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Continuous biosorption of Cd(II) ions from aqueous solutions by sesame waste: thermodynamics and fixed-bed column studies

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ABSTRACT

The present study explored the ability of sesame waste biomass in removing Cd(II) from aqueous solutions in a fixed-bed column. The biosorbent was characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). There were hydroxyl group, carboxyl group, etc. on the surface of the adsorbent from FTIR. A continuous study was carried out to evaluate the effects of flow rate, initial Cd(II) concentration, and bed height on breakthrough curves. The maximum uptake of Cd(II) in a fixed-bed adsorption column was 22.88 mg g^{-1} and the initial Cd(II) concentration, bed height, flow rate, and pH were 60 mg L^{-1}, 2 cm, 2.5 mL min^{-1}, and 5.5, respectively. Bohart–Adams, Thomas, and Yoon–Nelson models were applied to the data to predict breakthrough curves and find the characteristic parameters. Unique characteristic features of the mentioned models, such as adsorption capacity (Thomas model) and time required, for 50% breakthrough (Yoon–Nelson model) were achieved too.

Keywords: Sesame waste; Biosorption; Cadmium ion; Fixed-bed; Modeling; Thermodynamic

1. Introduction

Pollution of water environments by heavy metals is a universal environmental problem owing to their poisonous effects and accumulation through the food chain. Among the heavy metals, lead is one of the most dangerous contaminants charged into the water from different industrial activities such as electroplating, battery manufacturing, smelting, pigments, mining, and other applications. Wastewaters generated by related industries include high levels of this poisonous metal ion, which is required to be treated to safe limits before releasing into the environment. This contaminant is nondegradable and if taken in excess than the safe limit, it can result in many significant diseases such as hypertension, kidney damage, renal disorder, bone fraction, destruction of red blood cells, and ultimately, death.

To weaken the problem of aqueous contamination by heavy metals in the environment, several methods such as coagulation, flotation, reduction and precipitation, adsorption on activated carbon, ion exchange, reverse osmosis, and electrodialysis have been studied in order to eliminate heavy metals from wastewater [1–4]. In general, these methods are expensive or

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ineffectual, particularly when the metal concentrations are in the range of 1–100 mg/L [5].

Biosorption, as an alternate method, has become one of the most effective methods for the elimination of heavy metals from wastewater. The main advantages of biosorption over conventional treatment methods are: high efficiency, low cost, minimization of chemical or biological sludge, regeneration of biosorbents, and the possibility of metal recovery.

Several waste containing byproducts from agriculture and industry have been used as low-cost biosorbents, such as sesame leaf, banana peels, wheat straw, sugarcane bagasse, chitosan, aquatic plants, and seaweed and modified corn stalk [6–12]. Rice husk and rice polish, in their natural form as well as the modified forms, have been used for removing cadmium ions [13,14]. Plant biomass of Parthenium has also been tried for the biosorption of cadmium and removal efficiency has been determined [15]. Adsorption experiments have been performed for cadmium removal from aqueous solutions on other parts of the plants, such as peels of peas, fig leaves, broad beans, orange peels, medlar peels, and jack fruits as adsorbents, showing high removal efficiencies at acidic pH [16]. High efficiencies for the removal of cadmium have also been reported using hazelnut shells, peanut hulls, walnut shells, and green coconut shells [17]. Moreover, cadmium removal efficiencies varying from 50 to 98% have been obtained for adsorption studies directed on the activated carbon of bagasse pith, coir pith, peanut shells, and dates [18,19]. Recently, the removal of Cd(II) from industrial wastewater by macrofungus *Pleurotus platypus* was studied in a fixed-bed column and the breakthrough and exhaustion points were found to be earlier for the biosorption of Cd(II) in the presence of co-ions [20].

As mentioned, a number of studies in this area have used some other adsorbents rather than sesame waste for the removal of cadmium ions. On the other hand, only two biosorption studies have been reported using sesame waste [6,21] in a batch mode. The results have shown that sesame waste can be utilized as a promising biosorbent for Pb(II) removal. Hence, in this work, the capability of the sesame waste for removal of cadmium ions from aqueous solutions was investigated in a fixed-bed column for the first time.

Sesame waste includes leaf and stem parts usually disposed in the environment as a useless solid waste, which, in turn, causes environmental pollution. Thus, conversion of sesame waste to low-cost biosorbent is performed to achieve tow purposes. First, the unwanted cheap market waste is converted to some useful material; second, it may be efficiently used for the abatement of environmental pollution. Thus, in the present work, an attempt has been made to use low-cost sesame waste biosorbent to remove Cd(II) based on an adsorption technique in a fixed-bed column. Breakthrough curves were achieved at various flow rates, initial cadmium concentrations, and bed heights. Moreover, the data were examined using different kinetic models: Bohart–Adams model, Thomas model, and Yoon–Nelson model [22–24]. In addition, the effect of temperature on the process was studied, and the free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were also determined.

2. Methods

2.1. Preparation and characterization of sesame biosorbent

Sesame waste was collected from a local industrial center and washed thoroughly with distilled water to remove any dirt. It was then dried in an oven at 110°C until it reached a constant weight; it was cut into uniform lengths of 1 cm and fed to a mixer and grinder to be ground. Finally, it was sieved for a particle size of 0.21 mm.

The functional groups of the sesame waste were characterized by a Fourier transform infrared (FTIR) spectrometer (PE-1710, USA) using potassium bromide discs to prepare the sesame sample. The spectra of sesame were measured within the range of 4,000–400 cm^{-1} wave number. Scanning electron microscopic (SEM) studies were performed (Stereo Scan LEO, Model-400) to determine the surface characteristics of the sesame waste. Also, the BET (Brunauer, Emmett and Teller) surface area for the adsorbent was measured using Smart Sorbs 92 surface area analyzer.

2.2. Reagents

$\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was the heavy metal salt used. All other chemicals such as HCl and NaOH were of analytical reagent grade and supplied by Merck. Deionized water was used for the entire experiments.

2.3. Fixed-bed column biosorption study

Fixed-bed column experiments were carried out in a laboratory-scale glass column. The column was 2.2 cm in the internal diameter, and 30 cm in its length. Fig. 1 displays the experimental setup used for the present study.

