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Removal of cadmium from aqueous solutions by walnut green husk as a low-cost biosorbent

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ABSTRACT

In this study, the removal of Cd(II) ions by walnut green husk particles has been investigated by batch technique. The effect of initial solution pH, initial concentration of dissolved Cd(II), amount of adsorbent, and contact time on the removal efficiency and adsorption capacity were studied. The adsorption process was pH dependent, and the maximum adsorption of analyte was achieved at pH 7. Adsorption test results revealed that Cd(II) adsorption on the studied adsorbent could be fitted to Langmuir and Freundlich isotherms. The optimum amount of adsorbent was found to be 0.8 g L^{-1} of sample solution with initial Cd(II) concentration of 1.5 mg L^{-1} (i.e. 5.33 g L^{-1} for 10 mg L^{-1} Cd). In the optimum conditions, the removal efficiency of Cd(II) turned out to be 96.11%.

Keywords: Biosorbent; Walnut green husk particles; Heavy metal; Cadmium

1. Introduction

Industrial activity generates large volumes of aqueous effluents containing high levels of hazardous species. The species with the most toxicological relevance in the industrial effluents are the heavy metals, which do not biodegrade over time, being accumulated in the human body. Among the heavy metals, cadmium is one of the common contaminants; this metal, known to be a toxic element even at very low concentration, which tends to be concentrated in environmental systems and human bodies; it can cause dysfunction of the kidneys, liver, and lungs [1,2]. It could enter the water system through industrial discharge; thus, its removal from the various effluents has attracted much attention either from the scientific and technological or environmental points of view.

The conventional procedures for removing heavy metals from aqueous solutions include phytoremediation [3], chemical precipitation [4], lime coagulation [5], ion exchange [6], reverse osmosis [7], and solvent extraction [8]. Incomplete heavy metal removal, high reagent and energy requirement, generation of toxic sludge or other waste products are disadvantages in using these methods [9].

In order to remove the toxic heavy metals from waters and wastewaters, searching for new technologies has directed attention to biosorption based on metal-binding capacities of various biological materials. Recent studies have shown that common agricultural waste products or natural polymers can be used as potential biosorbents for the removal of heavy metals. Biosorption can be used for the treatment of wastewater with low heavy metal concentration as an inexpensive, simple, and effective alternative to conventional methods. The biosorption process involves a

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solid phase (biological material) and a liquid phase (solvent, normal water) containing dissolved species to be adsorbed (adsorbate, metal ions) due to higher affinity of biosorbent for the adsorbate species. The process of metal ion binding is comprised of many physicochemical processes such as ion exchange, complexation, microprecipitation, and electrostatic interactions [10].

Different parameters affect the biosorption mechanisms to various extents; pH is one of the most important parameters that can affect the solution chemistry of heavy metals, the activity of the functional groups in the biomass, and the competition of metallic ions. Metal affinity to the biomass can be improved by pretreatment of the biomass with alkalis, acids, etc., which leads to an increase in the amount of heavy metal uptake.

In recent years, a number of materials have been reported to be capable of removing Cd(II) from aqueous solutions with different efficiencies and capacities. Hasar and Cuci have reported activated carbon prepared from almond husk [11]; Pino et al. have used green coconut shell powder [12]; Zein et al. reported application of HNO_3-treated mangosteen shell with a low capacity [13]; Ho and Ofomaja reported HCl-treated coconut copra meal [14]; meranti wood sawdust was reported by Rafatullah et al. [15]; modified walnut sawdust was studied by Bulut and Tez [16]; Kumar et al. reported rice husk [17]; NaOH-treated Cedrus deodar sawdust was reported by Memon et al. [18]; Low et al. have studied the HCl-treated spent grain [19]; alkali-treated juniper fiber was used by Min et al. [20]; Karnitz et al. reported treated sugarcane bagasse [21]; Taty-Costodes et al. have used sawdust treated with Formaldehyde in H_2SO_4 [22]; Horsfall et al. have reported Cassava waste modified with thioglycollic acid [23]. However, the search for more efficient, cheaper, and freely available adsorbents continues.

As a pursuit of our previous works, i.e. transport of Cd(II) through the liquid membrane [24,25], the present work was an attempt to use an inexpensive adsorbent that is easily available in large quantities, for the removal of Cd(II). Iran produces approximately 290,000 metric tons (average 2001–2012) of walnut annually [26]. Consequently, walnut husk, as an agricultural by-product, is available in large quantities in this country. Walnut hull in its native form has been used for the removal of chromium(VI) in previous works [27]. Chemically modified plant wastes can enhance the adsorption of heavy metal ions by increasing adsorption capacity on the one hand and lowering the release of soluble organic compounds on the other hand [28,29]. However, in order to produce low-cost adsorbent, taking into consideration the cost of chemicals used for modification, we used walnut green husk (WGH) without chemical treatment for the removal of Cd(II) ions. Despite the numerous studies regarding the use of agricultural wastes including walnut hull as adsorbents, the thorough literature review indicated that this is the first report introducing the application of WGH as an adsorbent for Cd(II) removal. The objective of this study was to explore the feasibility of using untreated WGH to remove Cd(II) from aqueous solutions as well as waste samples. The effects of pH, contact time, adsorbent concentration, and salt were investigated and the adsorption isotherms, kinetics, and mechanism were studied. Later, the method was accessed by applying it to the leach solution of zinc plant purification cake and wastewater. Finally, a mechanism was suggested for the adsorption of Cd(II).

