Preparation, characterization and biosorption properties of chitosan-mwcnts nanocomposite for removal of cadmium from aqueous solution

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Abstract

The removal of Cd (II) ions from aqueous solution by synthesized chitosan-mwcnts (ch-mwcnts) was investigated in a batch adsorption system. The morphological of modified chitosan was characterized by scanning electron microscopy (SEM), fourier transfer infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). The effect of various factors such as; initial concentration of cadmium ions, initial pH and temperature of the solution for removal of Cd (II) was studied. The experimental isotherm data were analyzed by Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models. Equilibrium data agreed well with Langmuir isotherm, Based on this model, the maximum adsorption capacity of nanocomposite of ch-mwcnts for Cd (II) was obtained to be 24.27 mg/g at pH=6. A pseudo-second order model has been proposed to correlate the experimental data (R2= 0.996). The thermodynamic parameters such as standard Gibb’s free energy (ΔG˚), standard enthalpy (ΔH˚), standard entropy (ΔS˚) and activation energy (Ea) were evaluated by applying the Van’t Hoff and Arrhenius equations and were determined as -0.088 to -1.208 kJ/mol , 16.6 kJ/mol , 56 J/ mol. K and 5.58 kJ/ mol, respectively.

Keywords: Chitosan- mwcnts, Cadmium, Nanocomposite, Adsorption, Isotherms.

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1. Introduction

With the rapidly growing population of the world and development of industries; increasing number of reports on harmful effects on the environment [1]. Industrial effluents are directly or indirectly discharged into the environment increasingly, especially in developing countries [2]. Heavy metals are harmful pollutants that are not biodegradable and inclined to accumulate in an environment. Cadmium is a toxic metal and it has many common applications as a key component in various industries including pigments, stabilizers and coatings for rapidly growing applications in Ni-Cd batteries [3]. Recently, Several numbers of technologies have been used to removal of Cd (II) from aqueous solution such as; chemical precipitation [4] cementation [5] membrane and separation technique [6] ion exchange and solvent extraction techniques [7] and adsorption [8-11]. However, most of them have disadvantages such as secondary pollution, high operating and investment costs. Adsorption process is considered as the best methods to remove heavy metals from industrial effluents due to its ease of operation, insensitivity to toxic substances and low cost. Several adsorbents such as; activated carbon [12] zeolites [13] agricultural waste material [14] chitosan and modified chitosan [15-17] have been applied for removal of organic and inorganic pollutants. Chitosan and its derivatives have been widely investigated as low-cost bioadsorbents for the removal of heavy metals. The major structure of chitosan is a polysaccharide found in crustacean, insects and lower plants. Chitosan has advantages over polysaccharides due to its non-toxicity, hydrophilic and biodegradability. It has been used in several applications due to the outstanding properties [18]. The amine and two hydroxyl groups on each glucosamine monomer act as adsorption sites. In recent years, chemical modification of chitosan has been significant interest because the modification would not change the fundamental skeleton of chitosan, would keep the original physicochemical and biochemical properties and finally would bring new or improved properties [19-21]. Modification of chitosan has been progressively improved by the specific functionalization of these carbohydrate polymers [22, 23]. Multi-wall carbon nanotubes (mwcnts) is the attractive materials that are used for the modification of chitosan. Carbon nanotubes have high specific surface areas, unique size distributions, novel hollow-tube structures, electrical conductivity. Carbon nanotubes have a wide range of length scales and are capable of being oxidized and forming hydroxyl and carboxyl groups on their surfaces. Composites based on carbon nanotubes are advanced materials that are attracting much attention because of their unique structures and mechanical properties [24-25].

In this study, nanocomposite of ch-mwcnts was synthesized and characterized by SEM, FTIR and TGA. The effect of experimental parameters such as; initial pH, initial cadmium concentration and temperature of the solution on the adsorption of Cd (II) by synthesized ch-mwcnts nanocomposite were investigated. The experimental adsorption data were analyzed by four adsorption isotherm model and three different kinetics equation. The standard Gibb’s free energy (ΔG˚), standard enthalpy (ΔH˚), standard entropy (ΔS˚) and activation energy (Ea) as thermodynamics parameters were evaluated.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (mwcnts), with diameters of 10–30 nm, length 10μm was obtained from Research Institute of Petroleum Industry (Iran). Chitosan (85% deacetylated) purchased by Sigma–Aldrich had a molecular weight ranging from 190,000 to 375,000 g/mol. Salt of cadmium (CdSO₄.H₂O) and epichlorohydrin (ECH) of 99.6% purity were purchased from Merck.

