

Equilibrium and kinetic studies of chromium adsorption from wastewater by functionalized multi-wall carbon nanotubes

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Abstract The equilibrium and kinetics of hexavalent chromium adsorption on multi-wall carbon nanotube (MWCNT) functionalized with ethylenediaminetetraacetic acid (EDTA) and sulfuric acid have been studied. Adsorption kinetics was evaluated using pseudo-first order, pseudo-second order, and intraparticle diffusion models. Langmuir, Freundlich, and Temkin isotherms were used to analyze the equilibrium. The studies were carried out by considering the effects of the main operating parameters, such as contact time (0–250 min), adsorbent dosage (20–60 mg), and pH (3–9). Under the optimum conditions, the contact time, functionalized multi-wall carbon nanotube (*f*-MWCNT) dosage and pH were 150, 60 mg and 3. The Langmuir isotherm fits the experimental data ($R^2 = 0.996$) significantly better than the other isotherms. Kinetic studies showed that the adsorption followed a pseudo-second order reaction. The maximum adsorption efficiency was about 99.8 %. These results showed that *f*-MWCNT can be used as an efficient adsorbent for chromium removal.

Keywords Equilibrium · Kinetic · Chromium · MWCNT · Adsorption

Introduction

Carbon nanotubes are a new adsorbent in the carbon family and have been studied intensively for the removal of various pollutants [1]. They have attracted increasing interest since their characterizations. Their small size, large surface area, high mechanical strength and remarkable electrical conductivity indicate

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their potential for future engineering applications, such as adsorption, hydrogen storage, field emission, catalyst supports and composite materials [2, 3]. Multiwall and single wall are two main groups of carbon nanotubes. Multi-wall carbon nanotube (MWCNT), can be classified as concentric and closed graphite tubules with multiple layers of graphite sheets that define a hole typically from 2 to 25 nm separated by a distance of approximately 0.34 nm [4, 5]. MWCNT manufacturing methods are easy, and it can be produced on a large scale. Hence, MWCNT is a suitable candidate for the adsorption of pollutants from large volumes of wastewater [4]. It has been widely recognized that pollutant removal by adsorbents are due to the surface complex formation between the species and the surface functional groups. This is especially significant in the case of removing metals and inorganics from aqueous solutions [4, 6]. One of the techniques to improve the interaction between matrix and pollutants is submitting carbon nanotube to a process called functionalization. Functionalization is a chemical process that inserts functional groups on the sidewall of carbon nanotube. This technique can be helpful to obtain better interaction and dispersion of carbon nanotube into relevant matrices [7]. Carbon materials are usually functionalized by oxidative processes to generate change on the sidewalls and tube tips [8]. Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that was reported by some researchers for the functionalization of material surface. The four oxygen atoms in four carboxyl groups and two nitrogen atoms all have the ability to coordinate with metal ions due to their lone pairs of electrons [9]. On the other hand, special metals such as chromium are very important in industry due to their unique characteristics, and their presence in environmental and ecosystems has occurred due to waste discharges [10]. The main industrial sources of chromium include electroplating, fertilizers, pigments, tanning, mining and metallurgical process. Chromium exists in the environment as trivalent Cr(III) and hexavalent Cr(VI) forms, and Cr(VI) is considered highly toxic, carcinogenic and mutagenic. Chromium can cause diseases like liver, kidney, lung and gastrointestinal cancer [11]. Therefore, chromium treatment is necessary before any discharge. Adsorption is the preferred treatment technology due to its cost-effectiveness in operation and investment, ease of use, simplicity, and wide usage. The adsorption of chromium onto adsorbents is influenced highly by the presence of active site on the surface [4]. To the best of our knowledge and based on the literature search, this is the first report that examined the surface modification of MWCNT with EDTA and sulfuric acid and the production of functionalized carbon materials with high adsorption properties. Also, few works focused on the adsorption of pollutants on functionalized multi-wall carbon nanotube (*f*-MWCNTs) and simultaneously determining the equilibrium and kinetic properties. Hence, this work focuses on the equilibrium and kinetics of chromium adsorption on *f*-MWCNT. The main goal of this work was: (i) to present a novel technique for functionalized of MWCNT, (ii) to determine the adsorption efficiency of chromium from wastewater by *f*-MWCNTs, (iii) to find out the optimum conditions (such as pH solution, *f*-MWCNT dosage, initial concentrations and contact time), and (iv) to evaluate the isotherm and kinetics.