2. Material and methods

2.1. Chemicals and reagents

All the chemicals used in this study were of analytical grade and provided by Merck (Darmstadt, Germany). The stock solution of Cd(II) (1,000 mg L^{-1}) was prepared by dissolving 0.686 g of dried cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) salt in 250 mL of deionized water. Experimental solutions of the desired concentrations were obtained by successive dilutions of stock solution. The pH of the solution was adjusted with 0.1 mol L^{-1} HCl and/or NaOH solutions.

2.2. Apparatus

A Varian Model spectrAA220 atomic absorption spectrometer (Mulgrave, Victoria, Australia) equipped with deuterium lamp background corrector was used for metal analysis. The measurements were performed in an air-acetylene flame. The operating conditions were those recommended by the manufacturer, unless specified otherwise. A JULABO model MP5 circulating thermostatic water bath (Seelbach, Germany) was used for temperature control during the experiments. Magnetic stirrer, Heidolph model MR3001K (Schwabach, Germany), was used for agitation of the phases. The pH measurements were accomplished with a Metrohm model 692 pH/ion meter (Herisau, Switzerland) equipped with a combined glass-calomel electrode. Bench-top centrifuge (Hettich, Rotofix, Germany) was used for the separation of adsorbent from sample solution.

2.3. Preparation of adsorbent and real sample

The green walnut was collected from gardens of Maragheh-Iran; husks were removed and washed with distilled water to remove the impurities and air-dried. The dried husks were transferred to a mortar and grinded into small particles. In order to remove husk color and water soluble organics, the particles were soaked in warm distilled water (45˚C) while stirring magnetically for 8 h, then washed a few times with deionized water until colorless, and then dried in the oven at 60˚C till a constant weight of adsorbent particles was achieved. Finally, they were sieved and particles with diameter in the range 0.15–0.42 mm were selected and stored in an airtight container for further use.

The zinc plant cadmium cake and an industrial wastewater obtained from Calcimine Company at Dandy, a zinc industries region, at the suburb of Zanjan-Iran, were used as real samples. The cake sample (15 kg, collected randomly) was laid in the sunlight for 2 d and crashed into small pieces. Five samples of 100 g were sampled randomly (total 500 g) and dried in the oven at 110˚C for 2 h. Having been cooled to room temperature, the sample was ground, using a ball mill. Five samples of approximately 10 g each were collected randomly and mixed well. A total of 2.5 g portions were sampled in three replicates (3 samples), each sample leached in 100 mL HCl 2 mol L^{-1} at 100˚C for 1 h under reflux. Two of samples were analyzed by atomic absorption spectrometry and the average amounts of the content were found to be 20% Zn, 9% Cd, 4% Ni and minor amounts of cobalt and iron. The majority of Zn, Ni, Co, and Fe were precipitated using different reagents and pH adjustment (i.e. pH was adjusted at 9 using NH_3 and NH_4Cl and the four ions were precipitated as mixture of FeS, $Fe(OH)_3$, NiS, CoS, and ZnS upon addition of H_2S, while Cd(II) does not precipitate and is mainly present as $Cd(NH_3)_4^{2+}$ in solution. The residue was then removed by filtration and the filtrate was neutralized by 0.2 mol L^{-1} HCl solution). The third sample solution was diluted to 1,000 mL with distilled water. An industrial wastewater collected from the same zinc processing plant was filtered to remove any particulate matter. The metal contents was measured by atomic absorption spectrometry (metal contents of both samples are shown in Table 3). A total of 50 mL aliquots of each sample after pH adjustment were subjected to the extraction using 1.0 g WGH particles (Table 3).

2.4. Experimental method

In all sets of experiments (except real sample), an appropriate amount of WGH (of 0.15–0.42 mm) was placed in 25 mL solution of Cd(II) with known concentration and initial pH. The mixture was stirred at room temperature and 300 rpm for 80 min. At the end of the experiment, the solution was separated from the biomass by centrifuging and then the Cd(II) content was measured with the flame atomic absorption spectrometer. Each experiment was performed three times and the reported data in the figures are the averaged values.

The amount of metal bound to the sorbent and percentage removal (%R) from the solution were calculated by (Eqs. (1) and (2))

$$q = \frac{(C_i - C_e) \cdot V}{m} \tag{1}$$

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

where q is the amount of metal ion uptake (mg g^{-1}); C_i and C_e are the initial and final concentrations of metal ion in solution, respectively (mg L^{-1}); V is solution volume (L); m is dry mass of biosorbent (g). The difference between the initial and final metal concentration was assumed to be bound to the sorbent.

Adsorption kinetic experiments were performed at 25˚C by adding 0.02 g of WGH into 25 mL Cd(II) solution containing 1.5 mg L^{-1} of analyte (at pH 7.0) and stirred at constant rate (300 rpm). A total of 5 mL aliquots were taken from the suspension at certain time intervals of the reaction while separating the solution from sorbent with the aid of the centrifuge. The Cd(II) content of solution was analyzed by atomic absorption spectrometry and R (%) vs. reaction time was determined. Metal adsorption isotherms were studied at initial pH 7.0 with the initial cadmium concentrations at the range of 0.5–3 mg L^{-1} using 0.8 g L^{-1} of sorbent.

3. Results and discussions

3.1. Determination of the point of zero charge

Aliquots of 25 mL potassium nitrate (0.1 mol L^{-1}) solutions containing 100 mg of WGH were prepared whose initial pH values were adjusted within the range 1–9 using either 0.1 mol L^{-1} HCl or NaOH solutions. The suspensions were then stirred magnetically at 250 rpm for 1 h and the mixture was left for about 4 h. The final pH values of the supernatant liquids were measured and plotted vs. initial pH. The pH_{PZC} was obtained from the intersection of the two lines which indicated 4.0. Below this pH, the surface charge of the WGH particles is positive while above that it would have a net negative charge [30].