2.2. Characterization

The FT-IR spectrum was recorded with the KBr disc technique using BRUKER model Tensor 27
The thermal stability and weight ratio were confirmed by thermogravimetric analysis (TGA), conducted at BÄHR-Thermoanalyse GmbH from 25 to 1100 °C in an air atmosphere with heating rate of 10 °C/min. The TGA graph was plotted with weight (%) vs. temperatures.

2.3. Preparation of Ch- mwcnts nanocomposite

3 gr of chitosan was dissolved to 100 ml of acetic acid (2%v/v) and sonicated for 2 h until be homogeneous. 1 gr of mwcnts were suspended in 100 ml deionized water and sonicated for 2 hours. The solution of mwcnts was added dropwise to chitosan solution and the new solution was mechanically stirred for 1 h and then sonicated for 160 min to increase the homogeneity by ultrasonic homogenizer (400W, 20kHz). The dark solution of ch-mwcnts was precipitated by dropwise addition of NaOH 1M until the pH of the solution reached to 11. After 12 h, 3 ml of epichlorohydrine (ECH) as crosslinking agent was slowly added to the solution of ch-mwcnt under vigorous stirring and then the solution was stirred for 24 h. The resulted nanocomposite was filtered from the solution and washed with deionized water several times to remove impurities (unreacted ECH) until the pH of the solution reached to 7. Finally, the ch-mwcnts nanocomposite was left to dry 48 h in an oven at 70 °C followed mechanically grinding in ball mill (PM100 RETSCH, Germany). The ch-mwcnts nanocomposite is represented schematically in Fig. 1.

2.4. Batch adsorption

A stock solution containing 1000 mg/l cadmium ions was prepared by dissolving CdsO₄ in deionized water. The desired Cd (II) concentrations were prepared from the stock solution by diluting for each adsorption experiment. Adsorption studies were obtained by adding 0.08 gr of ch-mwcnts nanocomposite to 50 ml of Cd (II) ion solution. The solution of 0.1 M NaOH and 0.1 M H₂SO₄ were used to adjust the initial pH of the solution. The following equation can be used to calculate of the adsorption capacities (mg/g) and percentage of adsorption (Eq.1, 2):

\[ q_e = \frac{(C_0 - C_t) \times V}{M} \quad \text{Eq. (1)} \]

\[ A\% = \frac{(C_0 - C_t)}{C_t} \times 100 \quad \text{Eq. (2)} \]

Where \( q_e \) as adsorption capacities is the amount of the Cd (II) adsorbed (mg/g) on the adsorbent, \( C_0 \) and \( C_t \) are concentration of the metal ions (mg/l) at the initial time and at any time t, respectively, \( C_e \) is the equilibrium concentrations of Cd (II) (mg/l), \( V \) (ml) is the volume of Cd (II) solution and \( M \) (gr) is weight of ch-mwcnts nanocomposite.

3. Results and discussion

3.1. Characterization of ch-mwcnts

Fig 2 shows the SEM micrographs of the pure chitosan and nanocomposite of ch-mwcnts. As shown in Fig 2, Chitosan particles embedded on the mwcnts surface. The FT-IR spectroscopy is influential characterization techniques used to explain the changes in chemical structures. Fig. 3a shows the FT-IR spectroscopy of mwcnts, chitosan and ch-mwcnt nanocomposite. The peak of 1380cm⁻¹ indicated of CH bonding in mwcnts. The major peaks for pure chitosan in Figure 1a can be assigned as follows: 3443 cm⁻¹ (O-H and N-H stretching vibrations), 1643 cm⁻¹ (N-H deformation vibration), and 1397 cm⁻¹ (C-H symmetric blending vibration). The two characteristic absorption bands of
chitosan were centered at 1155 cm\(^{-1}\) and 898 cm\(^{-1}\) in the spectrum that the intensity of them was decreased in ch-mwcnt nanocomposite. The peaks of 1089 cm\(^{-1}\), 1559 cm\(^{-1}\) and 1658 cm\(^{-1}\) were indicated C–O–C bonds, the free NH\(_2\) groups, respectively. The new peak in ch-mwcnts nanocomposite at 1745 cm\(^{-1}\) indicated new functional group could be correspond to the C=O stretch in amide. The peak at 1532 cm\(^{-1}\) could be corresponding to the N–H bending of –NH of –NHCO– (amide I) \[14\]. The intense bands at 3428 cm\(^{-1}\) and 1049 cm\(^{-1}\) are attributed to the stretching vibration of N–H and C=O in -CONH, respectively, which confirm that the chitosan was implanted onto mwcnts via the amide linkage \[15\]. As seen in Fig. 3 b, the intensity of all of the functional groups transmittance (%) onto the surface of nanocomposite was decreased after adsorption of cadmium and some of the peaks disappeared compared to the peak of ch-mwcnts nanocomposite.