The sesame waste with the particle size of 0.21 mm was packed in the column between glass wool, preventing the sesame waste from being washed out and enabling a uniform inlet flow into the column. Column was packed with 4.00, 8.00, and 12.00 g of

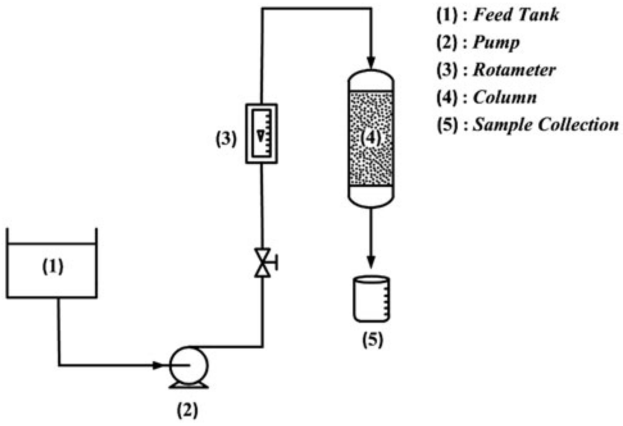

Fig. 1. Experimental setup.

sesame to achieve a particular bed height of the biosorbent (equiv. to 2, 4, and 6 cm of bed depth) at 298 K, thereby keeping flow rate and influent Cd(II) concentration constant at 3.5 mL/min and 60 mg/L, respectively. In addition, Cd(II) solution of known concentrations (20, 60, and 100 mg/L) at the pH of 5.5 was fed through the column at the flow rate of 3.5 mL/min, and the biosorbent bed height of 2 cm. To investigate the effect of flow rate on Cd(II) adsorption in the fixed-bed column, experiments were performed for the flow rates of 2.5, 3.2, and 4.5 mL min^{-1}, keeping bed height of the biosorbent and influent Cd (II) concentration constant at 2 cm and 60 mg/L, respectively. Effluent samples were collected during the time-course of the experiments to determine the metal concentration in the effluent solutions, and analyzed by atomic absorption spectrometry (Perkin Elmer model Aanalist 2300). Air-acetylene flame and Hollow Fiber Cathode as the light source with the linear range of 2 ppm were used for the determination of Cd(II) concentration by atomic absorption. Also, the working conditions such as wavelength and slit width were 228.8 nm and 0.7 nm, respectively. The flow to the column was continued until the Cd(II) concentration was close to the influent concentration.

2.4. Column data analysis

The breakthrough curves describe the performance of the fixed-bed column. The general shape of the breakthrough curve and the time for breakthrough appearance are known as the major characteristics to estimating the operation and dynamic behavior of an adsorption column [25,26]. The effluent concentration (C_2) from the fixed-bed column, which is extended to about 0.1% of the influent concentration (C_1), is usually known as the breakthrough point. The effluent concentration from the fixed-bed column with an extent of 90% is called the point of column exhaustion [27]. The breakthrough curve is generally defined by C_2/C_1 as a time function or outlet volume for a given bed depth [26]. The effluent volume, V_{eff} (mL), is evaluated as follows [28]:

$$v_{\text{eff}} = Q \times t_{\text{t}} \tag{1}$$

where Q and t_{t} are the volumetric flow rate (mL min^{-1}) and the total flow time (min), respectively.

The total value of metal ions adsorbed to the column, known as q_{t} (mg), can be evaluated from the following equation:

$$q_{\text{t}} = \frac{Q}{1,000}\int_{t:0}^{t:t_{\text{t}}} C_{\text{ad}}\, \mathrm{d}t \tag{2}$$

where C_{ad} expresses the concentration of metal removal (mg L^{-1}).

The maximum capacity of the column, known as q_{max} (mg g^{-1}), can be evaluated from the following equation:

$$q_{\text{max}} = \frac{q_{\text{t}}}{m} \tag{3}$$

where m refers to the dry weight of the adsorbent in the column (g). The total value of metal ion sent to the column (m_{t}) is evaluated as follows [29]:

$$m_{\text{t}} = \frac{C_0 q_{\text{t}} t}{1,000} \tag{4}$$

where C_0 is the inlet metal ion concentration (mg L^{-1}). Finally, the removal percentage of Cd(II) ions was attained as shown in the following equation:

$$\%\ Removal = \frac{q_{\text{t}}}{m_{\text{t}}} \times 100 \tag{5}$$

2.5. Thermodynamic study

To evaluate the thermodynamic parameters for the interaction of Cd(II)–sesame, the removal of Cd(II) from solution by sesame waste was investigated in a batch mode after 30 min of agitation at different temperatures, e.g. 25, 50, and 75℃. According to the results obtained from some preliminary experiments, they were performed at pH 6, cadmium concentration = 20 mg L^{-1}, stirring speed = 240 rpm, and adsorbent dose = 3.33 g dm^{-3}. The equilibrium adsorption capacity, Q_e, of Cd(II) aqueous solution was calculated according to the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{6}$$

where V is the sample volume (L), m is the mass of biosorbent (g), C_o is the initial concentration of Cd(II) in the solution (mg/L), and C_e is the equilibrium concentration of Cd(II) in the solution (mg/L). For time-dependent data, C substitutes C_e and Q substitutes Q_e in Eq. (6).

3. Results and discussion

3.1. Characterization of the biosorbent

The nitrogen adsorption–desorption isotherm of sesame waste was achieved. The BET surface area of sesame waste was found to be 6.666 $m^2 g^{-1}$. The total pore volume and the average pore diameter of sesame waste were 0.010 mL g^{-1} and 2.474 nm, respectively.

Scanning electron micrographs of sesame particles before and after cadmium uptake are displayed in Fig. 2(a) and (b).

SEM micrograph of sesame waste displayed a rough and irregular surface (Fig. 2(a)), indicating that the sesame waste had good characteristics to be used as an adsorbent for metal ion uptake. A significant change in the biosorbent surface was seen after the biosorption of cadmium. Moreover, a polishing/smoothening effect perceived in Fig. 2(b), showed that the adsorption of cadmium ions over biosorbent made the surface of biosorbent smoother than its original form.

To characterize the type of the functional groups effective for Cd(II) ions removal, FTIR spectra of the adsorbent were attained and showed in Fig. 3.

The FTIR spectrum of sesame waste showed a broad peak observed at 3,298 cm^{-1} and it could be assigned to the O–H stretching vibrations of cellulose, pectin, hemicellulose, and lignin [30]. The OH stretching vibrations took place within a broad range of frequencies, indicating the existence of free hydroxyl groups and bonded OH bands of carboxylic acids [31]. The bands at 2,924 and 2,854 cm^{-1} were assigned to the stretching vibration of $–CH_3$ and $–CH_2$, respectively. The strong peak near 1,658 cm^{-1} could be related to the stretch vibration of C–O from carboxyl group in the presence of intermolecular hydrogen bonding [32]. The peak around 1,541 cm^{-1} could be from the C–C stretching of aromatic ring [32]. The peak at 1,431 cm^{-1} was characteristic of the symmetric bending of $–CH_3$. The strong peak observed at 1,054 cm^{-1} displayed the vibration of C–O and stretching vibration in lignin structure of the sesame. The band around 1,245 cm^{-1} was also attributed to the presence of the C–O stretching of phenols.