3.2. Effect of pH

Fig. 1 shows the effect of pH on amount of Cd(II) ion adsorbed q (mg g^{-1}) and the removal efficiency (%R). Obviously, it was observed that the solution pH affects the adsorption. The metal ion uptake was found to increase from 0.7 to 1.73 mg g^{-1} for an increase in pH from 2 to 7 and then decrease mildly from 1.73 to 1.71 mg g^{-1} for an increase in pH from 7 to 9. Along with the increasing amount of q, the removal efficiency increases from 20 to 96.11% for an increase in pH from 2 to 7 and then decreases slightly to 94% at pH 9. Several reasons may be attributed to heavy metal ion adsorption behavior of the biosorbent relative to the solution pH. The surface of WGH particles may contain a large number of active sites and the solute (Cd(II)) uptake can be related to those sites and also to the chemistry of the solute in solution. As mentioned earlier, at low pH values the, WGH surface is positively charged and low adsorption of Cd(II) ions should be due to their electrostatic repulsion and competition between the metal and H^{+} ions in the solution. The negative charge density on the surface increases by increasing the pH, resulting in enhanced interaction with positively charged metal ions through electrostatic force of attraction. At pH values higher than 8, Cd(II) ions may transform to Cd(OH)$^{+}$ causing slight decrease in adsorption efficiency due to weakened attraction forces; therefore, pH 7.0 was chosen as the optimum value. The pH values higher than 9.0 was not tested due to possible Cd(OH)$_2$ formation, which may precipitate onto the sorbent.

3.3. Effect of initial adsorbate concentration

Fig. 2 shows that the equilibrium adsorption capacity increases from 0.51 to 5.8 mg g^{-1} with increasing initial Cd(II) concentration from 0.5 to 9 mg L^{-1}. This may be due to the increase in the number of Cd(II) ions competing for the available binding sites at the surface of the adsorbent. Whereas the percent Cd(II) removal is almost constant for an increase in initial Cd(II) concentration from 0.5 to 1.5 mg L^{-1} but then it decreases gradually from 96.11 to 58% for an increase in initial concentration from 1.5 to 9 mg L^{-1}. The decrease in removal efficiency (%R) may be ascribed to the fact that the number of active adsorption sites remains constant as increasing the adsorbate concentration increases its number to be accommodated (limited adsorption sites).

3.4. Effect of adsorbent mass

In order to study this parameter, 25 mL aliquots of 1.5 mg L^{-1} Cd(II) with initial pH of 7 were contacted with different amounts of WGH particles. The results shown in Fig. 3 depict that the amount of Cd(II) adsorbed gets varied with varying adsorbent mass. That is, q decreases from 5.63 to 1.73 mg g^{-1} for an increase in adsorbent mass from 5 to 20 mg, whereas the removal percentage increased from 77.33 to 96.11% with an increase in adsorbent mass at the same range. At higher biomass-solute concentration ratio, there is a very fast superficial sorption onto the adsorbent surface that produces a lower solute concentration in the solution than when this ratio is lower. This is because

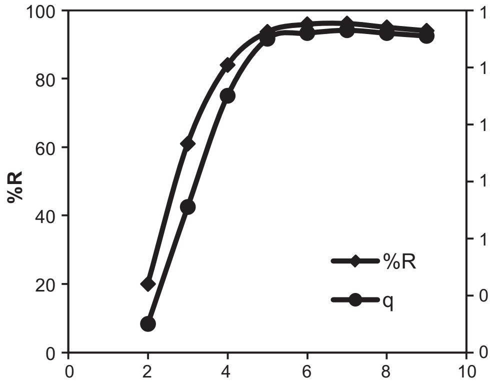

Fig. 1. The effect of initial solution pH on the adsorption of Cd(II); conditions: T = 24–26°C, 25 mL solution of 1.5 mg L^{-1} Cd(II) containing 0.02 g WGH (0.15–0.42 mm), contact time = 60 min.

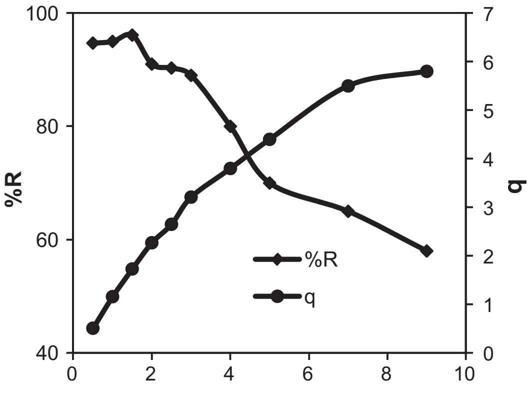

Fig. 2. Effect of initial Cd(II) ion concentration on its removal; conditions: Initial pH 7, T = 24–26°C, 25 mL solution with different concentrations of Cd(II) containing 0.02 g WGH (0.15–0.42 mm), contact time = 60 min.