The thermal stability of chitosan, mwcnts and ch-mwcnt nanocomposite were estimated by thermogravimetric analysis (TGA). As seen in Fig 4, the high thermal stability of net mwcnts is 425 °C and then they decomposed around 1000 °C. Meanwhile, the pure chitosan decomposed in several steps \[25\]. The first stage represents the evaporation of water adsorbed by the surface, and the second stage is the condensation of hydroxyl and carboxyl groups. At the 350 °C, 40% of the chitosan removed and at the around temperature of 1000 °C, the chitosan was completely decomposed. On the other hand, the nanocomposite of ch-mwcnts is more stable compared to net chitosan and pristine mwcnts at end of experiment. By comparing TGA curves of the chitosan, mwcnts and ch-mwcnts nanocomposite in the temperature of 1100 °C, 32% of the ch-mwcnts nanocomposite remained as residual however, all the mwcnts and chitosan were decomposed and ch-mwcnts nanocomposite was still stable.
3.2. Effect of time, pH, Cd (II) concentration and temperature

The adsorption of Cd (II) by ch-mwcnts nanocomposite as a function of contact time is shown in Fig. 5a. The time of equilibrium is important parameters in the adsorption process. The adsorption efficiency gradually increased with the adsorption time until an equilibrium state is achieved. The adsorption rate was fast until 60 min and then adsorption equilibrium was achieved within 180 min. As seen in Fig. 5a, $q_t$ increased to 18.25 mg/g at 180 min. The absorption rate was initially rapid and then slows, maybe the presence of a large number of vacant sites on the surface of nanocomposite was affected on the rate of adsorption Cd (II) at primary times.

The pH of the solution is an important factor because it affects the surface charge of adsorbents. The pH can influence the adsorption of charged ions. The effect of pH on the $q_e$ is shown in Fig. 5b. Under various pH, the removal of cadmium ions by the ch-mwcnts nanocomposite was evaluated. The equilibrium adsorption capacity increased from 9 to 18 when the initial pH varied from 3 to 6, then at pH>6 cadmium precipitated in solution. A decrease of cadmium adsorption in pH>6 was due to formation of dissolved hydroxyl groups [15].

The effect of initial Cd (II) concentration on the adsorption percent and equilibrium adsorption capacity is shown in Fig. 5c. As presented in fig. 3c, A% was decreased from 47.8% at 20 ppm of Cd (II) to 16.25% at 200 ppm of initial cadmium concentration and equilibrium adsorption capacity was increased from 6 mg/g to 20.3 mg/g. The increased $q_e$ at higher initial concentration attributed to enhanced driving force. At low initial Cd (II) concentration, the surface area and the availability of adsorption sites were relatively high, and the Cd (II) ions were easily adsorbed [27]. Temperature is the significant factor for in the adsorption process.

The adsorption batch solution was carried out at three different temperatures. As seen in Fig. 5d, it is observed that the adsorption capacity increased with increase in temperature, indicating the endothermic nature of the adsorption reaction of cadmium onto ch-mwcnts nanocomposite. The reason may be that the physical bonding between Cd (II) molecules and the active sites of the adsorbent weakened at high temperature.
3.3. Adsorption isotherms

Interaction between adsorbent and adsorbate described with adsorption isotherms. Several models of adsorption have developed to describe adsorption equilibrium. In this study, four isotherms have investigated including by Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin models.

Langmuir isotherm is a general model to describe of monolayer adsorption. It assumes that adsorbed layer is one molecule in thickness and that all sites are equal, resulting adsorbent surface has a finite number of adsorption sites and each site can hold only one adsorbate molecule. This model does not take into account interaction between adsorbed molecules and the strength of the intermolecular attractive forces is believed to fall off rapidly with distance [28]. This equation (Eq.3.) for the Langmuir is as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} C_e
\]