3.2. Underlying mechanism of adsorption

The surface binding-sites of the adsorbent and the presence of hydrogen ion in solution are known to have a significant effect on the adsorptive uptake of metal ions. Due to the value of solution pH, the adsorbent surface undergoes protonation or deprotonation [33]. At lower pH values, stiff competition between hydrogen and cadmium cations for the active sites could reduce Cd(II) adsorption. In this situation, high positive charge density of the adsorbent made the Cd (II) adsorption unfavorable due to electrostatic repulsion. Reversely, at higher pH values, the presence of hydrogen ions in the aqueous solution was reduced and the adsorbent surface was also deprotonated, thereby resulting in the increased adsorption of Cd(II). It is necessary to point out that according to the above discussion and some preliminary experiments, the results of adsorption were obtained at pH 6. Finally, deprotonation of the adsorbent surface underwent electrostatic attraction for Cd(II), resulting in the formation of metal–ligand complexes. On the other hand,

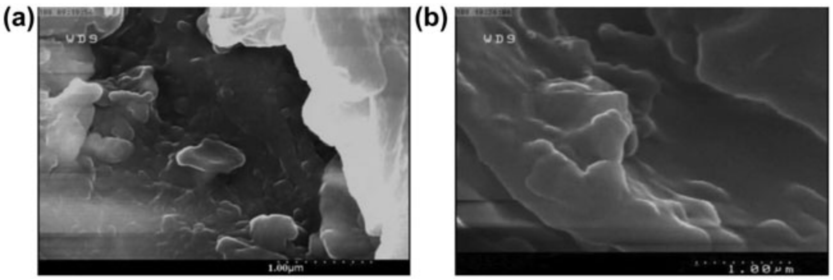

Fig. 2. Scanning electron micrograph of biosorbent (a) before Cd(II) adsorption and (b) after Cd(II) adsorption.

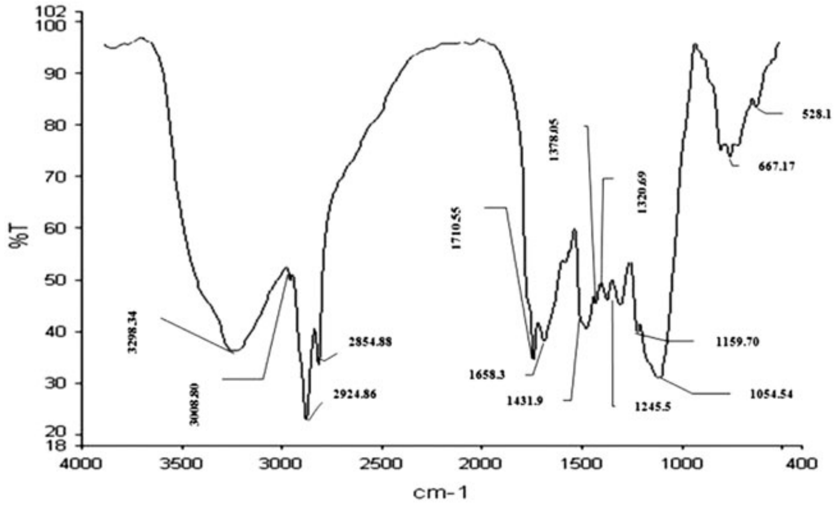

Fig. 3. FTIR spectra of sesame waste.

the functional groups present in biomass molecules such as carbonyl, phenolic and carboxyl had the affinity for metal complexation [34]. In the present work, multi hydroxyl groups on sesame, as perceived by FTIR spectra, played the main role in the Cd(II) adsorption. As a result, complexation and ion exchange appeared to be the governing mechanism of the adsorption. In this regard, the sorption of Pb(II) and Cd(II) ions by nitric acid-treated wild cocoyam biomass was studied and the sorption was reported to occur by ion-exchange mechanism containing hydroxyl groups [35].

3.3. Thermodynamic parameters

3.3.1. The effect of temperature

Temperature plays a crucial role in the adsorption process. Firstly, the rising temperature decreases the viscosity of the solution, which, in turn, improves the diffusion rate of the adsorbate molecules across the external boundary layer of the adsorbent, leading to higher adsorption. Secondly, temperature variations may affect the equilibrium adsorption capacity of the biosorbent. For example, the adsorption capacity will be reduced upon raising the temperature for an exothermic reaction; on the other hand, it is improved for an endothermic one. Therefore, an investigation of the temperature effect on biosorption processes can offer substantial data about the standard Gibbs free energy, enthalpy, and entropy variations related to adsorption. Experiments were performed in this regard to find the optimum temperature and determine thermodynamic parameters on the adsorption of Cd(II) ions onto sesame waste at three different temperatures of 298, 313, and 328 K. The results are shown in Fig. 4.

As can be seen in Fig. 4, the value of Cd(II) adsorbed was reduced as the temperature was increased. This reduction implied that the adsorption process was an exothermic one. This could be according to the tendency of Cd(II) molecules to discharge from the sorbent to the aqueous solution with an enhancement in temperature. A similar result was also found in a sorption study of lead using kaolinite clay as the sorbent [36].

3.3.2. Calculation of the free energy change (ΔG)

Free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were determined in order to

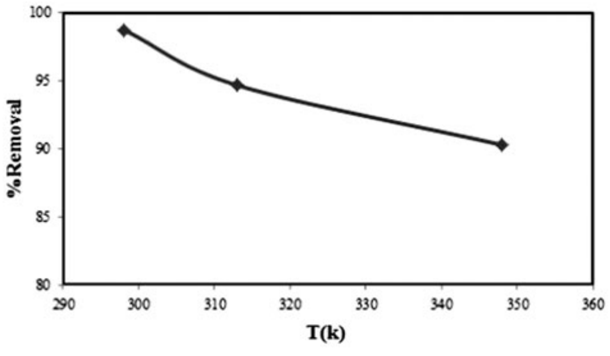

Fig. 4. The effect of temperature on the removal of Cd(II) (the initial Cd(II) concentration of 60 mg L^{-1}, the pH of 6; the stirring speed of 240 rpm and the adsorbent dose of 3.33 g dm^{-3}).

evaluate the effect of temperature on the biosorption of Cd(II) ions on sesame waste. The apparent equilibrium constant k'_c of the biosorption can be defined as [37]:

$$k'_c = c_{ad,e}/c_e \tag{7}$$

where $c_{ad,e}$ represents the concentration of the adsorbate on the biosorbent at equilibrium ($mg\,L^{-1}$). The value of k'_c can be substituted in the following equation to achieve the change of Gibbs free energy of adsorption (ΔG).

$$\Delta G = -RT \ln k'_c \tag{8}$$

Subsequently, the change of enthalpy (ΔH) and entropy (ΔS) can be determined from the slope and intercept of van't Hoff equation of ΔG vs. T.