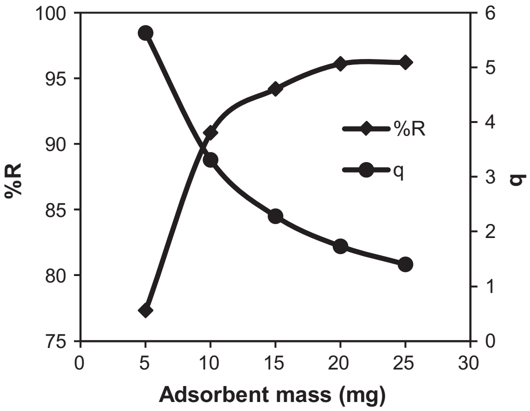

Fig. 3. Effect of WGH mass on the Cd(II) uptake; conditions: $T = 24–26^\circ C$, 25 mL solution of 1.5 mg L^{-1} Cd(II) containing different amounts of WGH, initial pH 7, contact time = 60 min.

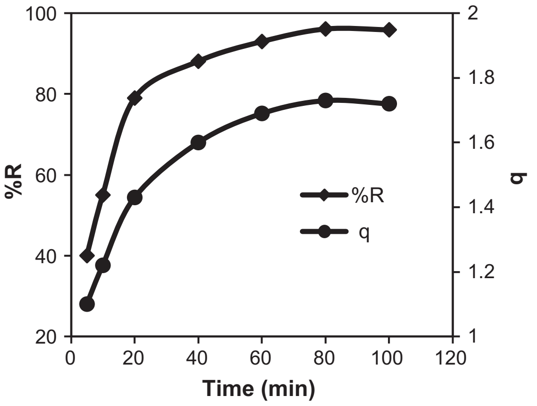

Fig. 4. Effect of contact time on Cd(II) ion removal; conditions: $T = 24–26^\circ C$, 25 mL solution of 1.5 mg L^{-1} Cd(II) containing 0.02 g of WGH, initial pH 7, different contact time.

a fixed mass of biomass can only adsorb a certain amount of Cd(II) ions. Therefore, the more the adsorbent dosage, the larger will be the volume of effluent that a fixed mass of biomass can purify. The decrease in the amount of Cd(II) adsorbed q (mg g^{-1}) with increasing adsorbent mass is due to the concentration gradient between solute concentration in the solution and the solute concentration at the surface of the adsorbent. Thus, with increasing adsorbent mass, the amount of Cd(II) adsorbed onto unit weight of adsorbent gets split causing a decrease in q value. Similar results were reported by several workers [15,27,31].

3.5. Effect of contact time

The influence of contact time on the uptake of Cd(II) ions was studied across the range of 5–100 min. As shown in Fig. 4, the amount of adsorption (q, mg g^{-1}) and the removal efficiency (%R) of Cd(II) ions were increased from 1.1 to 1.73 mg g^{-1}, and 40 to 96.11%, respectively, for an increase in contact time from 5 to 80 min after which the equilibrium is approached. However, it can be seen that Cd(II) sorption occurred in two stages: an initial fast phase which lasted for 20 min, followed by the slower second phase which continued until the equilibrium was reached. Initially, the concentration gradient between the liquid phase and the solid surface was large and, as such, the solute movement to the solid surface was faster. As contact time increased, intra-particle diffusion became predominant. Therefore, the solute took more time to diffuse into the internal sorption sites through the pores. On the other hand, because the increase of solute concentration resulted in the increase of the sorption capacity (q), 80 min was selected as contact time to ensure the equilibrium for entire concentration range.

3.6. Effect of ionic strength on Cd(II) removal

Wastewaters often contain significant quantities of salts and hence high ionic strength. Therefore, the effect of ionic strength was investigated with different concentrations of NaCl in the range of 0–60 g L^{-1}.

The results (not shown) indicated that increasing NaCl concentration leads to a significant decrease in the equilibrium adsorption capacity (q) and consequently in the removal efficiency (%R). This observation can be attributed to: (1) increasing Na^+ ions concentration and therefore increasing competition for the adsorption sites on the WGH and (2) decreasing activity of Cd(II) ions in solution due to increasing non-ideality of solution. This non-ideality is due to the interaction between Cl^- and Cd(II) ions [27].

3.7. Adsorption equilibrium isotherms

To characterize the biosorption of metal ion, Langmuir, Freundlich, and Temkin isotherm models were used. The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy [32], whereas the Freundlich model deals with heterogeneous multilayer adsorption and the model does not consider the biosorbent saturation [33]; and the Temkin model contains a factor that explicitly takes into account adsorbing species adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions and (ii) adsorption is characterized by uniform distribution of binding energies, up to some maximum binding energy [34].

3.7.1. Langmuir isotherm

Langmuir equation of adsorption is

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

It is linearized to the form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e} \tag{4}$$

where $K_L = q_m \times b$.

The terms q_m and b are the Langmuir constants, and q_e and C_e are the amount of metal adsorbed per unit mass of adsorbent (mg g^{-1}) and equilibrium concentration of metal ion (mg L^{-1}), respectively. The quality of biosorbent is estimated by the heavy metal uptake (biosorption capacity), q_m.

From Fig. 5(a) and high correlation coefficient of curve ($R^2 = 0.9907$), it was observed that the adsorption of Cd(II) ions onto WGH particles is consistent with Langmuir isotherm and shows that the adsorption is monolayer.

3.7.1.1. Favorability of Langmuir isotherm. The essential characteristics of the Langmuir isotherm can be represented in terms of dimensionless constant separation factor or equilibrium parameter, R_L given by the equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{5}$$

The parameter R_L indicates the shape of isotherm as follows:

$R_L > 1$, Unfavorable;
$R_L = 1$, Linear;
$0 < R_L < 1$, Favorable;
$R_L = 0$, Irreversible.