Experimental

Materials

MWCNT with 10–40 nm diameters and 1–25 μm length was obtained from the Research Institute of the Petroleum Industry, Iran. The characteristics of MWCNT are shown in Table 1. EDTA, sulfuric acid, 1, 5-diphenylcarbazine, NaOH, HCl, H_2O_2 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and acetone were purchased from Merck, Germany. All chemicals used in this study were of analytical reagent grade. Deionized water was used for all dilution.

MWCNT functionalization

In the first step, 1 g of MWNCT was placed in a 500 ml round bottom flask and 300 ml of EDTA (1 M) was added at room temperature. The mixture was stirred using a magnetic stirrer for 2 h, then dried at 120 $^\circ\text{C}$. For the second step, the sulfuric acid was added to the MWCNT. Treated MWCNT with EDTA was immersed in a 1 M H_2SO_4 for 12 h at room temperature. The *f*-MWCNT was washed several times using deionized water and it was used in the experiments.

Adsorption experiments

The experiments were conducted by adding the *f*-MWCNT to 50 ml of different chromium test solutions in an erlenmeyer flask (200 mL capacity). All experiments were carried out at ambient temperature. The initial solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. The flasks were agitated at 100 rpm in a rotary shaker for different contact time (0–250 min). The *f*-MWCNT was separated from the test solution. The amount of chromium adsorbed at equilibrium, q_e (mg/g), was calculated from the difference in chromium concentrations in the aqueous phase before and after adsorption, as per the following Eq. 1:

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

Here, V is the volume of solution, C_i and C_e are the initial and equilibrium concentrations of chromium in solution (mg/L), respectively, and m is the mass of adsorbent [12]:

The langmuir isotherm model

The adsorption data were analyzed using the Langmuir isotherm model. This model is valid for monolayer adsorption onto a surface containing a finite number of identical sorption sites and is represented by the following Eq. 2 [11]:

$$q_e = \frac{q_m K_c C_e}{1 + K_c C_e} \quad (2)$$

Table 1 The MWCNT characteristics

| Characteristic | Unit | Value |
|-----------------------------|-------------------|-------|
| Specific surface area (BET) | m ² /g | 270 |
| Length | μm | 10 |
| Diameter | nm | 10–30 |
| Thermal conductivity | w/mV | 1,500 |

Here, q_e is the amount of chromium adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration in the solution (mg/L), and q_m is the maximum amount of chromium required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_c) by the following Eq. 3 [4]:

$$\frac{C_e}{q_e} = \frac{1}{K_c q_m} + \frac{C_e}{q_m} \quad (3)$$

The equilibrium data were analyzed using the linearized form of the Langmuir adsorption isotherm Eq. 3. The Langmuir constant, K_c , and monolayer sorption capacity, q_m , were calculated from the slope and intercept of the plot of C_e/q_e and C_e .

The Freundlich isotherm model

The Freundlich equation is purely empirical, based on sorption on a heterogeneous surface, and is commonly described by the following Eq. 4 [11]:

$$q_e = K_f C^{1/n} \quad (4)$$

K_f and $(1/n)$ are the Freundlich constants (representing the adsorption capacity and adsorption intensity, respectively). Equilibrium constants were evaluated from the intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown in Eq. 5 [4]:

$$\log q_e = \log(K_f) + \frac{1}{n} \log(C_e) \quad (5)$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. 5. Values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favorable adsorption.

The Temkin isotherm model

The Temkin isotherm has been generally applied in the following Eq. 6 [11]:

$$q_e = \left(\frac{RT}{b} \right) \ln(k_t C_e) \quad (6)$$

It can be linearized as Eq. 7:

$$q_e = B \ln k_t + B \ln C_e \quad (7)$$

Here, $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol), B is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

Kinetics of adsorption

Various kinetic models, namely pseudo-first order, pseudo-second order and intraparticle diffusion models, have been used for their good fit to experimental adsorption data for chromium onto *f*-MWCNT. To investigate changes in the adsorption with shaking time, the kinetic data of chromium sorption onto *f*-MWCNT was subjected to the pseudo-first order Eq. 8 [4]:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \tag{8}$$

Here, q_e is the sorbed concentration at equilibrium and k_1 is the first order rate constant. The linear plot of $\log(q_e - q_t)$ against time ‘ t ’ demonstrates the applicability of the above equation to chromium adsorption onto *f*-MWCNT.