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

where T is absolute temperature, K and R refer to universal gas constant, which is $8.314\ J\,mol^{-1}\,K^{-1}$. The linear plot of $\ln k'_c$ vs. $1/T$ is presented in Fig. 5. Values of thermodynamic parameters for the adsorption process are presented in Table 1.

It should be noted that the negative values of ΔG at all temperatures show the spontaneous nature of the adsorption of Cd(II) on sesame waste. The negative value of ΔG was reduced with an enhancement in temperature, proving that a better adsorption was attained at lower temperatures. It should also be noted that the negative value of ΔH indicated the exothermic nature of adsorption. In addition, the positive value of ΔS showed the enhanced randomness at the solid–solute interface during the adsorption process, thereby indicating that the solution system tended toward stability while the biosorption of Cd(II) on the biosorbent surface happened due to the second law of thermodynamics [6,37]. On the other hand, it was found that systems were always evolved toward thermodynamic equilibrium, a state with maximum entropy. This observation suggested that cadmium ions substituted some water molecules from the aqueous solution before being adsorbed on the surface of adsorbent. These substituted molecules gained more translation entropy than that lost by the adsorbate ions, thereby causing the prevalence of randomness in the system [38]. It has also been proposed that the positive values of entropy show some structural changes in the adsorbent and adsorbate [39]. The low value of ΔS also points to the fact that no significant changes happened on entropy.

Table 1
Thermodynamic parameters of the Cd(II) adsorption on sesame waste

T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ molK)
298.15	−24.94	−6.754	0.061
323.15	−26.47		
348.15	−27.99		

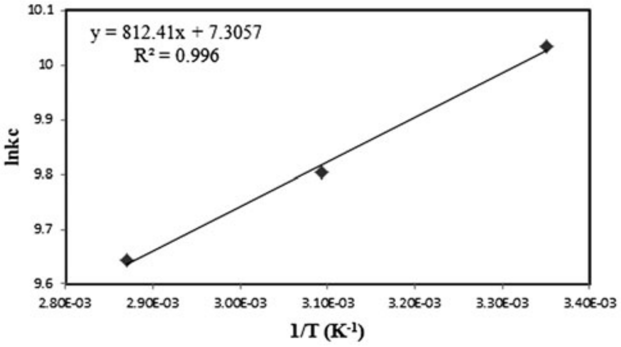

Fig. 5. Linear plot of $\ln k_c$ vs. $1/T$ (the initial Cd(II) concentration of $60\ mg\,L^{-1}$; the pH of 6; the stirring speed of 240 rpm and adsorbent dose of $3.33\ g\,dm^{-3}$).

3.3.3. Estimation of activation energy

Knowledge of the type of sorption can be obtained with the magnitude of activation energy. Two main types of adsorption are considered: physical and chemical. Activated chemical adsorption occurs when the rate varies with temperature according to finite activation energy (8.4–$83.7\ kJ\,mol^{-1}$) in Arrhenius equation. In the nonactivated chemical adsorption, the activation energy is close to zero [37].

The activation energy for sesame waste adsorption was estimated by Arrhenius equation:

$$K = k_0 e^{\frac{-E_a}{RT}} \tag{10}$$

where E_a is the apparent activation energy of the reaction of adsorption in $J\,mol^{-1}$, k_0 is the temperature independent factor in $g\,mg^{-1}\,min^{-1}$, T is the adsorption absolute temperature, K and R are the gas constants, $8.314\ J\,mol^{-1}\,K^{-1}$. The linear form of Arrhenius equation is:

$$\ln k = -\frac{E_a}{RT} + \ln k_0 \tag{11}$$

The plot of ln k vs. $1/T$ gives a straight line, and energy of activation (E_a) can be estimated from the slope of the linear form of Arrhenius equation. The value of activation energy was found to be -37.58 kJ mol^{-1} for Cd(II). As mentioned before, the magnitude of activation energy may imply the type of adsorption. Usually, in physical adsorption the equilibrium is rapidly achieved and easily reversible as the energy requirements are slight. The activation energy obtained for physical adsorption is typically less than 4.2 kJ mol^{-1}, because the forces involved in physical adsorption are weak. In contrast, chemical adsorption is specific and includes forces much stronger than those in physical adsorption. Therefore, the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions. Moreover, two kinds of chemical adsorption are defined: activated and less frequently, nonactivated. The first one happens when the rate varies with temperature due to finite activation energy (between 8.4 and 83.7 kJ mol^{-1}) in the Arrhenius equation. But in the second one, chemisorption happens very quickly, suggesting that the activation energy is near zero [40]. So the obtained value (-37.58 kJ mol^{-1}) for activation energy is of the same magnitude as that of the activation energy of activated chemical sorption [32,37]. In this regard, Ho and Ofamaja have indicated that the value of activation energy of 22 kJ mol^{-1} suggests that chemisorption is the main process in the adsorption of copper onto HCl-treated palm kernel fiber [41]. In addition, the negative value of activation energy was found to confirm that an increase in temperature did not favor the adsorption, and that adsorption process could be naturally exothermic.

3.4. The effect of bed depth

The effect of bed depths on the breakthrough curves is exhibited in Fig. 6. In the present work, the breakthrough times and the charge times corresponded to $C_2/C_1 = 0.1$ and 0.9, respectively, where C_1 and C_2 were the inlet and outlet Cd(II) concentrations in the column, respectively [42]. It was illustrated that the charge time was enhanced with an increase in the bed depth.

