

Kinetic and Thermodynamic Study of Chromium Picolinate Removing from Aqueous Solution onto the Functionalized Multi-Walled Carbon Nano Tubes

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ABSTRACT: *In the present research, the Functionalized Multi-Walled Carbon Nano Tubes (FMWCNTs) were functionalized and then were characterized by using the Fourier Transform infrared spectroscopy (FT-IR), X-Ray powder Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer–Emmett-Teller and Barrett-Joyner–Halenda (BET/BJH) and Particle Size Analyzer (PSA) techniques. Subsequently, the functionalized multi-walled carbon nanotubes were used to remove chromium picolinate (ChP) drug from the aqueous media, and its ability for ChP adsorption was also evaluated. To achieve this purpose, the effects of the various parameters such as pH, initial concentration of the sorbate, sorbent dosage, temperature, and contact time on the removal percentage of ChP drug onto the FMWCNTs adsorbent were studied and reported. Based on the experimental results, the optimum conditions to perform the adsorption experiments were determined. In addition, the experimental results were examined using some suitable isotherm models, and it was found that the Langmuir isotherm model is more suitable for fitting the results of the considered adsorption process. Finally, the kinetic and thermodynamic behavior of the ChP adsorption onto the FMWCNTs sorbent were considered and the related results indicated that the studied adsorption process is exothermic and exergonic and almost is physical adsorption. In addition, the kinetic results showed that the adsorption of ChP onto the FMWCNTs adsorbent obeys the pseudo-first-order reaction law from the kinetic point of view.*

KEYWORDS: *Functionalized multi-walled carbon nanotubes; Adsorption; Isotherm; Chromium picolinate; kinetics and thermodynamics.*

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INTRODUCTION

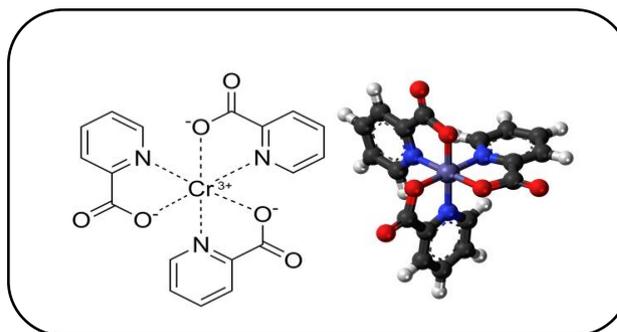
Environmental pollution as a consequence of technological development has become one of the most vital for the worldwide population. The first news on the existence of pharmaceutical pollutants in surface waters and effluents were reported by United States in the 1970s [1]. Pharmaceuticals are extensively used to treat many infections and are considered as water and wastewater pollutants because of their high diversity, high consumption, stability and their resistance to degradations in environment [2-4].

Chromium picolinate (Chp) with chemical formula of $\text{CrC}_{18}\text{H}_{12}\text{N}_3\text{O}_6$ is one of the important compounds among the different pharmaceuticals (scheme 1). Cr (III) in Chp is an essential element for adjusting the blood glucose in the patients with type 1 and 2 diabetes [5]. Indeed, Cr (III) in Chp plays a main role in the insulin performance, resulting in enhanced glucose transport into tissues and appropriate control of blood glucose. In addition, Cr contributes in lipid, protein and carbohydrate metabolism. During insulin function, Chromium in Chp causes to improve the tyrosine kinase property, insulin receptor in the internal membrane of the cells, and facilitates the entrance of glucose into the cells by activating the glucose transporter (GLUT), resulting in decreasing the blood glucose [6, 7].

The bacteria resistant to pharmaceuticals are a basic threat to the environment, because it interferes with antimicrobial therapy and increases disease and mortality [8]. Due to risk of microorganism resistance and side effects of exposure which decreases the capability to treat infections, it is important to pay attention to the issue of removal of pharmaceutical pollutants from waste waters.

Up to date, the various physical, chemical and biological treatment methods such as ozonation (ozone addition), Fenton, Photo- Fenton, Electrochemical, Electron radiation, nanofiltration, chemical coagulation, ion exchange, microbial biodegradation and adsorption methods have been employed for the pharmaceutical residues removal from water and wastewater [9-17].

Among the treatment techniques, the adsorption process is considered as an efficient technique for pollutants removal from contaminated aquatic sources, because this technique has some important advantages such as simplicity, low cost and easy operation, high efficiency, not producing toxic and harmful substances and



Scheme 1. Structural formula of chromium picolinate.

applicability for the numerous types of pollutants than the others [18, 19].

Conventional adsorbents have been applied widely for treatment purposes [20]. However, application of these materials has been limited due to their high cost, low adsorption efficiency and low mechanical and chemical stability. Therefore, to solve some limitations of traditional sorbents, nanomaterials especially carbon nanostructures with outstandingly high surface area are introduced as the new adsorbents for the removal of various pollutants from aqueous solutions [21-23].