The kinetic data of chromium sorption onto *f*-MWCNT was subjected to the pseudo-second order model of Eq. 9 [4]:

$$\frac{t}{qt} = \frac{1}{(Kq_e)^2} + \frac{t}{q_e} \tag{9}$$

The rate constant k_2 was calculated from the slope of the straight line with a correlation factor. Intraparticle diffusion kinetics was the other kinetic model investigated. The linear form of intraparticle diffusion is shown in Eq. 10 [4]:

$$\log q_t = \log k_{id} + a \log(t) \tag{10}$$

Here, q_t is the sorbed concentration of chromium at time ‘ t ’ and k_{id} is the constant of intraparticle diffusion.

Analysis

All experiments were performed in triplicate in order to minimize errors, and average values were analyzed. The concentration of chromium was analyzed by spectrophotometry at the wavelength of 540 nm, using diphenylcarbazide [CO(NHNHC₆H₅)₂] as chromogenic reagent, H₂SO₄ and H₃PO₄ as buffering agent. Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups involved in functionalization before and after the treatment.

Results and discussion

Surface functionalities of MWCNT

Chemical functionalization is a procedure used in materials science to improve the surface of materials. Several researchers use this technique to promote carbon nanotube properties [7, 8]. The addition of functional groups on carbon nanotube is

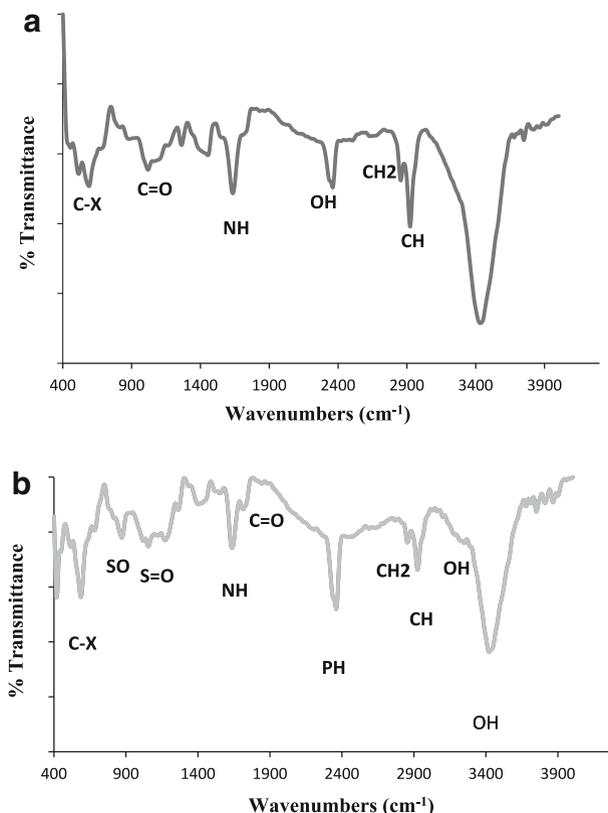


Fig. 1 FTIR spectra of MWCNTs (**a** MWCNT, **b** *f*-MWCNT) [C-X: carbon halogen stretches (Alkyl Halides), S-O/S = O: sulfoxide, sulfone, sulfonic acid, sulfonyl chloride or sulfate groups, NH: Amines, C = O saturated aldehyde and ketone, PH: phosphine, C-H/CH₂ : Alkenes/Alkanes (usually sharp), O-H: Carboxylic Acids (very broad)]

commonly made by immersing it in strong acids such as sulfuric acid or nitric acid [13]. Choi et al. [14] used 5-phenoxyisophthalic acid, phosphorous pentoxide, and polyphosphoric acid to functionalized carbon nanotubes [14]. In addition to the above mentioned methods, there are still other methodologies that function as alternative routes to functionalize carbon nanotubes [8]. FTIR is mainly used to identify the presence or absence of functional groups. Figs. 1a and b show the FTIR results of the MWCNT obtained before and after chemical functionalized. The region below 1,400 cm⁻¹ is named fingerprint region and is hardly used to identify compounds due its complexity [7]. The band at 3,419 is attributed to the presence of hydroxyl groups (-OH) on the surface of the MWCNT, which are believed to result from either ambient atmospheric moisture bound to the MWCNT or oxidation during the purification of the raw material [9]. For the *f*-MWCNT (Fig. 1b), a new band appeared at 1,713, which are attributed to the C O stretching vibrations of the carboxylic groups. Also, two new bands appeared at 1,055 and 1,171 cm⁻¹, which