where \(q_e\) is the amount of adsorbent adsorbed by a unit mass of adsorbent at equilibrium (mg/g adsorbent), \(C_e\); the concentration of adsorbate remaining in the solution at equilibrium (mg/L), \(k_L\); the constant related to the adsorption net enthalpy, \(q_m\) is the maximum adsorption capacity (mg/g). Constants \(k_L\) and \(q_m\) can be evaluated from the plot of \(C_e/q_e\) versus \(C_e\). The plots of \(C_e/q_e\) versus \(C_e\) for cadmium adsorption at different pH are shown in figure 6a and linear isotherm parameters are presented in table 1. The maximum sorption capacity, \(q_m\) which is the monolayer adsorption capacity showed that the ch-mwcnts nanocomposite had a mass capacity for Cd (II) 24.27 (mg/g), 22 (mg/gr), 17 (mg/gr) at pH 6, 5 and 3, respectively. The \(k_L\) that is related to the apparent energy of sorption was \(36\times10^{-3}\) L/g at pH 6 that greater than of pH 5 (\(20.3\times10^{-3}\) L/g) and pH 3 (\(23\times10^{-3}\) L/g).

The fundamental description of the Langmuir model can be expressed \(R_L\) terms that predicting the favorableness of an adsorption system.

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \(K_L\) (L/mg) is the Langmuir constant, and \(C_0\) is the initial Cd(II) concentration (mg/L). The values of \(R_L\) indicated the isotherm shapes, which can be unfavorable (\(R_L>1\)) or favorable (\(0 < R_L < 1\)). The \(R_L\) value for adsorption of Cd (II) on ch-mwcnts nanocomposite are shown and listed in fig 6b and table
1. The smaller $R_L$ indicates a higher favorable adsorption [29].

Table 1. Langmuir, Freundlich, D-R and temkin isotherm constants for the Cd (II) adsorption onto ch-mwcnt .

<table>
<thead>
<tr>
<th></th>
<th>Temkin</th>
<th>D-R</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_L$</td>
<td>$b_L$</td>
<td>$A$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH3</td>
<td>0.60</td>
<td>0.60</td>
<td>0.03</td>
</tr>
<tr>
<td>pH5</td>
<td>0.60</td>
<td>0.60</td>
<td>0.03</td>
</tr>
<tr>
<td>pH6</td>
<td>0.60</td>
<td>0.60</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Freundlich's equation is based on heterogeneous adsorption over independent sites and this model predicted multilayer adsorption [30]. This isotherm assumes that with increasing of ion concentration in the solution caused an increase to adsorbent capacity. This model was stated for amorphous surfaces. The amount adsorbed is the summation of the adsorption of all sites, each having bond energy. Equation of this isotherm is as follows (Eq.5.):

$$q_e = K_f, c_e^{1/n}$$  \hspace{1cm} Eq. (5).

where $K_f$ and 1/n constants depend on the temperature and properties of absorbent and adsorbent. These constants can be determined from the slope and intercept when ln($q_e$) is plotted versus ln($C_e$), according to the linearized form of Eq. (6).

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f$$  \hspace{1cm} Eq. (6).

The values of 1/n less than 1 represent a favorable adsorption. The experimental data from adsorption cadmium ion on ch-mwcnt nanocomposite were plotted. The plot of log $C_e$ versus log $q_e$ has shown in figure 6c. The freundlich constants $K_f$ and 1/n were calculated. As presented in table 1. The $K_f$ value at pH 6 (2.5) is greater than pH 5 (1.3) and pH 3 (1.6).

The D–R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character, involves Vander Waals forces and is applicable for physical adsorption processes [31]. This isotherm does not assume a homogenous surface or constant sorption potential. The linear form of D–R isotherm model is expressed as:

$$\ln q_e = \ln q_m - KE^2$$  \hspace{1cm} Eq. (7).

Where $e$ is equal to $RT\ln(1 + \frac{1}{c_e})$, $q_m$ is the maximum adsorption capacity (mg/g), $K$ is related to mean adsorption energy ($E$ in kJmole$^{-1}$) as followed equation and shown figure 6d:

$$E = \frac{1}{\sqrt{2R}}$$  \hspace{1cm} Eq. (8).

One of the isotherm equations could be described of adsorption model is Temkin isotherm. The Temkin isotherm assumes that the heat of adsorption of all the molecules in layer linearly decreases with coverage due to adsorbent-adsorbate interaction [32]. Equation of this isotherm is as follows (Eq.9.):
\[ q_e = \left( \frac{RT}{b_T} \right) \ln A + \left( \frac{RT}{b_T} \right) \ln C_e \quad \text{Eq. (9).} \]

Where, \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (8.314 J/mol.K), \( A \) is the equilibrium binding constant (L/mg), and \( b_T \) is the variation of the adsorption energy (kJ/mol). \( B_T \left( \frac{RT}{b_T} \right) \) is Temkin constant related to the heat of adsorption (kJ/mol). Constants \( b_T \) and \( A \) can be evaluated from the plot of \( q_e \) versus \( \ln C_e \). The plots of \( q_e \) versus \( \ln C_e \) are shown in figure 6e and table 1.