Carbon NanoTubes (CNTs) with cylindrical carbon structure as one of the highlighted nanomaterials discovered by researching group of *Iijima* in 1991 [24, 25]. These nanomaterials have received intensive attention by researchers as extremely potential adsorbents for application in the field of environmental remediation because of their remarkable properties such as unique structure, high theoretical specific surface area, exceptional electrical and thermal conductivity and excellent mechanical, thermal and chemical stability [26, 27]. However, dispersion of CNTs nanoparticles into aqueous media is restricted due to their hydrophobic surfaces and may limit their application [28]. Therefore, surface modification of CNTs with various hydrophilic groups and nanoparticles can increase their dispersion into aqueous solutions and improve their adsorption properties for suitable interaction with the different pollutants [29, 30]. Recently, many works have been carried out and reported on the removal of types of pollutants from water and wastewaters by functionalized CNTs and multi walled CNTs nanostructures [31-35]. For example, *Sharifi et al.* designed a modified ZnS:Mn/MWCNTs nanocomposite for the effective photocatalytic removal of organic pollutants [36]. *Gupta et al.* reported COOH-MWCNTs

as functionalized adsorbent for advanced Cu(II) adsorption [37]. Sadegh *et al.* suggested Carboxylate group functionalized multi-walled carbon nanotubes for Microwave-assisted removal of malachite green [38]. Treatment of MWCNTs with strong acids can be led to the oxidation of MWCNTs surface and emergent of the functional groups containing oxygen such as OH and COOH on the MWCNTs surfaces.

In the present research, we have reported modification of MWCNTs surfaces by treatment with strong acids (HNO_3 and H_2SO_4) to convert hydrophobic carbon surfaces to hydrophilic surfaces for effective removal of Chp from aqueous solutions. The effect of the various experimental parameters such as pH, initial concentration of adsorbate, adsorbent dose, contact time and temperature on the adsorption process has been well examined. Thermodynamic study of the adsorption process was also performed. The pseudo-first order and pseudo-second order models were selected to represent the adsorption kinetics data of Chp adsorption onto the functionalized MWCNTs. Also, the experimental equilibrium data were analyzed using the Langmuir and Freundlich isotherm models and the related thermodynamic points were considered.

EXPERIMENTAL SECTION

Chemicals

Chromium picolinate was purchased from 21st Century Company; Multi-walled carbonnanotubes were obtained from Iranian Nanomaterials Company; Nitric acid, Sulfuric acid and other needed reagents were Purchased from Merck Company and were used without further purification.

Instruments

Atomic absorption spectrometer, Model PG-990 from England; Ultrasonic set, Model DK203H from Germany; pH-meter, Model 827 from Switzerland; Four-decimal balance form Germany, FT-IR spectrometer manufactured by Perkin Elmer, XRD device, BET equipment and the other necessary apparatus.

Functionalizing

The adequate amounts of multi-walled carbonnanotubes and 3-molar nitric acid and 1-molar sulfuric acid were mixed at room temperature, and stirred for 2 hours using a magnetic stirrer. Then, the product was placed in an ultrasonic bath for 24 hours, and finally

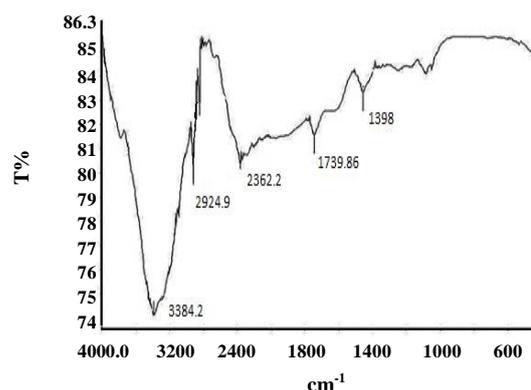


Fig. 1: FT-IR Spectrum of the functionalized multi-walled carbonnanotubes.

was filtered and washed several times with distilled water and ethanol, and after that was dried in an oven at 80°C .