Table 2 Calculated constants of adsorption isotherms

| Isotherm | R ² | qmL, nF, B1 | kc, kf, kt |
|------------|----------------|-------------|------------|
| Langmuir | 0.996 | 6.33 | 1.11 |
| Freundlich | 0.834 | 4.24 | 3.40 |
| Temkin | 0.850 | 1.09 | 3.35 |

are attributed to the S–O and S–O stretching vibrations of the sulfate groups, respectively. All these observations confirm that the surface of the MWCNT has been functionalized by the EDTA and sulfuric acid.

Isotherm studies

Isotherm studies are used for estimation of the quantity of total chromium that could be adsorbed onto *f*-MWCNT. Chromium adsorption data were analyzed using the Langmuir, Freundlich and Temkin adsorption isotherm models. The constants of each isotherm are shown in Table 2. According to these results, the maximum adsorption capacity (q_m), K_f and B_1 were determined to be about 6.33 and 4.24 mg/g (l/mg)^{1/n} and 1.09. The regression coefficients indicated a better fit with the Langmuir isotherm. This correlation of experimental data with the Langmuir model was determined by higher values of the correlation coefficient ($R^2 = 0.996$). The Langmuir isotherm is based on two assumptions: first that a single adsorbate binds to a single site on the adsorbent and second, that all surface sites on the adsorbent have the same affinity for the adsorbate. A comparison of equilibrium constants of various pollutants for varying carbon nanomaterials is shown in Table 3. As shown in this table, the adsorption of metal ions by carbon nanomaterials is best correlated with the Langmuir isotherm.

Kinetic evaluation

In order to evaluate the adsorption dynamics, three models, pseudo-first order, pseudo-second order and intraparticle diffusion or Weber Morris kinetics were considered. Adsorption dynamics are used to describe the sorption rate of chromium at the *f*-MWCNT-wastewater interface. The complete details of kinetic models for each concentration (5, 10 and 20 mg/l) are provided in Table 4. Based on the regression coefficients, a better fit is found with the pseudo-first and second order models. The best adsorption dynamics fit occurred at lower concentrations for the pseudo-first and second order models. However, the best fit for intraparticle diffusion kinetics occurred at higher ion content. Moreover, higher q_e values are observed at higher chromium concentrations.

Effect of contact time

Among the adsorption parameters, contact time was limited to a period of 4 h. The contact time should be considered as an important factor for the interactions between

Table 3 Comparative evaluation of equilibrium constants for various adsorbates

| Adsorbent | Adsorbate | Equilibrium values and constants | References |
|--------------------------|-------------------------------------|---|---------------|
| f-MWCNT | Total chromium | Langmuir, $q_m = 6.33$ (mg/g) | Present study |
| MWCNT | Cr^{+6} | Langmuir, pH 2.88, $q_m = 3.04 \pm 0.02$ (mg/g) | [4] |
| CNT | Pb^{2+} | Langmuir, $q_m = 17.44$ (mg/g) in pH 5 | [18] |
| MWCNT | Ni^{2+} | Freundlich, $K_F = 2.921$ (mg/g) | [19] |
| MWCNT | Pb^{2+} | Langmuir, $q_m = 28.86$ (mg/g) | [20] |
| | Co^{2+} | Langmuir, $q_m = 21.44$ (mg/g) | |
| | Cd^{2+} | Langmuir, $q_m = 55.89$ (mg/g) | |
| SWCNT | Pb^{2+} | Langmuir, $q_m = 96.02$ (mg/g) | [21] |
| | Cu^{2+} | Langmuir, $q_m = 77.00$ (mg/g) | |
| | Cd^{2+} | Langmuir, $q_m = 24.29$ (mg/g) | |
| CNT | Direct dyes DY ₈₆ | Freundlich, $K_F = 5.14$ (mg/g) | [22] |
| | Direct dyes DR ₂₂₄ | D–R, $X_m = (8.2–12.5) \times 10^{-4}$ (mol/g) | |
| CNT | Reactive dye (procion red MX-5B) | Langmuir, 301 K, pH 6.5, $q_m = 39.84$ (mg/g) Langmuir, 301 K, pH 10, $q_m = 35.21$ (mg/g) | [23] |
| MWCNT | Phenol | Freundlich, $K_F = 17.24$ (mol ^{1–n} L ⁿ /g) | [24] |
| | Catechol | Freundlich, $K_F = 16.49$ (mol ^{1–n} L ⁿ /g) | |
| | Pyrogallol | Freundlich, $K_F = 38.71$ (mol ^{1–n} L ⁿ /g) | |
| CNTs- x % O ₂ | Toluene | Langmuir, 3.2 % O ₂ , $q_m = 99.47$ (mg/g) | [25] |
| | Ethylbenzene | Langmuir, 3.2 % O ₂ , $q_m = 115.63$ (mg/g) | |
| | Xylene | Langmuir, 3.2 % O ₂ , $q_m = 112.19$ (mg/g) | |