The calculated R_L values vs. initial Cd(II) concentrations are represented in Fig. 5(b). From this figure, the adsorption was found to be favorable at all studied initial Cd(II) concentrations. Also, higher R_L values at lower Cd(II) ion concentrations showed that adsorption was more favorable at lower concentration.

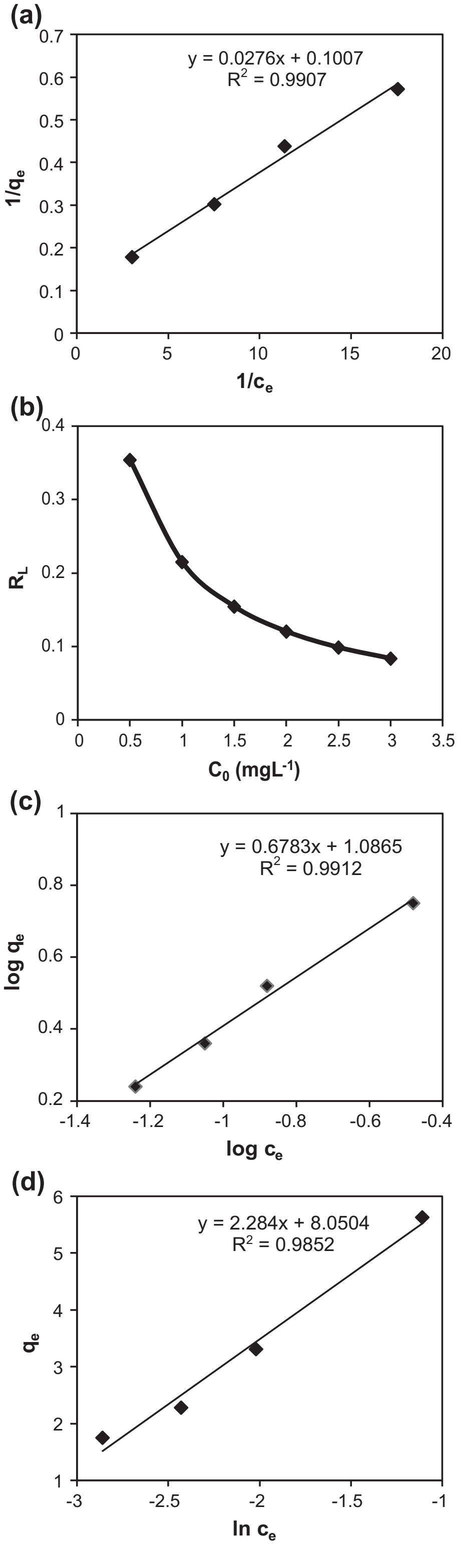

Fig. 5. Adsorption isotherms of Cd(II) ions at 25˚C; (a) Langmuir isotherm, (b) separation factor for adsorption of Cd(II) ions according to Langmuir model, (c) Freundlich isotherm, and (d) Temkin isotherm.

3.7.2. Freundlich isotherm

The Freundlich equation of adsorption isotherm is

$$q_e = K_F \times C_e^{1/n} \tag{6}$$

Its linearized form is represented by the (Eq. (7)):

$$\log\ q_e = \log\ K_F + \frac{1}{n} \log\ C_e \tag{7}$$

where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg g^{-1}), K_F and n are isotherm constants indicating the relative adsorption capacity (mg g^{-1}) and adsorption intensity, respectively; C_e stands for the equilibrium concentration of metal ion (mg L^{-1}). The plot of log q_e vs. log C_e is linear, and the constants K_F and $1/n$ can be obtained from the intercepts and slopes of the plot.

As shown in Fig. 5(c), it was obviously observed that the adsorption of Cd(II) ions onto WGH particles has higher consistency with the Freundlich isotherm ($R^2 = 0.9912$) in comparison with the Langmuir and Temkin isotherms (the values of R^2 are regarded as a measure of the goodness of fit of experimental data on the isotherm's models). The consistency with this isotherm means that the adsorption of solute (Cd(II)) is multilayer and also the surface of biosorbent (WGH particles) has heterogeneous sites for adsorption.

3.7.3. Temkin isotherm

The Temkin isotherm is represented by the following equation:

$$q_e = \left(\frac{RT}{b}\right)\ \ln(A \cdot C_e) \tag{8}$$

Its linear form is

$$q_e = \left(\frac{RT}{b}\right)\ \ln\ A + \left(\frac{RT}{b}\right)\ \ln\ C_e \tag{9}$$

The adsorption data can be analyzed according to (Eq. (9)). Therefore, a plot of q_e vs. ln C_e enables one to determine the constants A and b. A is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy and constant b is related to the heat of adsorption. The plot of this isotherm is shown in Fig. 5(d). The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions.

High regression correlation coefficients (>0.99) show that both Freundlich and Langmuir models are suitable for describing the biosorption equilibrium of Cd(II) by WGH in the studied concentration range. Nevertheless, according to order of R^2 values, the applicability of the three isotherm models for the present data follows the order:

Freundlich > Langmuir > Temkin.

However, an adsorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the sorbent and can also be used to find the sorptive capacity of biomass. The calculated Langmuir, Freundlich, and Temkin isotherm constants are given in Table 1. As can be seen here, the magnitude of K_F and n (Freundlich constants, 12.2 and 1.47) showed easy uptake of Cd(II) from aqueous solutions with high adsorptive capacity of WGH, at 25˚C. The value of n is greater than unity, indicating that Cd(II) ions are favorably adsorbed at the temperature studied.

