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.

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

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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 ($\Delta G°$), standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$) and activation energy (E_a) 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 ($CdSO_4.H_2O$) 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 (Germany). 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,

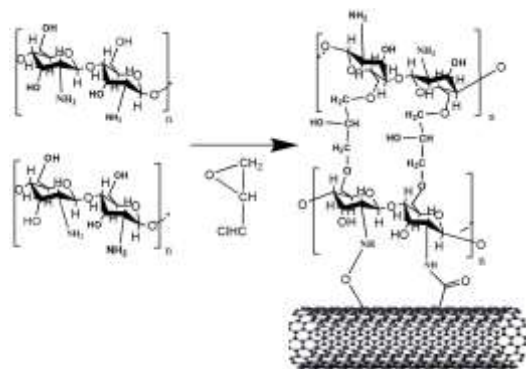Germany). The ch-mwcnts nanocomposite is represented schematically in Fig. 1.

Fig.1. structure of chitosan-mwcnts nanocomposite.

2.4. Batch adsorption

A stock solution containing 1000 mg/l cadmium ions was prepared by dissolving $CdSO_4$ 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 H_2SO_4 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.):

$$q_e = \frac{(C_\circ - C_e) \times V}{M} \qquad Eq.(1).$$

$$A\% = \frac{(C_\circ - C_t)}{C_t} \times 100 \qquad Eq.(2).$$

Where q_e as adsorption capacities is the amount of the Cd (II) adsorbed (mg/g) on the adsorbent, $C_\circ$ and C_t are concentration of the metal ions (mg/l) at the iginitial 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 nanocmposite.

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 nanocamposite. 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 1089cm^{-1} ,1559cm^{-1} and 1658cm^{-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.
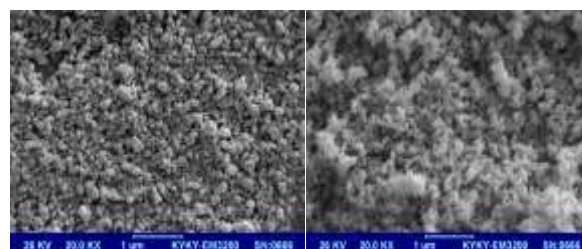

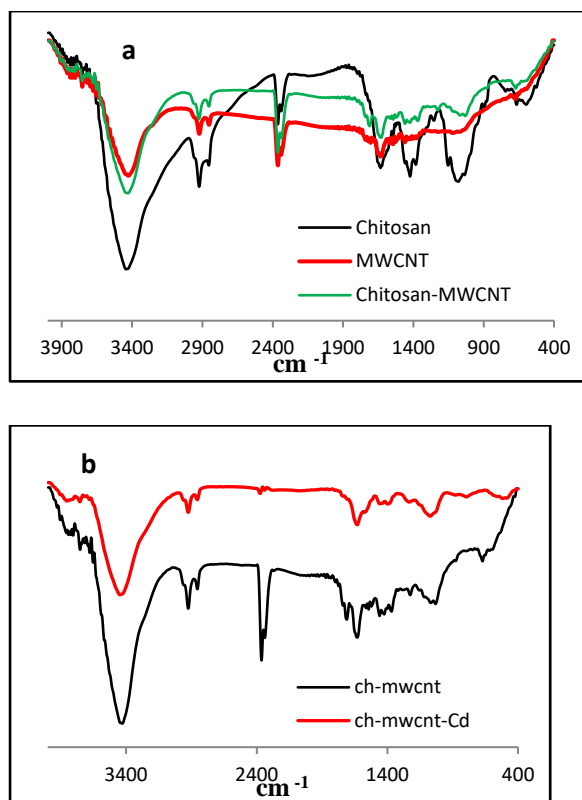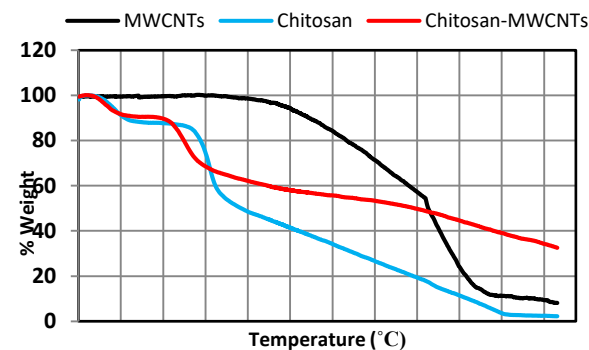**Fig.2.** SEM of pure chitosan (left) ch-mwcnts nanocomposite (right).