Table 4 Calculated constants of adsorption kinetics

| Kinetic models | Chromium conc. (mg/L) | R ² | | | q _e (mg/g) |
|-------------------------|-----------------------|----------------|--|--|-----------------------|
| | | R ² | Constants (k ₁ , k ₂ , k _{id}) | | |
| Pseudo first-order | 5 | 0.9856 | 0.0212 | | 4.4695 |
| | 10 | 0.9856 | 0.0186 | | 5.3635 |
| | 20 | 0.7102 | 0.0269 | | 6.6586 |
| Pseudo second-order | 5 | 0.9996 | 0.0574 | | 4.6111 |
| | 10 | 0.9986 | 0.0404 | | 5.5968 |
| | 20 | 0.4829 | 0.0362 | | 7.1572 |
| Intraparticle diffusion | 5 | 0.8948 | 1.8127 | | – |
| | 10 | 0.9077 | 0.6093 | | |
| | 20 | 0.9721 | 1.8127 | | |

pollutant and adsorbent [15]. To find equivalent times, the adsorption behavior was investigated for three initial chromium concentrations. Fig. 2 shows the effect of contact time during the process. According to the plot trend, the obtained equivalent time was 150 min; this is marked with a dashed line for each concentration. Regarding these results, it can be found that a higher removal efficiency is obtained for a lower concentration of chromium. The maximum removal for 5 mg/L of total chromium was

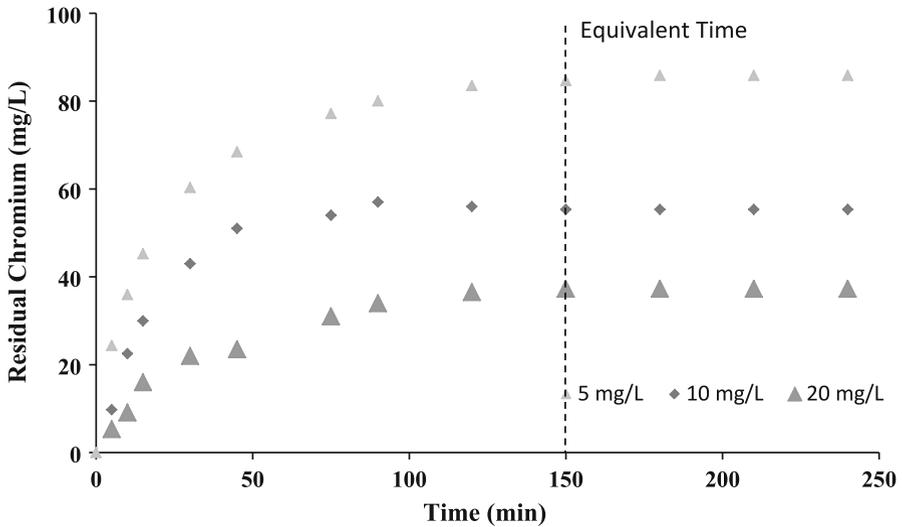


Fig. 2 The effect of contact time on the adsorption process at three values of total chromium over 250 min (adsorption conditions: pH 3, 50 mg *f*-MWCNT dosage, 100 rpm shaking, 25 ± 1 °C)

about 85 %. The adsorption efficiency for 10 and 20 mg/L is estimated at 55.33 and 37.27 %, respectively. Hu et al. [4] used oxidized-MWCNTs to reach 100 % adsorption efficiency with 3 mg/l of hexavalent chromium at 280 h of contact time, reporting that the removal efficiency of hexavalent chromium is closely related to the initial concentrations [4]. At lower concentrations, the removal percentage is increased, because of ion competition caused by a decrease of electronic repulsion, and the effect of interferents is negligible [16].

