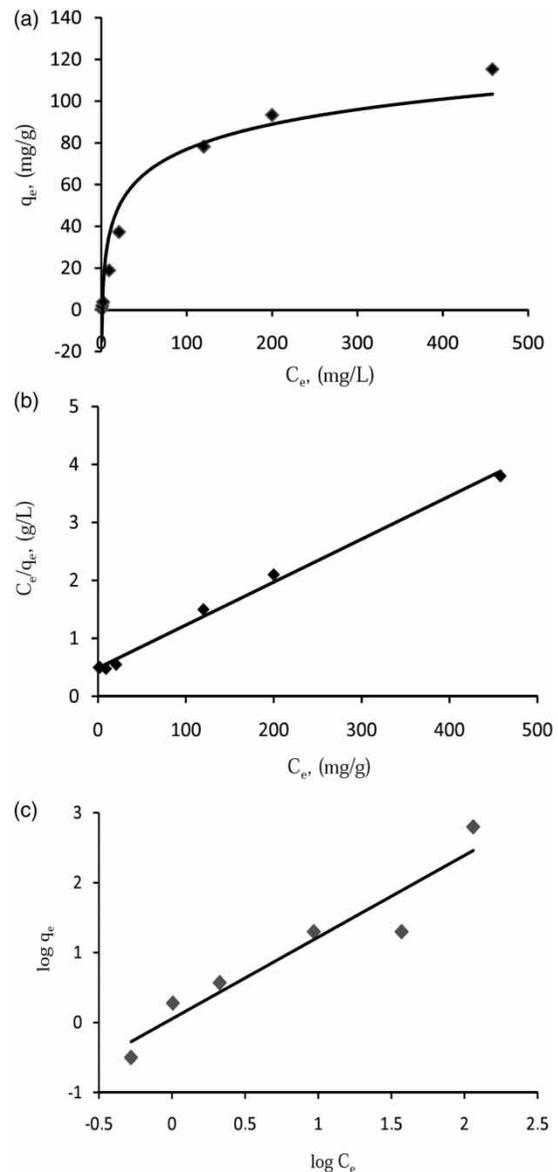


Figure 5 | (a) Langmuir isotherm for adsorption of Hg^{2+} (5 g/L almond shell, contact time: 20 min at pH 5.5 ± 0.1). (b) The linearized Langmuir isotherm for adsorption of Hg^{2+} (5 g/L: almond shell, contact time: 20 min at pH 5.5 ± 0.1). (c) The linearized Freundlich isotherm for adsorption of Hg^{2+} (5 g/L almond shell, contact time: 20 min at pH 5.5 ± 0.1).

Adsorption data of Hg^{2+} on almond shell have been analyzed using Langmuir and Freundlich models to evaluate the mechanism details of the adsorption processes. The correlation coefficients, maximum capacity of the sorbent (q_m), energy of adsorption (b) (Langmuir parameters), adsorption capacity (K_F) and adsorption intensity (n) (Freundlich parameters) have been calculated and the results are presented in Table 3. The most precise match was acquired using the Langmuir model. The correlation coefficient r^2 of the linearized equation of the Langmuir model for the

Table 3 | Correlation coefficient and constants of isotherm models for the adsorption of Hg^{2+} on almond shell

Langmuir q_m (mg/g)	b (L/mg)	r^2	Freundlich K_F (mg/g)	n	r^2
135.13	0.00737	0.994	1.13	0.856	0.907

Table 4 | Natural biosorbents investigated for mercury removal from aqueous solution

Adsorbent	q_m (mg/g)	Reference
Heat inactivated fungus	403.0	Bayramoglu & Arica (2008)
Live fungus	336.3	Bayramoglu & Arica (2008)
Coir pith	154	Namasivayam & Kadirvelu (1999)
Walnut shell	151.5	Zabihi et al. (2009)
Almond shell	135.13	Present study
<i>Terminalia catappa</i>	94.43	Inbaraj & Sulochana (2006)
Moss biomass	94.4	Sari & Tuzen (2009)
Eucalyptus bark	33.11	Ghodbane & Hamdaoui (2008)
<i>Ceiba pentandra</i> hulls	25.88	Rao et al. (2009)
<i>Phaseolus aureus</i> hull	23.66	Rao et al. (2009)
<i>Cicer arietinum</i>	22.88	Rao et al. (2009)

adsorption of Hg^{2+} was 0.9944, which was higher than the r^2 (0.9070) value of the Freundlich model. Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. These results confirmed that the adsorption of Hg^{2+} onto the almond shell is monolayer (Bulut & Tez 2007).