Fig. 3. (a) FT-IR spectrum of chitosan, mwcnts, ch-mwcnt nanocomposite; (b) ch-mwcnt before and after Cd (II) adsorption;

The thermal stability of chitosan, mwcnts and ch-mwcnts nanocamposite were estimated by thermogravimetric analysis (TGA). A 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.

Fig .4. Thermogravimetric analysis for chitosan, mwcnts, ch-

mwcnts nanocomposite.

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.5 d, 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.
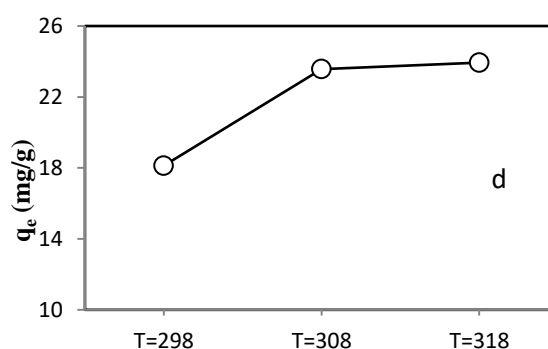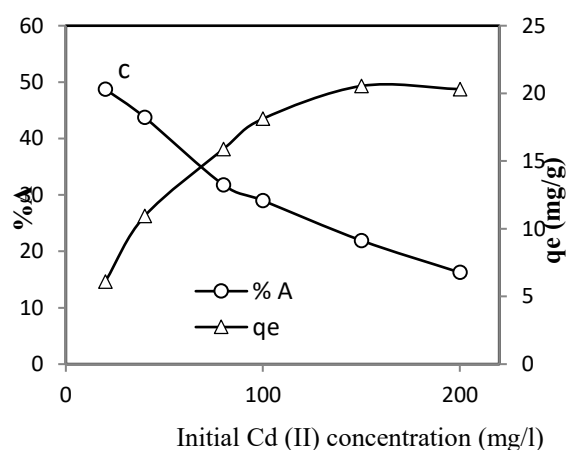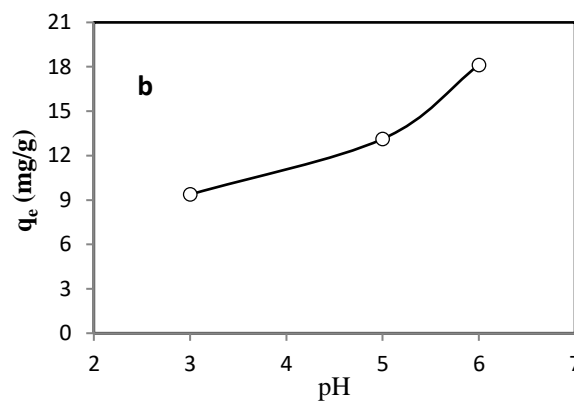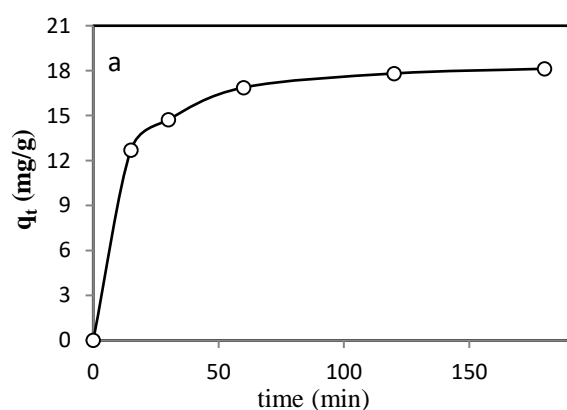

Fig.5. (a) Effect of contact time, (b) Effect of pH, (c) Effect of Cadmium concentration, (d) Effect of temperature on the Cd (II) adsorption by ch-mwcnts nanocompositeadsorbent dose: 0.08 g, V : 50 ml, contact time: 180 min.