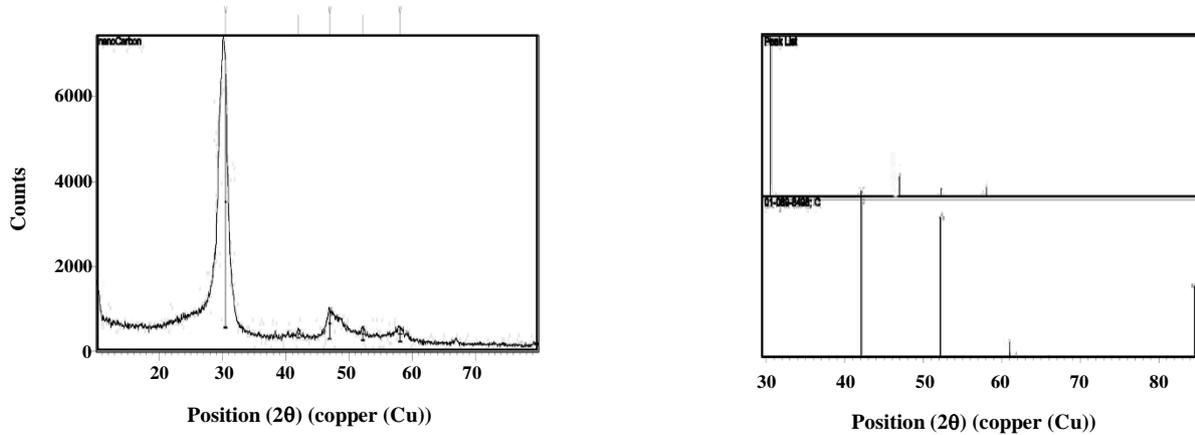
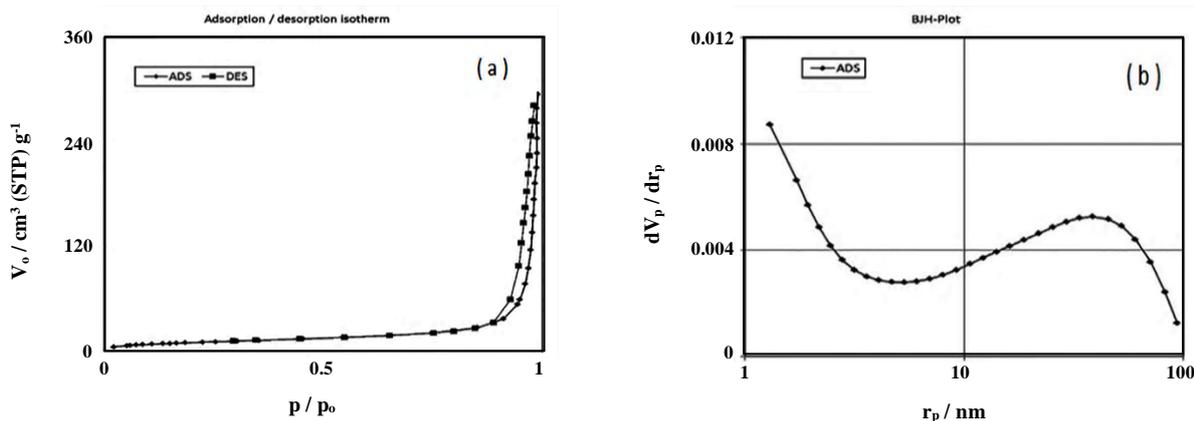
The obtained functionalized multi-walled carbonnanotubes (FMWCNTs) were characterized by FT-IR (Fig. 1), XRD (Fig. 2), BET/BJH (Fig. 3a, 3b and Table 1) and SEM (Fig. 4) methods. Fig. 1 reveals some characteristics of the functional groups such as O-H, C-OH, O=C-OH, -COOH and -C=O bonds of the functionalized multi-walled carbonnanotubes. Some other characteristics of FMWCNTs such as specific surface area, total pore volume and mean pore diameter are shown in Table 1 indicating good qualities of FMWCNTs for adsorbing several sorbates. In turn, XRD pattern shows some specifications of prepared FMWCNTs (Fig. 2). The peaks at 42° , 52.6° and 85° in Fig. 2 are related to the carbon structure in the prepared FMWCNTs. Peak list and patterns list of XRD are shown in Table 2(a) and 2(b), respectively. The morphologies of the functionalized multi-walled carbonnanotubes were examined using SEM technique (see Fig. 4). Accordingly, it showed that the prepared FMWCNTs have very smooth surfaces and the mean outside diameters of the particles were approximately between 20-30nm, and the mean length of a few micrometers.

RESULTS AND DISCUSSION

To evaluate the FMWCNTs ability for Chp removal, the effects of pH solution, sorbate concentration, adsorbent dosage, contact time and temperature on the removal percentage of chromium picolinate were studied, and along with the optimized conditions were also determined.

Table 1: Some characteristics of the Functionalized Multi-Walled Carbonnanotubes obtained using BET/BJH experiment.

Characteristic	Specific surface area (BET),m ² /g	Total pore volume, cm ³ /g	Mean pore diameter, nm
Value	39.338	0.4515	45.912

**Fig. 2: XRD pattern of FMWCNTs indicating some characters of the prepared adsorbent.****Fig. 3. (a) BET/BJH adsorption /desorption isotherms of the Functionalized Multi-Walled Carbonnanotubes at 77.0 K. (b) BJH plot of the Functionalized Multi-Walled Carbonnanotubes ($R_p = 82.35$ nm).**

In addition, the experimental results were analyzed using the suitable isotherm models and the adsorption thermodynamics and kinetics of the studied process were discussed.

Designing a typical adsorption experiment

The procedure of performing a typical adsorption experiment is very important. In general, the common procedure (batch method), which is very frequent is as following: A suitable dose of sorbent (e.g.0.05 g) is mixed with the desired volume of sorbate solution with a known

concentration (e.g.100 mL with the concentration of 10 mg/L). The temperature and the solution pH should be fixed at desired values (e.g. 25.0 °C and 5.0, respectively). The mixture should be stirred during the optimum contact time (e.g.100 min), and under the other optimum conditions. The ultimate mixture should be filtered (using a paper filter with high quality). Finally, the concentration of the filtered solution (the obtained solution upon filtering) must be determined using an effective method such as spectrophotometric measurement, atomic absorption method, etc. In addition, the initial

Table 2(a): Peak list of XRD examination of prepared FMWCNTs.

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width	Matched by
30.489400	5940.423000	0.246000	2.93197	100.00	0.2952	
42.047300	191.158000	0.393600	2.14893	3.22	0.4723	01-089-8498
46.924930	704.328300	0.393600	1.93631	11.86	0.4723	
52.192450	305.499800	0.393600	1.75261	5.14	0.4723	01-089-8498
58.040740	337.499500	0.787200	1.58917	5.68	0.9446	

Table 2(b): List of the Identified Patterns of the prepared FMWCNTs.