The maximum adsorption capacity of the Langmuir isotherm q_m was 135.13 mg Hg^{2+} /g sorbent. The capacity of the sorbent is the most important parameter for a sorption system. Values of the adsorption capacity for other adsorbents originated from agricultural by-products from the literature are given in Table 4 for comparison. It is clear from this table that the adsorption capacity of almond shell for Hg^{2+} is much better than some adsorbents and in some cases is comparable with the other adsorbents.

Kinetic study

In order to predict the sorption kinetics of Hg^{2+} , the data that are presented in Figure 2, were analysed using pseudo-first-order and pseudo-second-order models to

investigate the mechanism of biosorption. The pseudo-first-order reaction equation of Lagergren has been widely used for the adsorption of liquid/solid system on the basis of solid capacity (Ahmadpour et al. 2009). Its linear form is generally expressed as the following:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (8)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption amount at equilibrium and time t (min), respectively. K_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process. The constant was determined experimentally by plotting of $\log(q_e - q_t)$ versus t (Figure 6(a)).

The pseudo-second-order model proposed by Ho and McKay is based on the assumption that the adsorption follows second order sorption (Ho & McKay 1998). The linear form of the equation can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (9)$$

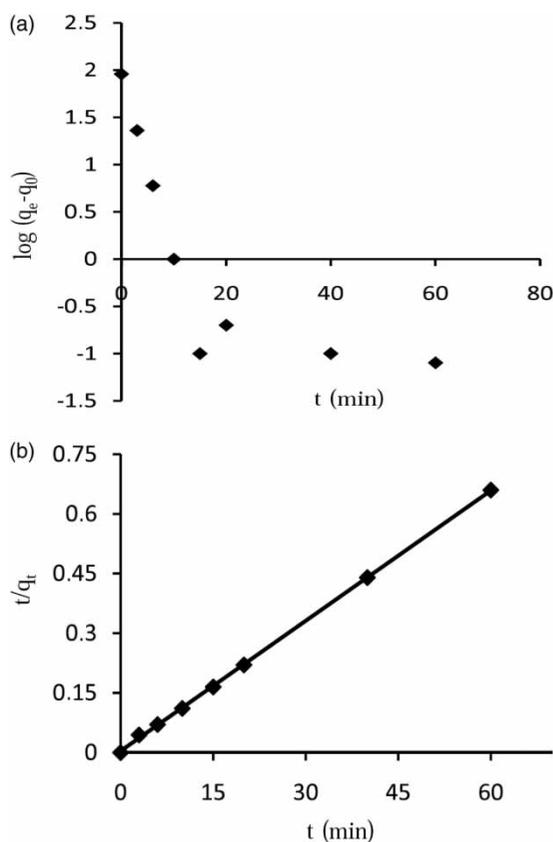
**Figure 6** | (a) Pseudo-first-order sorption kinetics of Hg^{2+} onto almond shell. (b) Pseudo-second-order sorption kinetics of Hg^{2+} onto almond shell.

Table 5 | Kinetic parameters for Hg²⁺ adsorption at 100 mg/L initial concentrations

Parameters	Pseudo-first order	Pseudo-second order
q_{cal}	7.63	91.76
K_1 (min ⁻¹)	0.10	-
K_2 (g/mg min)	-	0.031
h_0 (mg/g min)	-	260.91
r^2	0.5799	0.9998

where k_2 (g/mg min) is the rate constant of adsorption. By plotting a curve of t/q_t against t (Figure 6(b)), q_e and k_2 can be evaluated. The initial adsorption rate, h_0 (mg/g min) is defined as:

$$h_0 = k_2 q_e^2 \quad (10)$$

The values from the kinetic studies are listed in Table 5. The value of the correlation coefficient r^2 for the pseudo-second-order adsorption model is much higher (0.9998) than the value of r^2 for the pseudo-first-order model (0.5799). Therefore, it was concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of Hg²⁺ uptake by almond shell.

Adsorption thermodynamic

The Gibbs free energy change of the adsorption process (ΔG^0) can be related with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b , by the following equation (Silva et al. 2004):

$$\Delta G^0 = -RT \ln b \quad (11)$$

where ΔG^0 is the standard free energy change (J/mol), T absolute temperature (K) and R gas universal constant (8.314 J/mol/K).