The maximum monolayer adsorption capacity, q_m of WGH particles determined from the Langmuir isotherm defines the total capacity of the biosorbent for Cd(II) ions (9.93 mg g^{-1}). A large value of b also implies strong bonding of Cd(II) to the WGH at 25˚C. Hence, the results exhibit heterogeneous surface conditions and monolayer adsorption [35]. Based upon the Temkin values of equilibrium binding constant (A, 34) and heat of adsorption (b, 1,085), it can be concluded that the biosorption process includes surface adsorption besides complexation and electrostatic interactions.

3.8. Adsorption kinetics and kinetic modeling

The nature of adsorption process depends on physical or chemical characteristics of the adsorbent and also on the adsorption system conditions. Fig. 6 shows the plot of the amount of Cd(II) adsorbed (mg g^{-1}) vs. contact time for different initial Cd(II) concentrations. From the figure, it was observed that for an initial Cd(II) concentration of 1.5 mg L^{-1}, the maximum amount (approximately 88.11% of total amount of Cd(II) removed) of Cd(II) was adsorbed within the first 40 min and continued at slower rate up to 80 min. A similar trend was observed for the remaining range of initial Cd(II) concentrations (i.e. 0.5–3 mg L^{-1}) studied. The first rapid portion of the curve may be due to increased number of vacant sites available at the initial stages, as a result, there exists an increased concentration gradient between adsorbate in solution and adsorbate at the adsorbent surface. This increase in concentration gradient tends to increase in Cd(II) adsorption rate at initial stages. As time proceeds, this

Table 1
Constant values of adsorption isotherms for Cd(II) onto WGH particles

Isotherm	$q_{\max}$ (mg g^{-1})	b (L mg^{-1})	q_e (mg g^{-1})	K_F (mg/g)(L/mg)$^{1/n}$	$1/n$	A (L/mg)	b
Langmuir	9.93	3.65	1.73	–	–	–	–
Freundlich	–	–	1.73	12.2	0.68	–	–
Temkin	–	–	1.73	–	–	34	1,085

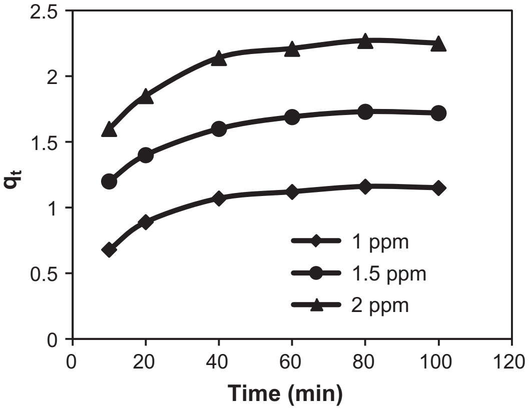

Fig. 6. Time effect on adsorption of different concentrations of Cd(II); conditions: T = 24–26°C, 25 mL solution of 1, 1.5, and 2 mg L^{-1} Cd(II) containing 0.02 g of WGH, initial pH 7, different contact time.

concentration in solution gets reduced due to the accumulation of Cd(II) ions in the vacant sites, leading to decrease in adsorption rate at later stages, i.e. from 40 to 80 min. The kinetics of Cd(II) adsorption onto WGH particles was analyzed using two simple kinetic models of pseudo-first order and pseudo-second order, and intraparticle diffusion model.

3.8.1. Pseudo-first-order model

The adsorption kinetic data of Cd(II) adsorption were analyzed using the Lagergren rate equation [36], which considers that the rate of occupation of biosorption sites is proportional to the number of unoccupied sites, therefore:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (10)$$

Integrating (Eq. (10)) between limits $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, (Eq. (11)) is obtained:

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \quad (11)$$

where q_e and q_t are the amounts of adsorbed Cd(II) ions on the biosorbent at equilibrium and at time t (mg g^{-1}), respectively, and k_1 is the equilibrium rate constant of pseudo-first-order adsorption. The slope and intercept of the plot $\log(q_e - q_t)$ vs. t were used to obtain the first-order rate constant k_1 and equilibrium adsorption q_e, respectively (Fig. 7(a)). The Lagergren first-order rate constant k_1 and q_e determined from the model indicated that this model had failed to estimate q_e since the experimental values of q_e differ from estimated ones (Table 2). This shows that the adsorption of Cd(II) ions onto WGH particles was not appropriate to describe the entire process and it was not a first-order reaction.

3.8.2. Pseudo-second-order model

This kinetic model is based on the assumption that the biosorption process follows a second-order mechanism; therefore, the occupation rate of adsorption sites is proportional to the square of the number of unoccupied sites and can be expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (12)$$

where k_2 is pseudo-second-order rate constant. After integration and applying the same boundary conditions $t = 0$ and $q_t = 0$ to t = t and $q_t = q_e$ at equilibrium, (Eq. (12)) takes the following form:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (13)$$

The second-order rate constant k_2 and q_e values were determined from the intercept and slope of the plot t/q_t vs. t presented in Fig. 7(b), the correlation coefficients (R^2) are indicative of the strength of the linear relationship. The theoretical q_e values (i.e. $q_{e,cal.}$) agree well with the experimental q_e values (i.e. $q_{e,exp.}$), suggesting that the sorption data tend to follow second-order kinetics for Cd(II) adsorption onto WGH particles (Table 2).