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-089-8498	77	Carbon	-0.143	0.026	C

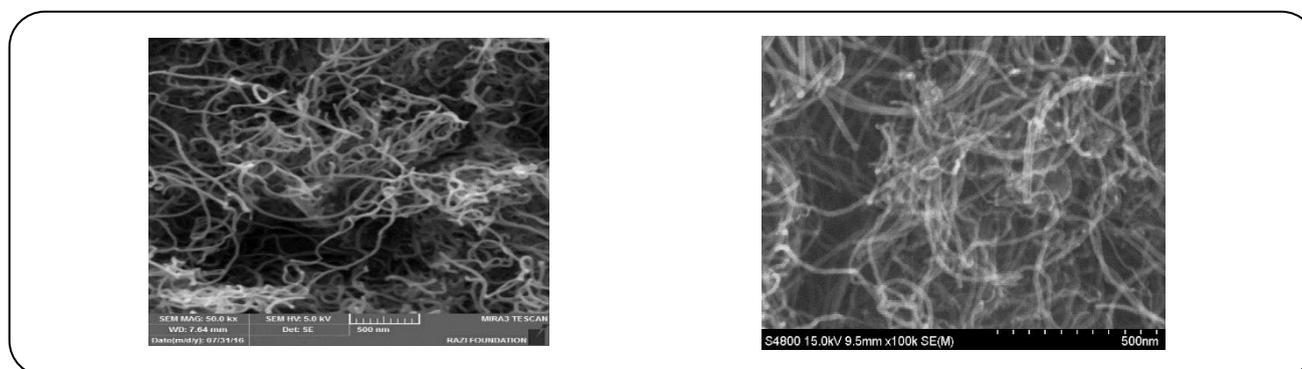


Fig. 4: SEM Micrographs of the Functionalized Multi-Walled Carbonnanotubes.

concentration should also be measured by the same instrument to achieve a high reliable precision.

Using the obtained results of such measurements, we can determine the removal percent (or %Ad), adsorption capacity (q; the amount of the sorbate (in mg) adsorbed per g of sorbent) and the other related parameters.

$$\text{Removal percent (\% Ad)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (3)$$

where C_0, C_t and C_e (in mgL^{-1}) represent the initial concentration of the sorbate, the concentration of the sorbate at time t , and the respect concentration of the sorbate at equilibrium, V is the volume of the solution containing the sorbate in terms of liter, m is the dosage

mass of the sorbent in gram. It is necessary to notice that the large value of the removal percent or q_e is a reliable indicator of the efficiency of the studied adsorption process.

Here, it should be noticed that, determining the optimum conditions such as the initial concentration of the sorbate, the dosage of the sorbent, the contact time, the solution pH and the temperature are very important to perform the adsorption experiments, and then selecting a suitable isotherm model to fit the experimental data, and also concluding the reasonable thermodynamic parameters and rate laws for the adsorption kinetics. Therefore, we investigated the mentioned optimum conditions with respect to the considered adsorption process, and based on the obtained results, we constructed the reasonable isotherm models for finding out the thermodynamic and kinetic parameters of the adsorption process.

The effect of pH solution

The pH parameter is one of the most important factors affecting the adsorption phenomena. Indeed, it has serious influences on the adsorbent surface binding sites and the adsorbate state. At low pH, H^+ (aq) ions and at high pH, OH^- (aq) ions may be adsorbed on a portion of the free adsorption sites of the adsorbent and compete with the main adsorbate. At the same time, the pH factor may seriously affect the chemical character of the sorbate and results in a considerable change in the adsorption study. Therefore, finding the optimum pH is very important in every adsorption investigation. To investigate the effect of pH on the adsorption capacity, the solution pH was changed from 3 to 9, during 4 experiments, and the maximum efficiency was also obtained at pH=5.0. Fig. 5(a) shows the plot of the experimental results (The constant parameters were as: $C_0 = 10.0$ mg/L, Sorbent dosage=0.050g, Temperature=25.0 °C, Contact time=480 min).

The effect of the sorbate concentration

The adsorption experiments were conducted at the several initial concentrations of chromium picolinate (the initial concentration range was: 10.0, 20.0, 30.0, 40.0 and 50.0 mg/L, the constant parameters were as: pH=5.0, Sorbent dosage=0.050g, Temperature=25.0 °C, Contact time=480 min). The removal percentages of the sorbate onto the FMWCNTs sorbent were evaluated after eq.(1) and are shown in Fig. 5 (b). As we can see from Fig. 5 (b), by increasing the concentration of the initial sorbate (increasing the adsorbate mass), the removal percentage decreases. The reason is at higher initial concentration of the sorbate, there will be relatively the lower free sites for adsorption phenomenon. (while the mass of the sorbent is constant). Therefore, a suitable low concentration of the sorbate will be preferred. Accordingly, we choose the initial concentration of 10.0 mg/L as a suitable initial concentration.

The effect of the sorbent dosage

The dosages were selected as: 0.0050, 0.010, 0.0150, 0.020, 0.030, 0.050 g, where, monitoring the other conditions remain constant, the constant parameters were as followings: ($C_0 = 10$ mg/L, pH=5.0 Contact time=480.0 min, Temperature=25.0 °C). As it was indicated by the experimental results shown in (Fig. 5(c)), along with increasing the sorbent dosage, the removal percentage

increases and then it remains fairly constant, because by increasing the sorbent dosage, there will be more free adsorption sites available to the sorbate molecules. From the plot of Fig. 5(c), it may be concluded that the optimum dose is 0.050g.