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:

$$\frac{C_e}{q_e} = \frac{1}{q_m . k_L} + \frac{1}{q_m} . C_e \qquad Eq.\ (3).$$

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 36×10^{-3} L/g at pH 6 that greater than of pH 5 (20.3×10^{-3} L/g) and pH 3 (23×10^{-3} L/g).

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

$$R_L = \frac{1}{1 + K_L . C_o} \qquad Eq.\ (4).$$

where K_L (L/ mg) is the Langmuir constant, and C_0 is the initial Cd^{2+} concentration (mg/ L). The values of R_L indicated the isotherm shapes, which can be unfavorable ($R_L > 1$) or favorable ($0 < RL < 1$). 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 .

	Langmuir				Freundlich			D-R			Temkin		
	q_m (mg/g)	k_L (L/g)	R^2	R_L	K_F (mg/g)	$1/n$	R^2	q_m (mg/g)	E (kJ/mol)	R^2	A (l/mg)	b_T (kj/mole)	R^2
pH3	17.00	0.023	0.903	0.178	1.60	0.437	0.802	3.61	7.45	0.802	2.50	11.08	0.842
pH5	22.00	0.020	0.993	0.197	1.30	0.520	0.954	3.40	7.71	0.905	5.37	12.50	0.986
pH6	24.27	0.036	0.995	0.122	2.50	0.438	0.935	5.46	7.45	0.868	0.69	13.70	0.976

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.):

$$q_e = K_f . C_e^{1/n} \qquad\qquad \textit{Eq. (5).}$$

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).

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

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 Ce 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 homogeneous surface or constant sorption potential. The linear form of D–R isotherm model is expressed as:

$$\ln q_e = ln q_m - K\varepsilon^2 \qquad\qquad \textit{Eq. (7).}$$

Where ε is equal to $RTln(1+\frac{1}{C_e})$, 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:

$$E = \frac{1}{\sqrt{-2K}} \qquad\qquad \textit{Eq. (8).}$$

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.):

$$q_e = \left(\frac{RT}{b_T}\right) \ln A + \left(\frac{RT}{b_T}\right) ln C_e \qquad\qquad \textit{Eq. (9).}$$

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). $B_T (\frac{RT}{b_T})$ 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 6 e and table 1.
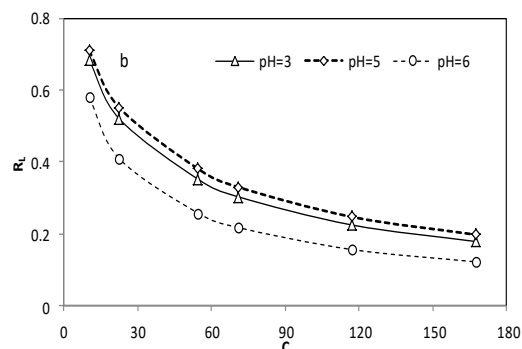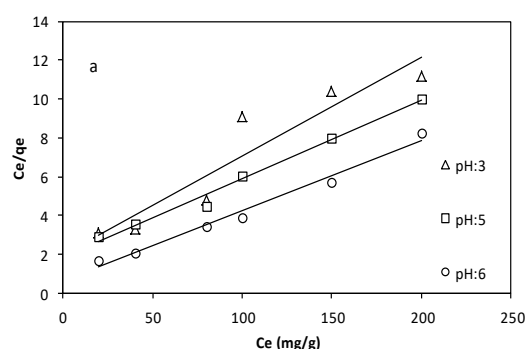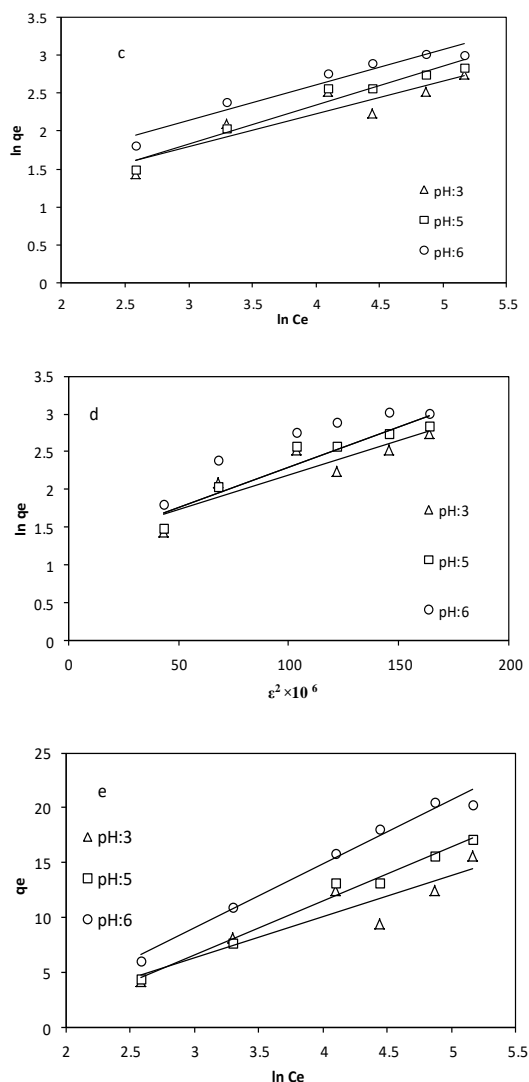
Fig.6. (a)Langmuir plot, (b) Plot of R_L versus initial Cd(II) concentration , (c) Freundlich plot, (d) D-R plot (e)Temkin.