As presented in table 1, the Langmuir isotherm model given the best fit with the highest \( R^2 \) value (0.99) compared to the other three models. The values of \( K_L \) were 0.023, 0.020, 0.036 L/mg at pH 3, 5 and 6, respectively. From table 1, the adsorption capacities of ch-mwcnts nanocomposite for Cd (II) vary in the range of 17 – 24.47 mg/g. Some previously researchers investigated several adsorbents for the adsorption of Cd (II) from aqueous solutions. The adsorption capacity for cadmium using ch-mwcnts nanocomposite is comparable with other reported adsorbents as shown in table 2. [17].
Table 2. Comparison of Cd (II) adsorption on different sorbents from the literature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Ref.</th>
<th>Lagergren (mg/L)</th>
<th>Freundlich</th>
<th>Pseudo-second-order</th>
<th>Intraparticle mass transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan crosslinked with ECH-TiPP</td>
<td>[33]</td>
<td>6.20</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chitosan-alginate</td>
<td>[34]</td>
<td>6.55</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chitosan</td>
<td>[35]</td>
<td>5.25</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chitosan coated cotton fiber</td>
<td>[36]</td>
<td>5.75</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chitosan nanowires</td>
<td>Present research</td>
<td>24.37</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4. Adsorption kinetics

Kinetics of adsorption is a significant characteristic in explaining the efficiency of adsorption. Three common kinetic models, Lagergren-first-order kinetic model, pseudo-second-order kinetic models and Intra-particle diffusion model were used to research the Cd (II) adsorption kinetic behavior onto ch-mwcnts nanocomposite.

Lagergren-first-order kinetic model represented by following Equation [33, 34]

\[
\log (q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad Eq. (10).
\]

where \( q_e \) and \( q_t \) are the amounts of Cd (II) adsorbed (mg/ g) at equilibrium and time t (min), respectively; \( k_1 \) is the rate constant of Lagergren-first-order kinetic model (min\(^{-1}\)). Values of \( k_1 \) can be calculated from the plots of \( \log (q_e - q_t) \) versus t for Eq.(2).

A linear form of pseudo-second-order kinetic model was expressed by Eq. (11)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad Eq. (11).
\]

where \( k_2 \) is the rate constant (g mg\(^{-1}\) min\(^{-1}\)) of pseudo-second-order kinetic model for adsorption. The slope and intercept of the linear plots of \( t/q_t \) against t yield the values of \( 1/q_e \) and \( \frac{1}{k_2q_e^2} \). Intra-particle mass transfer diffusion model proposed by Weber and Morris can be written as follows:

\[
q_t = k_1 t^{1/2} + C \quad Eq. (12).
\]

where C (mg/g) is the intercept and \( k_i \) is the intra-particle diffusion rate constant (mg (gmin\(^{-1}\))), which can be calculated from the slope of the linear plots of \( q_t \) versus t\(^{1/2}\).

The kinetic parameters of Cd (II) adsorption onto ch-mwcnts nanocomposite are shown in the table 3. Plots of Lagergren-first-order, pseudo-second-order kinetic models and intra-particle mass transfer diffusion model are shown in Fig. 7a, b and c.

Table 3. Kinetic data for for the adsorption of Cd(II) on ch-mwcnt nanocomposite

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Lagergren-first-order</th>
<th>pseudo-second-order</th>
<th>intra-particle mass transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_e ) (mg/g)</td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( Q_e ) (mg/g)</td>
</tr>
<tr>
<td></td>
<td>5/86</td>
<td>0.004</td>
<td>17/64</td>
</tr>
</tbody>
</table>

Experimental data showed that pseudo-second-order kinetic model has higher correlation coefficient values (R\(^2\) = 0.996) and more valid to describe the adsorption of Cd (II). The values of \( q_e \) calculated from the pseudo-second-order kinetic models were in good agreement with those obtained from experiment. This confirmed
that the adsorption process was dominated by chemical reactions involving valence forces through sharing or exchanging of electrons. To pseudo-second-order kinetic model, the \( q_e \) value obtained were 17.64 mg/g. On the other hand, the results obtained from pseudo-first-order kinetic model and intra-particle mass transfer diffusion model showed \( q_e \) values, and the correlation coefficients were lower compared with that of pseudo-second-order kinetic model.