The effect of the contact time

The adsorption experiments were performed at several contact times, while the other conditions were constant ($C_0 = 10.0$ mgL⁻¹, Sorbent dosage=0.050 g, pH=5.0, Temperature=25.0 °C). The experimental results are shown in Fig. 5(d) (the selected contact times were: 30, 60, 120, 180, 240, 300, 420 and 480 min). It is clear that, the adsorption process will be completed along with increasing of the contact time, so regarding the results, 480 minutes was selected as the optimum time. The rate of increasing of adsorption percent with respect to time beyond 480 min was low, so selected optimum time (480 min) is fairly reasonable.

The effect of temperature

The effect of temperature on the removal percentage was examined at 25.0, 35.0, 45.0, 55.0, 65.0 and 75.0°C, where the other conditions were constant ($C_0 = 10.0$ mg/L, Sorbent dosage=0.050 g, pH=5.0, Contact time=480.0 min). The results showed that, the removal percentage was decreased with the temperature rising, therefore based on the experimental feasibility, we selected 25.0°C as a suitable temperature to perform the adsorption experiments in this study. Indeed, based on the thermodynamic arguments, temperature affects the adsorption process in such a way, where an endothermic process is more favorable at higher temperature, while an exothermic one behaves inversely. Therefore, the present adsorption process should be an exothermic one.

ADSORPTION ISOTHERMS

Adsorption isotherms are the most effective criteria for evaluating and representing the adsorption experimental data. Indeed, the reasonable experimental data should be well-fitted by one or more of these isotherm models.

The results of this work, were examined under the optimized conditions with two isotherm models; one the Langmuir isotherm, and the another one was the Freundlich isotherm. "Linear Langmuir isotherm" is as following:

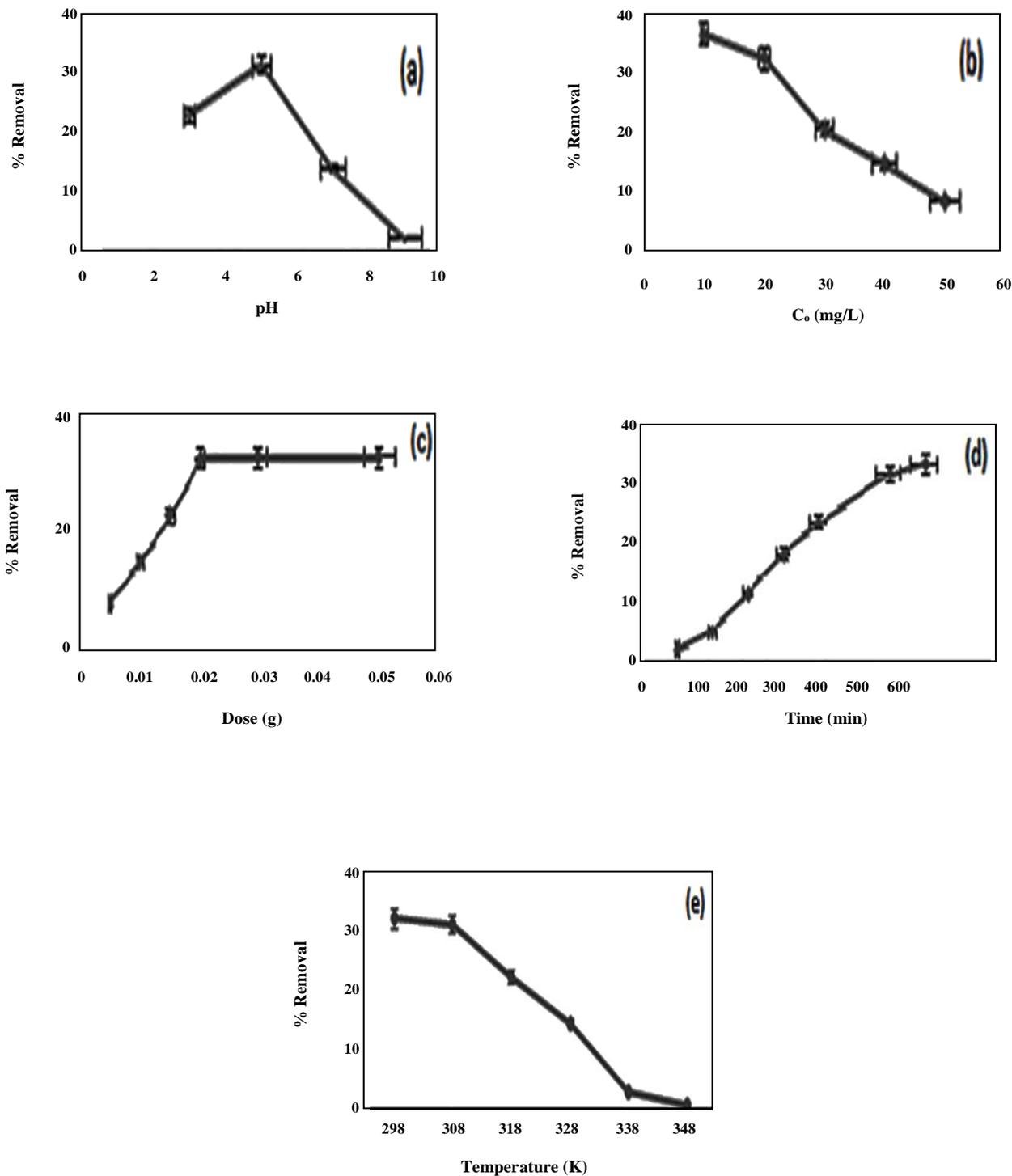


Fig. 5: (a).The effect of pH solution on the removal percentage of chromium picolinate by FMWCNTs (b). The effect of initial sorbate concentration on the removal percentage (c). The effect of adsorbent dosage on the removal percentage of chromium picolinate by FMWCNTs (d).The effect of contact time on the removal percentage of the studied sorbate onto FMWCNTs (e). The effect of temperature on the removal percentage of the studied sorbate onto FMWCNTs.

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \left(\frac{1}{C_e} \right) + \left(\frac{1}{q_m} \right) \quad (4)$$

or :

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (5)$$

Freundlich isotherm is presented as equation (6) or (7):

$$q_e = K_F C_e^n \quad (6)$$

or:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Where, C_e is the equilibrium concentration mg/L of the adsorbate, q_e is the equilibrium amount (mg) of the adsorbed sorbate per g of the adsorbent, q_m is the maximum value of q_e , K_L is the Langmuir equilibrium constant,

K_F and n are the model constants of the Freundlich isotherm [39-42]. Figs. 6 and 7 indicate the plots of (C_e/q_e) with respect to C_e for the Langmuir model and $\ln q_e$ with respect to $\ln C_e$ for the Freundlich model, respectively. The results of this work were fairly better fitted with the Langmuir model compared to the Freundlich isotherm. (The initial concentration was changed from 10 mg/L up to 50 mg/L where the other conditions were constant: pH=5.0, Sorbent dosage=0.050g, Temperature=25.0 °C, Contact time=480.0 min). Based on the equation 5 and Fig. 6, the value of q_m from the slope of the plot 6 and K_L from its intercept can be concluded. In addition, K_F and n , which are related to the Freundlich isotherm (eq.7), can be deduced from the plot of Fig. 7. The constants of the Langmuir model and the Freundlich model after Figs. 6 and 7 and equations (5) and (6,7), are gathered in Table 3. As we can see, the Langmuir isotherm model which corresponds to the monolayer adsorption is reasonably appropriate for representing the experimental data of this study.

The obtained values of adsorption capacities for this work are comparable with those that are obtained in the references [43-45].

The dimensionless constant, R_L , or separation factor is an effective criterion for predicting the efficiency and usages of the Langmuir isotherm model:

$$R_L = 1 + \frac{1}{K_L C_0} \quad (8)$$

When the values of R_L are between 0 and 1 ($0 < R_L < 1$), the studied adsorption is reasonable (or favorable).

$R_L \geq 1$ indicate unfavorable cases, while $R_L = 0$, represents adsorption irreversibility [46]. The obtained values of R_L for the studied adsorption at 25.0°C are given in Table 3, showing that the studied adsorption is favorable from the Langmuir isotherm point of view.

Adsorption kinetics

In general, the kinetics of the adsorption phenomena can be almost explained by the pseudo-first order and the pseudo-second order reactions, while the other models are also available such as Elovich and Intraparticle diffusion, etc [47].

The kinetic results of this work were examined using the two first models.

Pseudo-first order kinetics

The linear form of the model [48-55] is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (9)$$

Where q_e and q_t are the adsorption capacity mg/g at equilibrium and at time t and k_1 is the rate constant of the pseudo-first order adsorption. Fig. 8 shows the plot of $\log(q_e - q_t)$ with respect to t . This plot is nearly linear, and fits fairly with the kinetic data of this study.

Pseudo-second order kinetics

The pseudo-second order equation was presented by Ho and Mckay [56]. The linear form of the equation is as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_t and q_e are the adsorption capacity at time t and at equilibrium and k_2 is the rate constant of the pseudo-second order adsorption [57-60]. By plotting t/q_t against t , we can achieve the pseudo-second order kinetic parameters (Fig. 9). This plot is nearly far from linearity, therefore, this kinetic model is not enough suitable for representing the data of this research.

Table 3: Values of R_L for ChP adsorption onto FMWCNTs at 298.0K.

C_0 (mg/L)	10.0	20.0	30.0	40.0	50.0
R_L	0.015	0.0013	0.0048	0.0036	0.0029

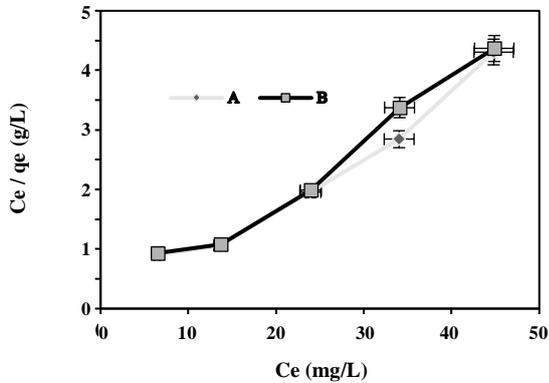


Fig. 6: The plots of the Langmuir model with respect to the experimental data, (A: at 25.0°C, B: at 35.0°C).