Effect of *f*-MWCNT concentration

The effect of *f*-MWCNT concentration during adsorption of chromium is displayed in Fig. 3. According to the trend in this diagram, for the concentrations of 20, 40 and 60 mg, removal efficiencies of 39.8, 61.76 and 90.80 % were obtained. In general, for similar ion concentrations, a higher removal percentage occurred with higher carbon nanotube content. Further adsorption is because of increased active sites and higher surface area in *f*-MWCNTs.

Effect of pH

pH is one of the parameters with the greatest influence on the adsorption of metallic ions [17]. In addition, the surface pH of MWCNTs is dependent on the charge density of the metallic species present [13]. The absorptive behavior of MWCNT at various pH values (3–8 and 9) in an initial concentration of 5 mg/l is illustrated in Fig. 4. It was determined that increasing the pH is associated with a loss of adsorbed ions. The maximum quantity of ions adsorbed at an acidic value of pH 3 was around 99.8 %. Higher removal at lower pH may be due to charging of the surface of *f*-

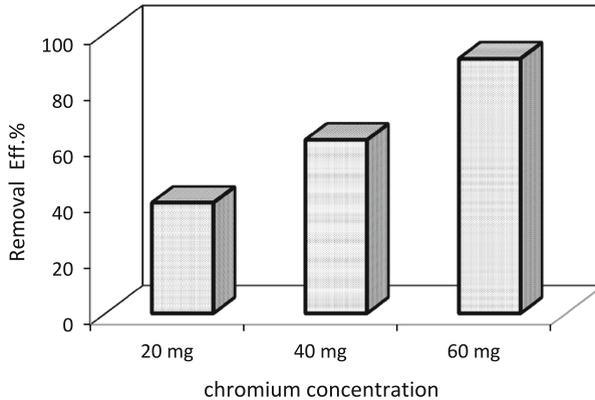


Fig. 3 The effect of *f*-MWCNT dosage on chromium adsorption (adsorption conditions: 150 min, pH 3, 5 mg/L total chromium, 100 rpm shaking, 25 ± 1 °C)

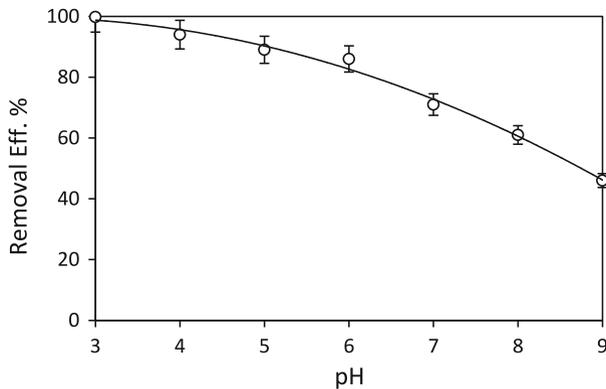


Fig. 4 The effect of pH on chromium adsorption (adsorption condition: 150 min, pH 3–9, 5 mg/L total chromium, 60 mg *f*-MWCNT dosage, 100 rpm shaking, 25 ± 1 °C)

MWCNTs with H^+ ions, creating a significantly strong electrostatic attraction between the positively charged carbon surface and anionic hexavalent chromium (as a main portion of total chromium). On the other hand, trivalent chromium ions (as the other important portion of total chromium) are present in cationic forms (Cr^{3+} , $Cr(OH)_2^+$ and $Cr(OH)_2^+$) at pH 3.6–6.5 and can result in considerable attraction to the negative surface charge on *f*-MWCNT.

Conclusion

Based on the findings from our work, the following can be asserted:

- (i) *f*-MWCNT can successfully achieve the removal of chromium from wastewater.

- (ii) In the process of adsorption of chromium, many parameters such as *f*-MWCNT concentration, contact time, initial pH and ion content can affect the removal efficiency of chromium.
- (iii) The Langmuir isotherm was determined to have the best correlation with experimental data, based on its higher correlation coefficient value ($R^2 = 0.996$).
- (iv) The pseudo-second order kinetic models provide a better fit with regards to regression coefficients.

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