It can be seen from Fig. 6 that the slope of breakthrough curve was reduced with an increase in bed depth, which caused a broadened mass transfer zone [25,43]. The sorption column data were evaluated as shown in Table 2. From the data shown in Table 2, one can conclude that the removal efficiency of Cd(II) ions had an increasing trend in column with the enhancement in the biosorbent mass. As reported in Table 2, the bed depth influenced the Cd(II) removal of 67.67, 75.88, and 77%, as obtained at 2, 4, and 6 cm, respectively. The rise in the removal percentage of Cd (II) with increasing the bed depth and consequently, enhancing biosorbent mass in the column could result from increasing adsorbent total mass transfer surface area, which supplied more binding sites for the adsorption [44,45]. But the results presented in Table 2 showed that the Cd(II) uptake capacity, $q_{e'}$ was decreased with increasing bed depth in the fixed-bed column. Moreover, when the bed depth was enhanced to 6 cm, a longer charge time was observed as shown in Table 2. These observations revealed that the bed depth of 2 cm provided an optimum breakthrough curve so that further experiments were performed with the bed depth of 2 cm.

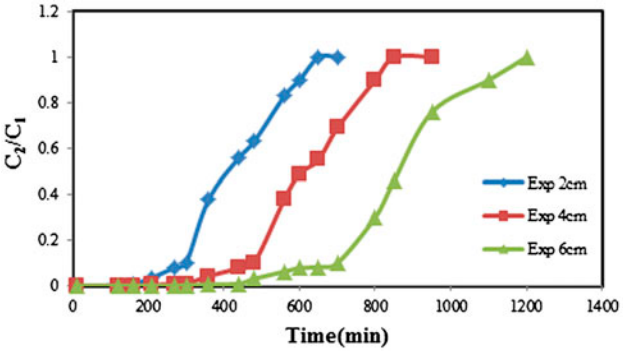

Fig. 6. The effect of bed depth on the breakthrough curve of Cd(II) adsorption on sesame waste (the initial Cd(II) concentration of 60 mg L^{-1}; the flow rate of 3.5 mL min^{-1}; the pH of 5.5).

3.5. The effect of flow rate

Experiments were performed by varying the flow rate between 2.5 and 4.5 mL min^{-1} in order to investigate the effect of the flow rate on Cd(II) adsorption in the fixed-bed column. The effect of flow rate on breakthrough performance is presented in Fig. 7.

It was obvious that for the flow rates of 2.5, 3.2, and 4.5 mL min^{-1}, the breakthrough times were 480, 300, and 160 min, respectively, while the charge times were found to be 850, 600, and 360 min, respectively. If the charge times were compared with each other, one could conclude that at low flow rate, it took more time to earn saturation. This is because at lower flow rates, the external film mass resistance at the biosorbent surface was increased and the residence time of the adsorbate in the column was enhanced; hence, Cd (II) ions have more time to diffuse into the biosorbent pores and this, in turn, resulted in higher removal efficiency. Similar results have been achieved by other researchers [42,46].

Table 2
Parameters in the fixed-bed column for the Cd(II) adsorption by sesame waste

Initial Cd(II) concentration (mg/l)	Flow rate (mL min^{-1})	Bed height (cm)	Breakthrough time (min)	Exhaust time (min)	m_{Total} (mg)	q_{Total} (mg)	q_e (mg g^{-1})	% Removal
20	3.5	2	520	900	62.37	45.78	11.44	73.41
60	3.5	2	300	600	113.68	76.93	19.23	67.67
100	3.5	2	160	440	153	87.54	21.88	57.2
60	2.5	2	480	850	124	91.54	22.88	73.77
60	4.5	2	160	360	94.6	60.55	15.13	64
60	3.5	4	480	800	165.2	125.35	15.66	75.88
60	3.5	6	700	1,100	227.15	175.08	14.58	77

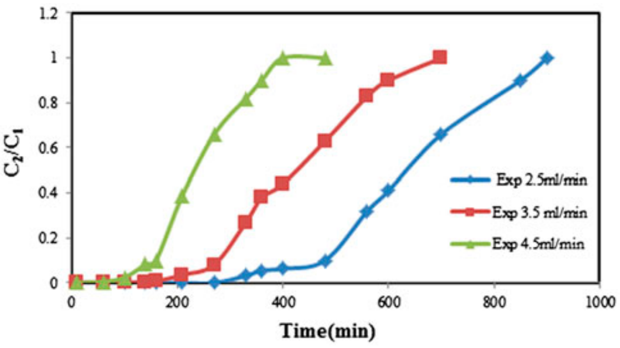

Fig. 7. The effect of flow rate on the breakthrough curve of Cd(II) adsorption on sesame waste (the bed depth of 2 cm, the initial Cd(II) concentration of 60 mg L^{-1}; the pH of 5.5).

Moreover, it can be concluded from data presented in Table 2 that the flow rate also affected the Cd(II) uptake capacity. As flow rate was enhanced from 2.5 to 4.5 mL/min, the extent of Cd(II) uptake (q_e) was reduced from 22.88 to 15.13 mg/g, This might be according to the reduction in insufficient contact time. Similar results have been reported by other researchers [47,48].

Moreover, from the literature reviewed above, it could be inferred that the biosorbents used in different investigations were compared in terms of maximum sorption capacities attained for the sorption of Cd(II) ions from aqueous solution in a fixed-bed column (Table 3) [10,20,49–52].

In this work, the maximum removal capacity of sesame waste for Cd(II) ions was found to be 22.88 mg g^{-1}, which was very much comparable with the adsorbents such as sphagnum peat moss, mollusk shells, and macrofungus *P. platypus* when they were tested for Cd(II) ions removal by other scientists [20,50]. In general, it can be indicated that sesame waste used in this study had a reasonable sorption capacity in contrast with other sorbents, with the additional advantage of abundant and economic.

3.6. The effect of initial adsorbate concentration

The adsorption performance of sesame waste was experienced at different Cd(II) influent concentrations of 20, 60, and 100 mg L^{-1}, and the breakthrough curves are presented in Fig. 8.

It can be seen from Fig. 8 that the breakthrough time was diminished with the enhancement in inlet Cd(II) concentration according to faster saturate sorption sites [42,46]. Moreover, for high inlet concentration (100 mg L^{-1}) of Cd(II), it took a shorter time (160 min) to attain the breakthrough, whereas at lower Cd(II) concentration (20 mg L^{-1}), the breakthrough happened within a long period (520 min). The exhaustion time for biosorbent was also reduced from 900 to 440 min when the inlet concentration of Cd(II) was enhanced from 20 to 100 mg L^{-1}. In addition, the breakthrough curve was sharp for the highest inlet concentration (100 mg L^{-1}), thereby suggesting a comparatively less zone of mass transfer and intraparticle diffusion control. Similar trends have been obtained by other researchers [2,10].