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-mwcnt 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.

Adsorbent	q_m (mg g^{-1})	pH	Temperature (°C)	isotherm	Kinetic model	Refs.
Chitosan crosslinked with ECH–TPP	83.75	7	25	Langmuir	–	[15]
Chitosan–alginate	6.60	3.5	25	Freundlich	–	[27]
Chitosan	10.00	6	25	Freundlich	Pseudo- second- order	[35]
Chitosan coated cotton fiber	15.75	6.5	25	Langmuir	–	[16]
Chitosan-mwcnts	24.27	6	25	Freundlich	Pseudo- second- order	Present research

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)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad Eq.\,(11).$$

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 $\frac{1}{k_2 q_e}$. Intra-particle mass transfer diffusion model proposed by Weber and Morris can be written as follows:

$$q_t = k_i t^{1/2} + C \qquad Eq.\,(12).$$

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 nancomposite 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

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.
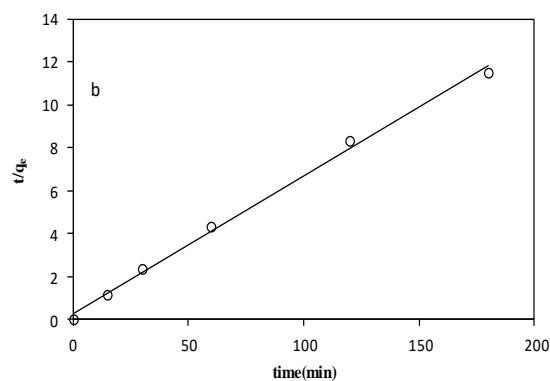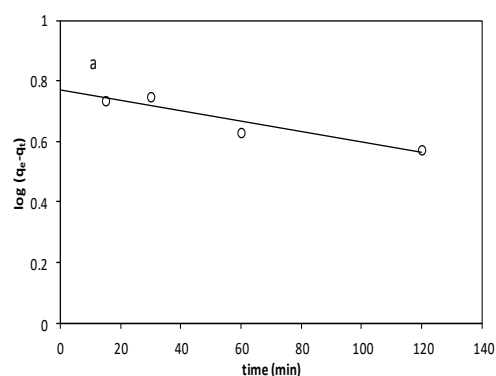
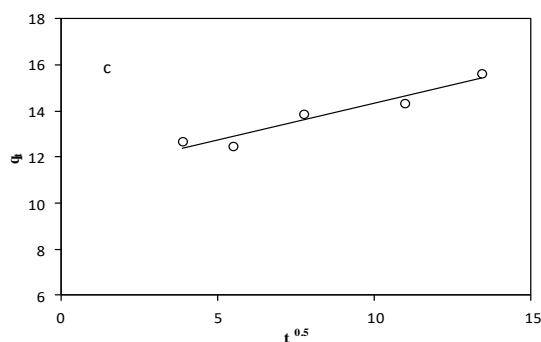| Lagergren-first-order		pseudo-second-order		intra-particle mass transfer	
Q_e (mg/g) k_1 (min^{-1}) R^2		Q_e (mg/g) k_2 (g.mg^{-1}.min^{-1}) R^2		C(mg/g) Ki(mg/gmin$^{0.5}$) R^2	
5/86 0/004		17/64		11/182	0/317
0/877		0/006	0/996	0/935	