The obtained kinetic parameters are shown in Table 4. The results of this work were better fitted with the pseudo-first order kinetics, compared to the pseudo-second order kinetics. In general, a great number of adsorption kinetics follow the Pseudo-first kinetic law, which has been used in many research papers dealing with the adsorption kinetics [61].

Adsorption thermodynamics

Based on the Langmuir adsorption isotherm, we can obtain some thermodynamic insight by considering the equilibrium between the chromium picolinate molecules in the solution phases and those adsorbed on the surface sites of FMWCNTs adsorbent. Therefore we may formally write the equilibrium reaction as following:



And the conditional equilibrium constant:

$$K = \frac{[ChPS]}{[ChP][S]} \tag{12}$$

Where $[ChP]$ is the concentration of chromium picolinate in the solution phase, $[S]$ is the number of unoccupied sites per unit area of the adsorbent surface and $[ChPS]$ is the number of occupied sites per unit area of the adsorbent surface.

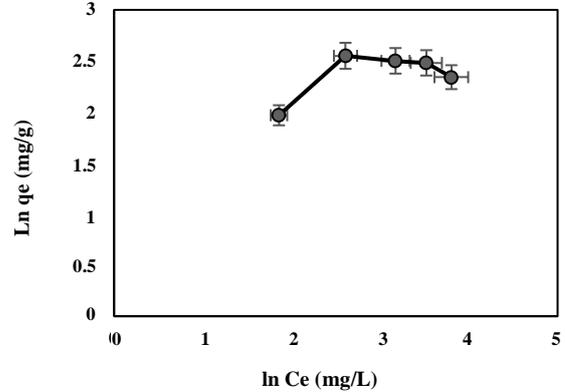


Fig. 7: The plot of the Freundlich model, in accordance with the experimental data of this work at 25.0°C.

It is quite easy to show that the above equilibrium constant coincides exactly with the Langmuir constant, K_L , in eqs (4) and (5).

In addition, by analogy with gas adsorption, we may consider the expression of K in the statistical mechanics as:

$$K = \frac{1}{[Chp]^0} q_{ChPS} e^{\frac{\mu^0}{kT}} \tag{13}$$

Where, $[Chp]^0$ is standard concentration of ChP in the solution phase, μ^0 is standard chemical potential of ChP at temperature T and q is molecular partition function of adsorbed ChP in the solution phase onto the surface of the adsorbent.

Statistical thermodynamic treatment of idea lattice gas (adsorbed gas on solid surface) gives a rigorous expression for Langmuir adsorption constant, K_L that is only temperature dependent as:

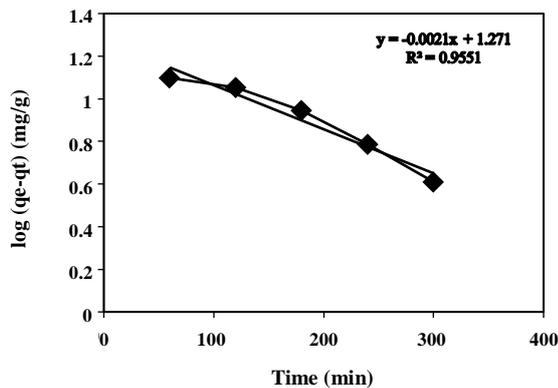
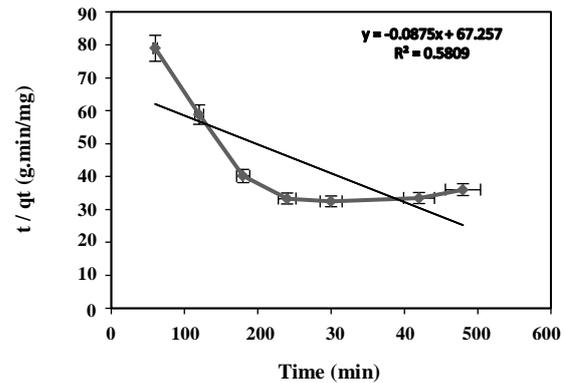
$$K_L = \frac{1}{p^0} q_{ad} e^{\frac{\mu^0}{kT}} = K(T) \tag{14}$$

Where, p^0 is the standard pressure, q_{ad} is molecular partition function of the adsorbed gas molecule, μ^0 is molecular chemical potential in gas phase and k is Boltzmann constant.

fter equation (13,14), constant K (or K_L) is only temperature dependent and can be considered as a

Table 4: The model constants for the Langmuir and Freundlich isotherms based on the experimental results of this work.

Temperature	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	K_L (L/mg)	R^2	$1/n$	K_F (mg/g)/(mg/L) ^{1/n}	R^2
298.0 K	11.16	6.84	0.96	0.185	4.92	0.36
308.0 K	10.49	4.76	0.97	-	-	-

**Fig. 8: The pseudo-first order kinetics plot of the chromium picolinate adsorption onto the FMWCNTs adsorbent at 25.0°C.****Fig. 9: Pseudo-second order kinetics plot of the chromium picolinate adsorption onto the FMWCNTs adsorbent at 25.0°C.**

thermodynamic constant, because all components in the right hand of eq. (13,14) are considered as only temperature dependent. Consequently, from the thermodynamic point of view, we can write:

$$\Delta G_{ad}^0 - RT \ln K_{ad} \quad (15)$$

where $K_{ad} \equiv K \equiv K_L$ and ΔG_{ad}^0 is the standard gibbs energy change related to the adsorption process (eq.11).