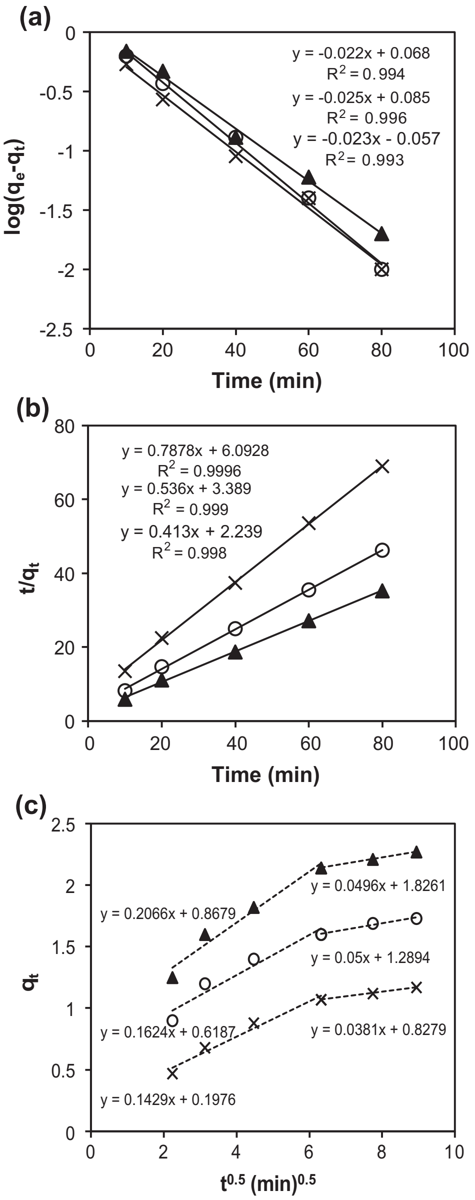

Fig. 7. Kinetic models for adsorption of Cd(II) onto WGH; (a) pseudo-first order, (b) pseudo-second order, and (c) intraparticle diffusion for different Cd(II) concentrations (×—1 ppm, O—1.5 ppm, ▲—2 ppm).

3.8.3. Sorption mechanism

Finding the rate limiting step is an important factor in sorption process. For solid–liquid sorption process, the sorption rate is shown to be controlled by several factors including the following processes:

(1) Transport of the solute from bulk solution to the adsorbent exterior surface (liquid film).
(2) Diffusion of solute from the film to particle surface and into the pores of the adsorbent except for a small quantity of sorption on the external surface.
(3) Sorption of solute on the interior surfaces of the adsorbent pores.
(4) Uptake which can involve several mechanisms, such as physicochemical sorption, ion exchange, precipitation, or complexation [37].

The overall rate of sorption is controlled by the slowest step, which can be either exterior surface diffusion or pore diffusion. However, the rate controlling step might be distributed between intraparticle and external surface transport mechanism. The third step is assumed to be a rapid equilibrium reaction and considered to be negligible. The sorption of Cd(II) ions onto WGH particles may be controlled due to exterior surface diffusion at earlier stages (assumed to be for the first 40 min) and as the adsorbent particles gets loaded with Cd(II) ions, the sorption process may be controlled due to intraparticle diffusion.

It is necessary to find the slowest step involved in the sorption process. For these processes, the external mass transfer controls the sorption rate for the systems that have poor mixing, low concentration of adsorbate, and small particle sizes of adsorbent, whereas the intraparticle diffusion controls the sorption rate for a system with good mixing, large particle sizes of adsorbent, and high concentration of adsorbate. In general, the external mass transfer is related to the initial solute uptake (in this study first 40 min).

The intraparticle diffusion coefficient for the sorption of Cd(II) ions was calculated from the slope of the plot between amount of Cd(II) adsorbed q_t (mg g^{-1}) vs. square root of time (min$^{0.5}$). Previous studies by various researchers showed that the plot of q_t vs. $t^{0.5}$ represents multilinearity, which characterizes the two or more steps involved in the sorption process. As shown in Fig. 7(c), at all three initial Cd(II) concentrations, the sorption process tends to be followed by two steps. The first step is initial linear portion that ended by second step with a low slope linear curve. These two steps suggest that the sorption process proceeds by both external surface sorption and the intraparticle diffusion. The initial portion of the plot indicates boundary layer effect or surface sorption while the second linear portion is due to intraparticle or pore diffusion [27].

The slope of second linear portion of the plot has been defined as the intraparticle diffusion rate constant k_{id} (mg g^{-1} min$^{-0.5}$). On the other hand, the intercept of the second step reflects the boundary layer effect. The larger the intercept, the greater is the contribution of the surface sorption in the rate limiting step as well as in the total process, i.e. the large

Table 2
Kinetic parameters for the adsorption of Cd(II) at different concentrations

		Initial Cd(II) concentration (mg L^{-1})		
Kinetic model	Kinetic parameters	1	1.5	2
Pseudo-first order	$q_{e(exp)}$ (mg g^{-1})	1.16	1.73	2.27
	$q_{e(cal)}$ (mg g^{-1})	0.81	1.33	1.2
	k_1 (min^{-1})	0.0537	0.0601	0.0511
Pseudo-second order	$q_{e(exp)}$ (mg g^{-1})	1.16	1.73	2.27
	$q_{e(cal)}$ (mg g^{-1})	1.28	1.90	2.47
	k_2 (g mg^{-1} min^{-1})	0.09136	0.06782	0.0578
Intraparticle diffusion	k_{id} (mg g^{-1} $min^{-0.5}$)	0.0381	0.0500	0.0496

amount of sorption takes place in initial part of the process and the intraparticle diffusion is not the sole rate limiting factor for the adsorption of Cd(II) [38]. The calculated intraparticle diffusion coefficient values (k_{id}) at different initial Cd(II) concentrations are shown in Table 2.