As observed in Table 2, adsorption capacity was improved from 11.44 to 21.88 mg g^{-1} with rising influent Cd(II) concentration. This can be explained by the fact that the driving force for the transfer process is improved when inlet Cd(II) concentration is increased, leading to overcoming the resistance of mass transfer. The removal percentage for Cd(II) was also reduced from 73.41 to 57.20% with the increase in the metal concentration sent to the fixed-bed column. This referred to the saturation of binding sites presented on the biosorbent for a finite mass of biosorbent, while the inlet concentration was enhanced. A similar tendency has been reported by Malkoc [53].

Table 3
Comparison of the sorption capacity obtained for the Cd(II) removal onto sesame waste and other types of biosorbents in a fixed-bed column

Biosorbent	q (mg g^{-1})	Ref.
Carbonaceous material (pyrolyzed sewage sludge)	22.9	Segura et al. [49]
Sphagnum peat moss	1.91	Li et al. [50]
Mollusk shells	8.15	Li et al. [50]
Grape stalk wastes	33.12	Miralles et al. [51]
Syzygium cumini L. leaf powder	29.08	Rao et al. [52]
Macrofungus *Pleurotus platypus*	13.25	Vimala et al. [20]
Plain chitosan	40.1	Sankararamakrishnan [10]
Sesame waste	22.88	This work

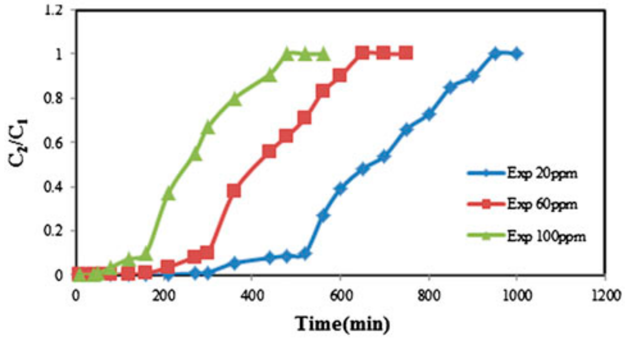

Fig. 8. The effect of the initial Cd(II) concentration on the breakthrough curve of Cd(II) adsorption on sesame waste (the bed depth of 2 cm; the flow rate of 3.5 mL min^{-1}; the pH of 5.5).

3.7. Models for adsorption in the column of sesame waste

3.7.1. Application of Bohart–Adams model

The Bohart–Adams model is one of the fixed-bed analysis methods used for the explanation of the initial section of breakthrough curve. This model can be employed to estimate the characteristic parameters such as kinetic constant (k_{AB}, L mg^{-1} min^{-1}) and the exhaustion concentration (N_0, mg L^{-1}). The model equation can be expressed as:

$$\ln\left(\frac{C_t}{C}\right) = K_{AB} \times C \times t - \frac{K_{AB} \times N_0 \times Z}{U_0} \tag{12}$$

where C and C_t are the influent and effluent concentrations, respectively. Z points to the bed height (cm) and U_0 is superficial velocity (cm min^{-1}). The values of $\ln(C_t/C)$ were plotted against time at various flow rates, initial biosorbate concentrations and bed heights to calculate the kinetic constant (k_{AB}) and exhaustion concentration (N_0) values. The model parameters, k_{AB} and N_0 values, were evaluated from the slope and intercept of the curves, respectively, as reported in Table 4.

As can be seen from Table 4, the value of N_0 was improved with increasing the initial concentration, and decreasing the flow rate and bed depth. Also the kinetic constants were improved with enhanced extents in the flow rate, reduction in the initial concentration and diminution in the bed height. Moreover, from data represented in Table 4 one can examine the curve-fitting capability of the Bohart and Adams model. This model, which is applicable only to the initial part of the breakthrough curve, assumes that the rate of adsorption is controlled by the surface reaction between adsorbate and the unsaturated adsorbent [22]. Therefore, such fit of the experimental data on Bohart model (R^2 range from 0.82 to 0.95) validates the simplistic modeling approach and suggests that the overall system kinetics can be controlled by external mass transfer in the initial zone of adsorption in the fixed-bed column [12,54].

3.7.2. Application of Thomas model

The maximum concentration of the solute on the adsorbent and the rate constant of adsorption through a continuous adsorption process in the column can be evaluated by Thomas model.

The linearized form of the model is expressed as:

$$\ln\left(\frac{C}{C_t} - 1\right) = \frac{K_{Th} \times q_0 \times m}{F} - K_{Th} \times C \times t \tag{13}$$

where k_{Th} is the Thomas rate constant (L mg^{-1} min^{-1}), q_0 is the solute maximum concentration (mg g^{-1}), m is the adsorbent amount (g) used in the column, and F is the volumetric flow rate (L min^{-1}).

The values of k_{Th} and q_0, as evaluated by plotting $\ln(C/C_t{-}1)$ against the effluent volume, are presented in Table 5.

The results showed that the bed capacity (q_0) was reduced and the coefficient (k_{Th}) was improved with a rise in the flow rate. As the initial Cd(II) concentration was enhanced, the value of q_0 was improved, whereas the value of k_{Th} exhibited a reverse behavior. It was due to the driving force for adsorption in the concentration difference. Moreover, it can be concluded that the kinetic coefficient and the bed capacity were improved with diminution in the bed height. Hence the higher influent concentration, the lower flow rate and the lower bed depth, thereby improving the adsorption of Cd(II) on the bed column to a limited extent. Also, the analysis of the regression coefficients showed that the regressed lines provided were well fitted to the experimental data with R^2 values ranging from 0.95 to 0.99. Comparing the values of R^2 as reported in Tables 4 and 5, indicated that the Thomas model provided a better fitting compared to Adams–Bohart model. This well fitting of the empirical data on Thomas model showed that internal and external diffusions were not the rate-limiting steps [52,54].

Table 4
Bohart–Adams model parameters

Parameter	$k_{BA} \times 10^{-4}$	N_0	R^2
Initial Cd(II) concentration (mg L^{-1})			
20	4.14	28,010.14	0.89
60	1.862	51,406.95	0.87
100	1.197	63,823.57	0.82
Flow rate (mL min^{-1})			
2.5	1.33	56,893.20	0.84
3.5	2.67	43,639.28	0.93
4.5	2.77	42,527.36	0.87
Bed height (cm)			
2	1.93	50,343.03	0.86
4	1.69	37,362.04	0.94
6	1.288	34,471.91	0.93

Table 5
Thomas model parameters

Parameter	$k_{Th} \times 10^{-4}$	q_0	R^2
Initial Cd(II) concentration (mg L^{-1})			
20	5.4	11.89	0.98
60	2.7	20.80	0.97
100	1.8	24.23	0.95
Flow rate (mL min^{-1})			
2.5	2.03	23.61	0.96
3.5	2.91	20.50	0.96
4.5	4.1	16.69	0.97
Bed height (cm)			
2	2.76	20.51	0.97
4	2.25	16.23	0.99
6	1.73	14.89	0.98