Fig.7. kinetics modeling; a: Plots of Lagergren-first-order, b: pseudo-second-order kinetic models, c: intra-particle mass transfer diffusion model

3.5. Adsorption thermodynamics

The free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were calculated for to evaluate the effect of temperature on Cd (II) onto ch-mwcnt nanocomposite. The thermodynamic parameters were estimated by following equations.

$$\ln K_e = \frac{\Delta S°}{R} - \left(\frac{\Delta H°}{R.T}\right) \qquad Eq.\ (13).$$

$$\Delta G° = \Delta H° - T.\Delta S° \qquad Eq.\ (14).$$

$$\ln K_e = \frac{q_e}{Ce} \qquad Eq.\ (15).$$

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 $\Delta G°$ and K_L, $\Delta H°$ and $\Delta S°$ 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-mwcnts nanocomposite are given in table 4 and figure 8. The negative value of $\Delta G°$ confirmed the spontaneous nature of the adsorption. The higher temperature, $\Delta G°$ 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 $\Delta H°$ and $\Delta S°$ 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-mwcnts 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.

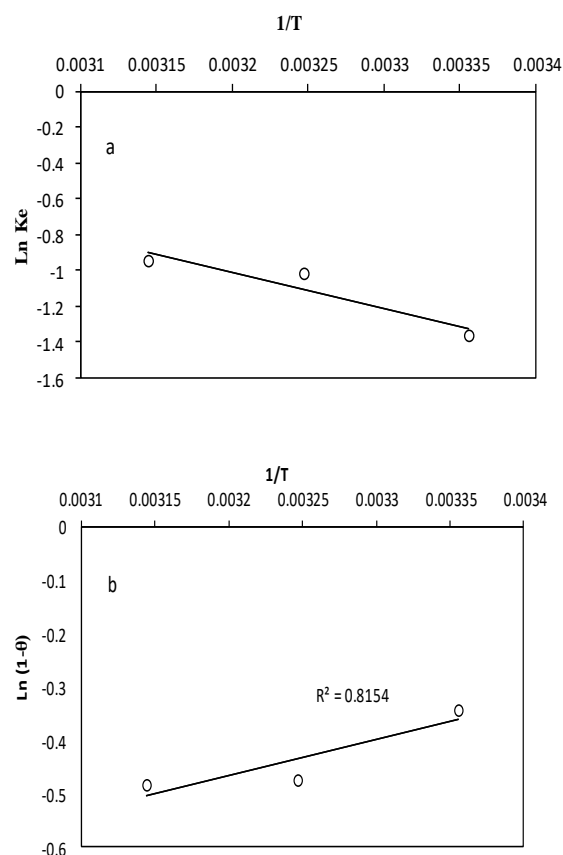| T (K)	$\Delta G°$ (kJ/mol)	($\Delta H°$) (kJ/mol)	($\Delta S°$) (J/mol K)	R^2
298	-0/088	16.6	56	0/886
308	-0/648			
318	-1/208			

Fig. 8. a: Van't Hoff plot of adsorption of cadmium onto ch-mwcnts nanocomposite, b:The plot of $\ln(1 - \theta)$ versus 1/T for the Cd (II) adsorption.

The Arrhenius equation is another significant equation in thermodynamic investigations. The Arrihenius equation described as follows:

$$S^* = (1 - \theta)\exp\left(-\frac{E_a}{R.T}\right) \qquad Eq.\,16.$$

$$\theta = 1 - \frac{C_e}{C_0} \qquad Eq.\,17.$$

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 $\frac{1}{T}$. The value of S^* and E_a were evaluated as 0.0743 and 5.58 kJ/mole (R^2=0.815), respectively. The E_a value is positive and it is compatible with the positive values of $\Delta H°$. 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 cross linking 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 ($R^2 = 0.996$). The maximum adsorption capacity of Cd (II) onto ch-mwcnts 24.27 mg/g at pH=6., the negative value of $\Delta G°$ and positive value of $\Delta S°$ show the spontaneous adsorption of Cd (II) and the positive value of $\Delta H°$ indicated that endothermic nature.

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