When the standard enthalpy change, ΔH_{ad}^0 , is nearly constant, the van't Hoff equation can be written as following:

$$\ln \left(\frac{K_{ad(2)}}{K_{ad(1)}} \right) = \frac{-\Delta H_{ad}^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (16)$$

from which the value of ΔH_{ad}^0 can be concluded. Finally, ΔS_{ad}^0 can be calculated as: [62-64]

$$\Delta G_{ad}^0 = \Delta H_{ad}^0 - T \Delta S_{ad}^0 \quad (17)$$

$$\Delta S_{ad}^0 = \frac{\Delta H_{ad}^0 - \Delta G_{ad}^0}{T} \quad (18)$$

The values of K_L at 298.0 K and 308.0K, which were estimated from the plots of Fig .6 and were given in Table 4 are as: 6.84 and 4.76, respectively.

By replacing this values in eq. (16), we get:

$$\Delta H_{ad}^0 = -27.66 \text{ kJmol}^{-1}$$

The value of ΔG_{ad}^0 at 298.0 K after eq. (15) is:

$$\Delta G_{ad}^0 = -4.76 \text{ kJmol}^{-1}$$

Then, using eq. (17) we get:

$$\Delta S_{ad}^0 = -0.0768 \text{ kJmol}^{-1}\text{K}^{-1}$$

The calculated values of ΔG_{ad}^0 , ΔH_{ad}^0 and ΔS_{ad}^0 are gathered in Table 6. It is worthy to notice the values of ΔH_{ad}^0 and ΔS_{ad}^0 were assumed to be constant and temperature independent, however ΔG_{ad}^0 is surely temperature dependent eq. (15).

The negative values of ΔG_{ad}^0 indicate that the studied adsorption process at the considered temperatures is spontaneous and exergonic, and the negative value of ΔH_{ad}^0 indicates that the studied adsorption process is exothermic. $\Delta S_{ad}^0 < 0$ indicates that the studied adsorption is accompanied with a decrease in the randomness.

In addition, on the basis of ΔH_{ad}^0 magnitude, we may conclude that the studied adsorption process is almost physical adsorption. Therefore, the van der Waals forces play a fundamental role in taking place the studied process,

Table 5: Kinetic parameters of the chromium picolinate adsorption onto the FMWCNTs adsorbent at 25.0°C

pseudo first order		Pseudo second order	
k/min ⁻¹	R ²	k/(g/mg.min)	R ²
4.83×10 ⁻³	0.955	1.14×10 ⁻⁴	0.581

Table 6: Thermodynamic parameters of the chromium picolinate adsorption onto the FMWCNTs sorbent.

T (K)	K _L (Lmg ⁻¹)	ΔG ⁰ _{ad} (kJ/mol)	ΔH ⁰ _{ad} (kJ/mol)	ΔS ⁰ _{ad} (kJ/mol.K)
298.0	6.84	-4.76	-27.66	-0.0768
308.0	4.76	-3.99	-27.66	-0.0768

and they are responsible for the spontaneity of the adsorption process.

CONCLUSIONS

The results of this research indicated that the functionalized Multi-walled carbonnanotubes are a good candidate for diminishing chromium picolinate from aqueous media. Therefore, the effect of the various parameters such as pH, initial concentration of the sorbate, sorbent dosage, temperature and contact time on the removal percentage of chromium picolinate onto the FMWCNTs sorbent were examined and the optimum conditions for performing the adsorption experiments were evaluated (pH=5.0, Sorbent dosage =0.050 g, Temperature= 25.0°C, C₀=10.0 mg/L, Contact time= 8.00hours). Each of these factors contributes to the adsorption percentage, but some of them are more effective for removing ChP from the solution phase onto the FMWCNTs adsorbent. The solution pH is almost more important, due to its influences on some physico-chemical properties of the adsorbate and adsorbent, which will alter the efficiency of the studied adsorption. In addition, at high or low pH values (above or below the optimum pH), the OH⁻ or H⁺ ions will compete with main adsorbate, which results in a reduction in the adsorption capacity. In turn, the other factors have also their own contributions in the affectivity of the adsorption efficiency, which were discussed through the text. The experimental results were analogized according to the Langmuir and Freundlich isotherm models, however the Langmuir isotherm fitted fairly better with the experimental results. The calculated values of R_L showed that the Langmuir isotherm is quite favorable for representing the related adsorption data of this research (0<R_L<1). Thermodynamic study of the considered

adsorption showed that the studied adsorption is exothermic and exergonic (ΔH⁰_{ad} < 0, ΔG⁰_{ad} < 0), so spontaneously, but with a reduction in the randomness during the adsorption of the sorbate onto the sorbent (ΔS⁰_{ad} < 0). We concluded that K_L, K_{ad} K are the same and only temperature dependent and can be used to estimate the values of adsorption thermodynamic functions.

To assess the kinetic behavior of the studied adsorption, the related experimental results were examined with the pseudo first order kinetics and the pseudo second order kinetics equations, and consequently, the first order kinetics was fairly better coincided with our experimental results. Based on the ΔH⁰_{ad} magnitude, we may conclude that the studied adsorption is a physisorption one, so, the van der Waals forces are responsible for taking place the studied process, and therefore, the adsorption mechanism is fairly simple and clear

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