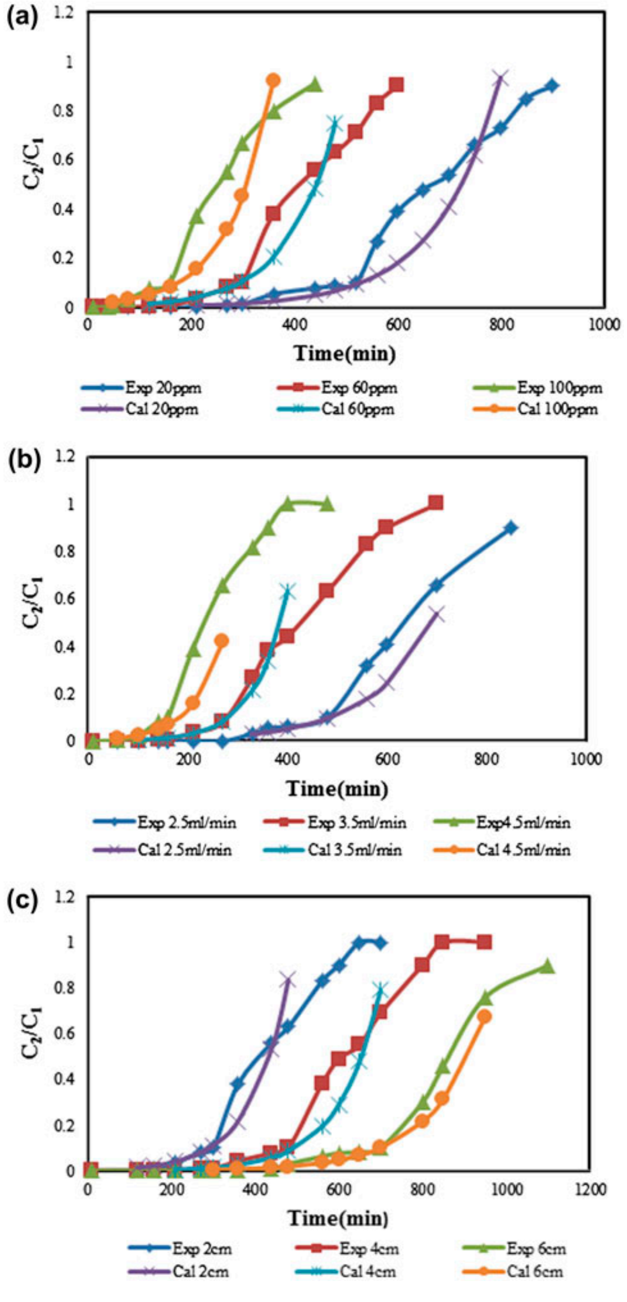

Fig. 9. Experimental and theoretical breakthrough curves based on Bohart–Adams model: the pH of 5.5 room temperature: (a) different flow rates, the influent Cd(II) concentration of 60 mg L^{-1}, the bed height of 2 cm, (b) different initial cadmium concentrations, the flow rate of 3.5 mL min^{-1}, the bed height of 2 cm, and (c) different bed heights, the influent Cd(II) concentration of 60 mg L^{-1}, the flow rate of 3.5 mL min^{-1}.

3.7.3. Application of Yoon–Nelson model

Yoon–Nelson model was also examined to study the breakthrough trend of Cd(II) on sesame waste. The model is based on the assumption that the rate of reduction in the probability of adsorption for any adsorbing specie is related to the chance of adsorbate adsorption and adsorbate breakthrough [24]. The model for a single component system is conveyed as:

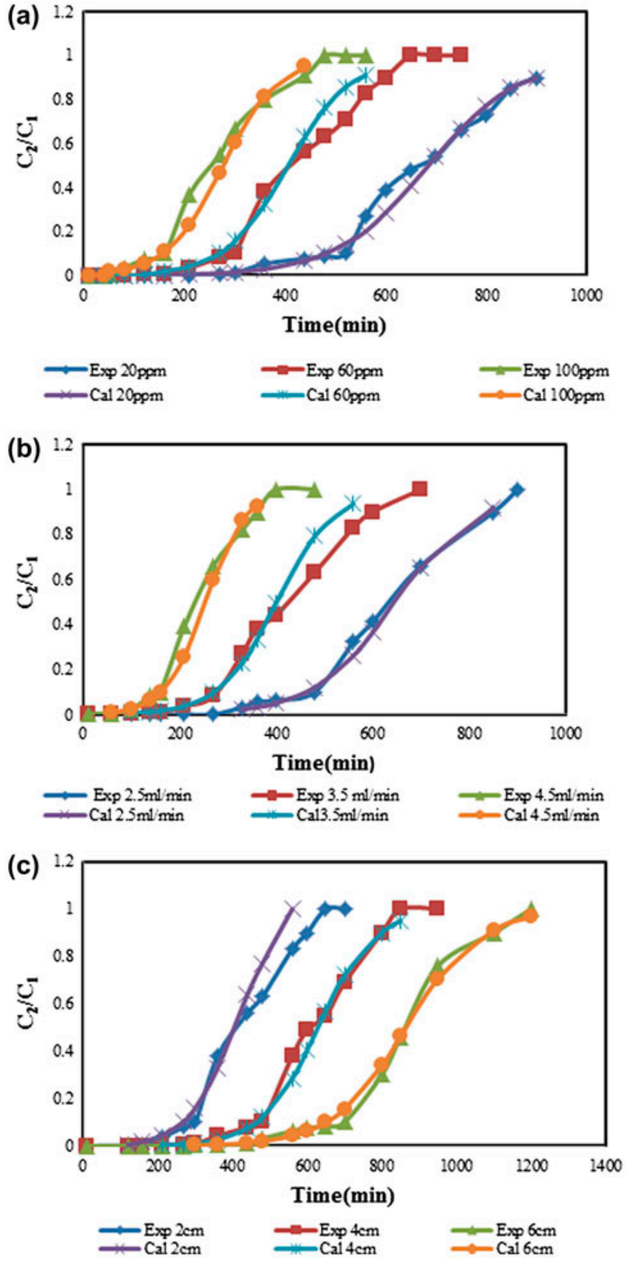

Fig. 10. Experimental and theoretical breakthrough curves based on Thomas model: at the pH of 5.5 and room temperature (a): different flow rates, the influent Cd(II) concentration of 60 mg L^{-1}, the bed height of 2 cm, (b) different initial cadmium concentrations, the flow rate of 3.5 mL min^{-1}, the bed height of 2 cm, and (c) different bed heights, the influent Cd(II) concentration of 60 mg L^{-1}, the flow rate of 3.5 mL min^{-1}.