Enthalpy (ΔH^0) and entropy (ΔS^0) changes can be estimated by the following equation:

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

where ΔH^0 is enthalpy change (J/mol) and ΔS^0 entropy change (J/mol/K). ΔH^0 and ΔS^0 can be calculated from the plot of $\ln b$ versus $1/T$ (not shown). The calculated thermodynamic parameters for the adsorption of Hg²⁺ onto almond shell are given in Table 6. The negative value of ΔG^0 indicates the feasibility of the process and spontaneous

Table 6 | Values of thermodynamic parameters for the sorption of Hg²⁺ on almond shell

T (K)	b (L/mol)	ln b	ΔG^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔH^0 (kJ/mol)
298	1,478.82	7.30	-18.08	144.43	25.10
318	2,347.25	7.76	-20.52		
333	4,052.14	8.31	-23.00		

nature of the adsorption. The positive value of ΔH^0 indicates the endothermic nature of the process, while the positive value of ΔS^0 shows the increased disorder and randomness at the solid-solution interface during the adsorption of mercury on the adsorbent.

Metal removal from synthetic effluent

Almond shell was employed for synthetic effluent treatment after optimization. The synthetic effluent has been made by spiking of Hg²⁺, Cd²⁺, Ni²⁺, Co²⁺, Zn²⁺, Fe³⁺, Cu²⁺, Al³⁺, Bi³⁺, Pb²⁺, and Mn²⁺ into the well water obtained from the eastern part of Tehran with the following chemical composition: Ca²⁺ 110 mg/L, Mg²⁺ 17.6 mg/L, Na⁺ 20.7 mg/L, Cl⁻ 17.8 mg/L, K⁺ 1.1 mg/L. The final concentrations of the above cations were 0.1 mM. All conditions for effluent treatment were adjusted according to the optimized parameters already defined (pH 5.5 ± 0.1, contact time 15 min at room temperature), except sorbent dose. The mass of the almond shell necessary to promote a good retention of Hg²⁺ was investigated to show the differences between the synthetic effluent and the standard solutions, and utilized for the optimization of the effluent treatment conditions due to the competitive adsorption of metal ions on almond shell from a mixed solution. The treated effluent is to be considered when the Hg²⁺ concentration is the same or lower than the concentration established by EPA (0.15 mg/L). For comparison, a sample of well water which was spiked by 0.1 mM Hg²⁺ was also treated. Values of Hg²⁺ concentration in both samples after treatment using different sorbent doses are shown in Table 7. The metal

Table 7 | Hg²⁺ concentration after synthetic effluent and well water were treated using different amounts of almond shell

Sorbent mass (g)	Hg ²⁺ concentration (mg/L)	
	Synthetic effluent	well water
0.5	7.30	2.73
1.0	4.07	0.93
1.5	1.85	0.10
2.0	0.14	0.10

adsorption from mixed solutions differed from their corresponding behavior in a single solution. It is clear that some of the metal ions compete with mercury ions for almond shell binding sites. Experimental results show mercury uptake is relatively unaffected by other metals in well water but mercury adsorption decreases in the presence of other heavy metals in synthetic effluent. The results indicate that 2 and 1 g of almond shell are enough for retaining Hg^{2+} when 100 mL of synthetic effluent and well water are treated, respectively. The concentration of Hg^{2+} obtained after effluent treatment was lower than the value established by EPA for the treatment of wastewater.

CONCLUSIONS

The ability of almond shell to act as a natural sorbent to remove Hg^{2+} from aqueous solution was investigated. In the batch mode of studies, adsorption of Hg^{2+} was a function of initial mercury ion concentration, contact time, sorbent dose and pH of the metal ion solutions. An equilibrium condition for Hg^{2+} loading on almond shell was achieved after 15 min of mixing of the solution and sorbent. Isotherm data for Hg^{2+} sorption onto the sorbent were modeled by both Langmuir and Freundlich isotherms. The results showed that the Langmuir model was more suitable than the Freundlich for adsorption equilibrium of Hg^{2+} . The maximum adsorptive capacity of almond shell for mercury ion was found to be 135.13 mg Hg^{2+} /g sorbent which was comparable to the other high quality natural sorbents. The experimental data was better fitted by a pseudo-second-order model than a pseudo-first-order model. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as ΔG^0 , ΔH^0 and ΔS^0 . The results indicated that adsorption of mercury on almond shell was spontaneous and physical in nature. The low cost and rapid adsorptive ability of this sorbent offers a promising technique for industrial wastewaters cleanup.

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