3.9. Desorption studies

Adsorption process can either be physisorption (physical bonding) or chemisorption (chemical bonding) or combination of both. If the adsorption is by physical bonding then the loosely bound metal ion can be easily desorbed with distilled water in most of the cases. However, if the mode of sorption is by chemical bonding or ion exchange or combination of both, then desorption can be affected by stronger desorbents like acid or alkali solutions. Distilled water (pH 6.8) was used to desorb Cd(II) from loaded WGH. The results revealed that the Cd(II) was not removed from biomass, this behavior was expected since the loading was performed at pH 7. Hence, the experiments were conducted with acid and alkali solutions. The Cd(II) ions were desorbed with acid solutions (HNO_3) and not with alkali solutions. About 94% of Cd(II) was desorbed using 0.1 moL^{-1} HNO_3. At low pH, hydrogen ions may release Cd(II) ions from the adsorbent following an ion exchange mechanism. Therefore, it can be concluded that the mode of biosorption of Cd(II) on WGH was chemisorption (chemical bonding or ion exchange) along with surface sorption. Hence, the rate of adsorption must be dependent upon chemical interaction too.

3.10. Application of the method

In order to access the applicability of the present optimized method, it was applied for the removal of cadmium from leach liquor of the zinc plant purification cake and wastewater. The results given in Table 3 depict the capability of the present method for the removal of Cd(II) from the real samples. However, the

Table 3
Removal of metal ions from real samples

Sample[a]	Cation	Initial concentration (mg L^{-1})	Removal (%)
Ni–Cd cake	Cd^{2+}	23.0 (±0.5)[b]	89.10
	Zn^{2+}	25.0 (±0.3)	65.50
	Ni^{2+}	6.0 (±0.4)	56.40
	Co^{2+}	1.0 (±0.1)	57.00
Wastewater	Cd^{2+}	8.0 (±0.6)	90.30
	Pb^{2+}	61.0(±0.5)	25.70
	Zn^{2+}	15.0 (±0.4)	63.00
	Ni^{2+}	4.5 (±0.5)	54.00

[a] Samples prepared as Section 2.3.

[b] Values in the parentheses are standard deviations for triplicate analysis.

Table 4
Comparison of different biosorbents for the removal of Cd(II)

Adsorbent	Modified with	$Q_{\max}$ (mg g^{-1})	Ref.
Rice husk	Water washed	8.58	[17]
	NaOH	20.24	[17]
Walnut sawdust	Formaldehyde in H_2SO_4	4.51	[16]
Cedrus deodar sawdust	NaOH	73.62	[18]
Spent grain	HCl	17.3	[19]
Juniper fiber	NaOH	29.54	[20]
Sugarcane bagasse	Ethylene diamine	189	[21]
Coconut copra meal	HCl	4.99	[14]
Sawdust (*Pinus sylvestris*)	Formaldehyde in H_2SO_4	9.29	[22]
Cassava tuber bark waste	Thioglycollic acid	26.3	[23]
Meranti wood	NA[a]	153–175	[15]
Mangosteen shell	Nitric acid	3.15	[13]
Walnut green husk	Water washed	9.93	This work

[a] Not available.

R% is lower (89–90%) compared to ≈96% obtained for standard solutions or synthetic samples (Sections 3.4 and 3.5). This decrease in efficiency is attributed to (i) the higher concentration of Cd(II)in the sample (same observation in Section 3.3); (ii) the presence of Zn(II), Ni(II), Pb(II), and Co(II) ions which compete with Cd(II) for the limited adsorption sites of the adsorbent; (iii) the inverse effect of salt on removal efficiency (Section 3.6). However, to enhance the efficiency, the adsorbent dose and contact time were varied, and >95% Cd(II) removal was achieved with 1.1–1.2 g WGH particles within 80 min.

3.11. Comparison with other adsorbents

Although the value of $q_{\max}$ is an important parameter and useful in scale-up considerations, the direct comparison of adsorbent capacity of walnut husk with other sorbents reported in the literature is difficult due to the varying experimental conditions employed in those studies. However, the walnut husk in this study possesses reasonable adsorption capacity for Cd(II) in comparison with other sorbents (Table 4).

4. Conclusions

As shown in this work, biosorption is a suitable procedure for the removal of heavy metals involved in wastewater. According to the experimental results, the WGH has high efficiency in uptake of heavy metals due to removal of >95% Cd(II) ions and co-extraction of Zn(II), Ni(II), and Pb(II) from the aqueous solutions and wastewaters (Table 3). Hence, it can be considered as an alternative to those methods that are not able to remove heavy metals with very low concentrations. The method is simple and cost-effective compared to many other methods due to easy availability and low cost of WGH. The amount of Cd(II) adsorbed was found to vary with initial solution pH, initial Cd(II) concentration, and adsorbent amount and contact time. The amount of Cd(II) uptake (mg g^{-1}) was found to increase with increase in the values of these parameters except adsorbent mass. This process was found to follow pseudo-second-order kinetic model. Equilibrium data although were fitted to all the three Langmuir, Freundlich, and Temkin isotherm models but fitted very well in the Freundlich isotherm equation that confirmed firstly the multilayer adsorption of Cd(II) onto WGH particles and secondly showed heterogeneous sites at surface of applied biosorbent. From the Langmuir isotherm, the biosorbent monolayer capacity (q_m) was obtained as 9.93 mg g^{-1}. The adsorption data were in line with both Freundlich and Langmuir models exhibiting heterogeneous surface conditions and monolayer adsorption. The Cd(II) uptake process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages. However, the chemisorption such as ion exchange also is to be considered.

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