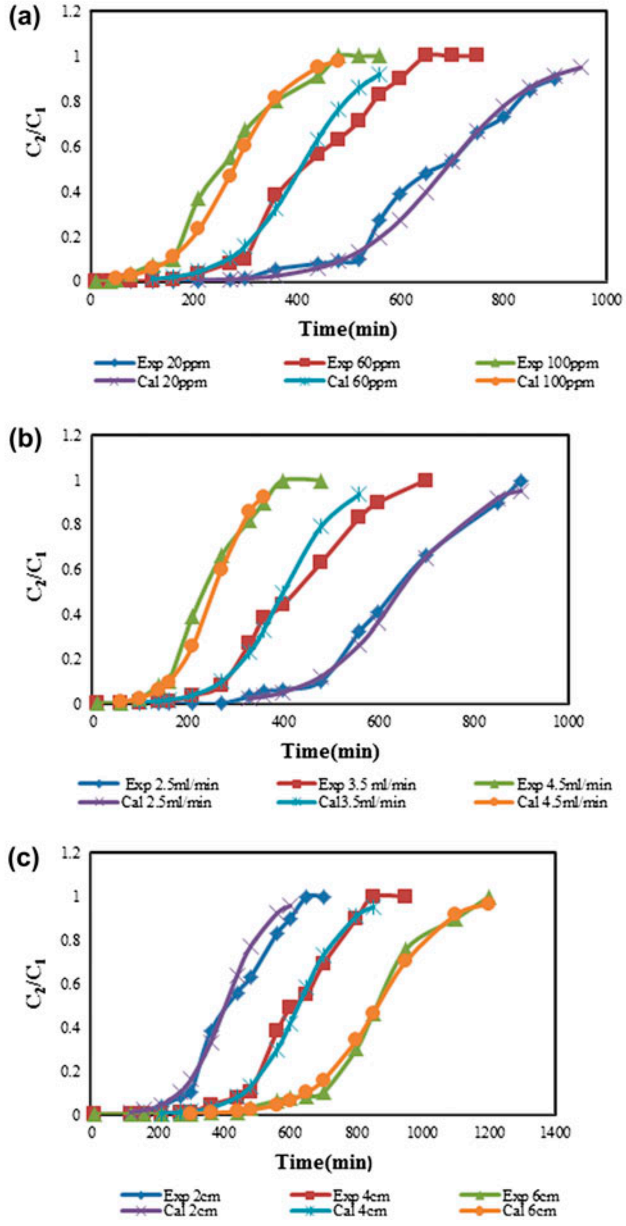

Fig. 11. Experimental and theoretical breakthrough curves based on Yoon–Nelson model: at the pH of 5.5 and room temperature (a): different flow rates, the influent Cd(II) concentration of 60 mg L^{-1}, the bed height of 2 cm, (b) different initial cadmium concentrations, the flow rate of 3.5 mL min^{-1}, the bed height of 2 cm, and (c) different bed heights, the influent Cd(II) concentration of 60 mg L^{-1}, the flow rate of 3.5 mL min^{-1}.

Table 6
Yoon–Nelson model parameters

Parameter	$k_{YN} \times 10^{-4}$	τ	R^2
Initial Cd(II) concentration (mg L^{-1})			
20	5.66	13,616.9	0.97
60	2.72	23,565.2	0.97
100	1.81	27,533.2	0.95
Flow rate (mL min^{-1})			
2.5	2.38	37,790.7	0.96
3.5	2.93	23,273.6	0.96
4.5	4.11	14,837.2	0.97
Bed height (cm)			
2	2.76	23,447.9	0.96
4	2.25	36,873.2	0.98
6	1.73	51,031.5	0.98

$$\ln\left(\frac{C_t}{C - C_t}\right) = k_{YN} \times t - k_{YN} \times \tau \qquad (14)$$

The rate constant, k_{YN} (min^{-1}), and the time needed for 50% adsorbate breakthrough, t (min), were determined from the plots between ln $\left(\frac{C_t}{C-C_t}\right)$ vs. time t at various flow rates, initial Cd(II) concentrations and bed heights. The values of k_{YN} were reduced with enhanced extents in bed height as well as initial Cd(II) concentrations, whereas corresponding values of t were enhanced (Table 6).

With a rise in the flow rate, the rate constant extents were found to be improved whereas the t indicated the reverse behavior. From the data reported in Table 6, it can be concluded that R^2 values higher than 0.95 showed the validity of Yoon–Nelson model for the present system. In a comparison of values of R^2, it was found that both Thomas and Yoon–Nelson models could be applied to predict adsorption performance for the adsorption of Cd(II) in a bed column.

3.7.4. Comparison of the applied models

Theoretical breakthrough curves achieved based on the kinetic models, were examined along with corresponding experimental ones, as are shown in Figs. 9–11.

From these figures, it can be concluded that Bohart–Adams model is valid only at the initial period of operation, but others are applicable for the entire range. Moreover, although the Adams–Bohart model offers a comprehensive and simple approach to estimate the sorption-column test, its validity is limited in the range of conditions applied [25,55]. If we consider the equations applied for Thomas and Yoon–Nelson models, it is evident that the characteristic parameters related to these models are different, but both of them should predict a basically similar uptake capacity for a specific data-set. Therefore, they would result in similar R^2 values as shown in Tables 5 and 6. In a comparison of the values of R^2, both Yoon–Nelson and Thomas models could be utilized to predict the adsorption performance for the adsorption of Cd(II) in a mini fixed-bed column.

4. Conclusions

This study revealed that locally available sesame waste could be used as a kind of biosorbent for the removal of cadmium from aqueous solutions in a fixed-bed column. The Cd(II) removal percentage was improved with an increase in bed height and reduced with the enhancement of Cd(II) concentration or flow rate. The increase in temperature reduced the removal efficiency of Cd(II). Thermodynamic parameters showed a spontaneous and exothermic process. The achieved experimental data were examined for Bohart–Adams, Thomas, and Yoon–Nelson models to predict breakthrough curves and evaluate the characteristic parameters of the fixed-bed column. The results showed that both Yoon–Nelson and Thomas models could be utilized to predict the adsorption performance for Cd(II) adsorption in a fixed-bed column. In general, it can be concluded that sesame waste has a reasonable sorption capacity with the additional advantage of abundant and economic.

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