**3.5. Adsorption thermodynamics**

The free energy change (\( \Delta G^\circ \)), enthalpy change (\( \Delta H^\circ \)), and entropy change (\( \Delta S^\circ \)) were calculated for to evaluate the effect of temperature on Cd (II) onto ch-\( \text{m} \)-\( \text{w} \)-\( \text{c} \)-\( \text{n} \)-\( \text{e} \)-\( \text{n} \)-\( \text{t} \) nanocomposite. The thermodynamic parameters were estimated by following equations.

\[
\ln K_e = \frac{\Delta S^\circ}{R} - \left( \frac{\Delta H^\circ}{R} \right) \frac{1}{T} \quad \text{Eq. (13)}.
\]

\[
\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad \text{Eq. (14)}.
\]

\[
\ln K_e = \frac{q_e}{C_e} \quad \text{Eq. (15)}.
\]

where \( K_e \) is the equilibrium constant (L/mol), \( R \) is the gas constant (8.314 J/mol K) and \( T \) is the temperature (K). Considering the relationship between \( \Delta G^\circ \) and \( K_L \), \( \Delta H^\circ \) and \( \Delta S^\circ \) were determined from the slope and intercept of the Van’t Hoff plots of \( \ln (K_L) \) versus \( 1/T \). Based on Eqs. (13)-(15), the calculated thermodynamic parameters for Cd(II) adsorption onto ch-\( \text{m} \)-\( \text{w} \)-\( \text{c} \)-\( \text{n} \)-\( \text{e} \)-\( \text{n} \)-\( \text{t} \) nanocomposite are given in table 4 and figure 8. The negative value of \( \Delta G^\circ \) confirmed the spontaneous nature of the adsorption. The higher temperature, \( \Delta G^\circ \) values become more negative and to decrease -0.088 to -1.208 kJ/mole, the reason may be the adsorption becomes easier and more favorable with increasing of temperature. The \( \Delta H^\circ \) and \( \Delta S^\circ \) calculated from the plot of \( \ln K_L \) versus \( 1/T \) as 16.6 kJ/mole and 56 J/moleK, respectively. The positive of the standard enthalpy indicated the endothermic nature of cadmium adsorption via nanocomposite of ch-\( \text{m} \)-\( \text{w} \)-\( \text{c} \)-\( \text{n} \)-\( \text{e} \)-\( \text{n} \)-\( \text{t} \) and positive of entropy implied that the adsorption process is driven entropy.
Table 4. Thermodynamic parameters for the Cd (II) adsorption onto ch-mwcnts at different pH.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG˚ (kJ/mol)</th>
<th>(ΔH˚) (kJ/mol)</th>
<th>(ΔS˚) (J/mol K)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-0.088</td>
<td>16.6</td>
<td>56</td>
<td>0.886</td>
</tr>
<tr>
<td>308</td>
<td>-0.648</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>-1/208</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where θ is surface coverage, E_a is activation energy, R is the universal gas constant (8.314 J/mole. K), T is the temperature (K) and C_e and C_0 are equilibrium and initial cadmium concentration, respectively. Based on the calculated date, fig. 6 b showed the plotting the Ln (1-θ) versus 1/T. The value of S^* and E_a were evaluated as 0.0743 and 5.58 kJ/mole (R²=0.815), respectively. The E_a value is positive and it is compatible with the positive values of ΔH˚. On other hand, the S^* value sets in the range of 0 < S^* < 1 for desirable process. The S^* parameter indicated the measure of the potential of an adsorbate to obtain on adsorbent indefinitely [29].

4. Conclusions

In this study, nanocomposite of ch-mwcnts was synthesized with ephychlorohydrin as crosslinking agent. The Ft-IR and TGA were used for characterization of ch-mwcnts morphology. The results confirmed the unique structure and high thermal stability of ch-mwcnts nanocomposite. The adsorption of Cd (II) on to ch-mwcnts followed of Freundlich isotherm. Batch adsorption experiments showed that the adsorption process followed the pseudo-second-order kinetic model (R² = 0.996). The maximum adsorption capacity of Cd (II) onto ch-mwcnts 24.27 mg/g at pH=6., the negative value of ΔG˚ and positive value of ΔS˚ show the spontaneous adsorption of Cd (II) and the positive value of ΔH˚ indicated that endothermic nature.

References


