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Removal of Cr(VI) from Waters by Multi-Walled Carbon Nanotubes: Optimization and Kinetic Investigations

Francisco J. Alguacil and Félix A. Lopez

Abstract

The adsorption of chromium(VI) from aqueous solutions onto multi-walled carbon nanotubes (MWCNTs) has been investigated under various experimental conditions of initial metal concentration, agitation speed, aqueous pH, temperature and adsorbent dosage to assess the equilibrium and kinetic parameters. It was found that the kinetic data were fitted with the pseudo-first- and pseudo-second-order models, whereas the chromium(VI) adsorption data were fitted with the Langmuir and Freundlich equilibrium models to give the characteristic parameters of each model. According with the evaluation, both isotherm models are useful to represent the measured adsorption data. The adsorption of chromium(VI) is also dependent on the temperature, and the corresponding thermodynamic parameters including ΔH° , ΔG° and ΔS° were estimated from the experimental data, indicating the exothermic and non-spontaneous nature of the metal adsorption onto the MWCNTs. Chromium(VI) desorption was investigated by the use of aqueous hydrazine sulfate solutions.

Keywords: chromium(VI), multi-walled carbon nanotubes, adsorption, desorption, kinetics

1. Introduction

Despite its toxic character, chromium(VI) is widely used in various industries, being its recovery from the corresponding liquid effluents a primary target before their discharge to natural waters. Several technologies have found application to remove and/or recover chromium(VI) from these process wastes: pseudo-emulsion strip dispersion pertraction [1, 2], adsorption onto activated carbons [3], liquid-liquid extraction [4], biomass adsorption [5, 6], adsorption onto natural zeolites [7], adsorption onto phosphates [8], ion exchange [9] and electro-assisted and photo-assisted technologies [10]. Among them, adsorption onto carbon nanotube (CNT) technology could be competitive when the metal is present at low concentrations in the aqueous solution. Various carbon nanotubes configurations can be found, being the most commonly used the single-walled carbon nanotubes (SCNTs) and multi-walled carbon nanotubes (MWCNTs) configurations, together with functionalized multi-walled carbon nanotubes. In either configuration, and

after the metal adsorption, a subsequent operation or elution is needed in order to recover the metal to a solution where it is concentrated and purified, and thus it can be conveniently recovered or even recycled to the original industrial process.

A number of examples using these CNTs for chromium(VI) recovery from aqueous solutions can be found in the literature. Naghizadeh [11] investigated the adsorption efficiency of activated carbon and multi-walled carbon nanotubes respect to cadmium(II) and chromium(VI) in the 3–12 pH range. Whereas both adsorbents presented high metal adsorption capacities over the whole pH range investigated, the experimental results indicated that MWCNTs had a greater potential for the removal of chromium(VI) and cadmium(II) from aqueous solutions than activated carbon. In an investigation by [12], oxidized (–COOH) multi-walled carbon nanotubes were used to remove Cr(VI) (hazardous element) and Au(III) (valuable element), from aqueous solutions. Experiments were performed in order to investigate the influence of different variables on the adsorption kinetics, i.e., the stirring speed ($250\text{--}2000\text{ min}^{-1}$) and adsorbent dosage ($0.25\text{--}1.5\text{ g/L}$) in the case of chromium(VI) as well as temperature ($20\text{--}60^\circ\text{C}$) and HCl ($0.1\text{--}10\text{ M}$) concentration in the case of gold(III). The performance of these carbon nanotubes was excellent in the removal of both elements, presented as the anions HCrO_4^- and AuCl_4^- , from the aqueous solutions.

Anastopoulos et al. [13] reviewed the removal of chromium(III) and (VI) from aqueous solutions by carbon nanotubes. In both cases, the pH of the solution seemed to control the adsorption process, with a maximum adsorption of Cr(VI) occurring at pH 1–4 (in the case of Cr(III), the above occurs at pH values of 5–8). Furthermore, it is stated that most of the investigations are reported using non-real wastewater, conditions that very often are not repeated in real wastewaters. Xing et al. [14] presented a novel remediation protocol for Cr(VI) featured with high-capacity adsorption and electrochemical regeneration of the adsorbent. In their study, MWCNTs modified carbon cloth (CC) is used as a useful carrier for electrodepositing polypyrrole (PPy) film and the resultant nanocomposite CC-MWCNTs-PPy is used as an adsorbent with high adsorption capacity and stability. CC-MWCNTs-PPy is electrically regenerated to reduce secondary wastes.

In the present work, results obtained for the adsorption of chromium(VI) using multi-walled carbon nanotubes are presented. Several variables that could affect the adsorption process, such as the stirring speed of the aqueous solution, metal concentration and adsorbent dosage, temperature, etc., are investigated. Several equilibrium, kinetics and thermodynamic parameters are also reported. The desorption of the Cr(VI)-loaded MWCNTs is accomplished using aqueous solutions of hydrazine sulfate.

2. Methods

2.1 Reactives and experimental procedure

The multi-walled carbon nanotubes were obtained from Fluka and were used without further purification; the main characteristics of the adsorbent are given in **Table 1**, with further characteristics (i.e., Raman data) of them published elsewhere [15]. The characteristics of other adsorbent-ion exchangers used in this investigation were described elsewhere: Dowex 1x8 resin [16], oxidized MWCNTs [12] and activated carbon [17].

Stock Cr(VI) solutions were prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck) in distilled water. All other chemicals were of AR grade.

Type	Multi-walled
Melting range	3652–3697°C
Density	2.1 g/mL
Appearance	Dust
Purity	≥98% carbon basis
Dimensions	10 ± 1 nm external diameter
Maximum adsorption	4.5 ± 0.5 nm internal diameter
BET	3–6 µm (length)
	1295 cm ³ /g
	263 m ² /g

Table 1.
Characteristics of the multi-walled carbon nanotubes.

Metal adsorption (and elution) studies were carried out in a glass reactor provided for mechanical shaking. Metal adsorption (or elution) was determined by monitoring concentration by AAS in the aqueous solution as a function of time, whereas the metal concentration in the adsorbent was calculated by mass balance.

2.2 Modeling of kinetic adsorption

2.2.1 Pseudo-first-order model

The pseudo-first-order equation [18] used in this work can be expressed accordingly with the next equation:

$$\ln([Cr]_{c,e} - [Cr]_{c,t}) = \ln[Cr]_{c,e} - k_1 t \tag{1}$$

where $[Cr]_{c,t}$ and $[Cr]_{c,e}$ are the chromium concentrations in the nanotubes at equilibrium and at an elapsed time, respectively, t is the time and k_1 is the constant related to this model.

2.2.2 Pseudo-second-order model

In this model, the equation used is

$$\frac{t}{[Cr]_{c,t}} = \frac{1}{k_2 [Cr]_{c,e}^2} + \frac{t}{[Cr]_{c,e}} \tag{2}$$

In this case, k_2 is the constant related to this model.

2.3 Modeling the rate law

Three possible adsorption mechanisms had been evaluated if the adsorption of chromium(VI) into the MWCNTs must be considered as a liquid-solid phase reaction which includes diffusion of chromium species from the aqueous phase to the adsorbent surface, the diffusion of ions within the nanotubes and the chemical reaction between ions and any functional group in the carbon nanotubes [19]. The rate equations for the above three cases are:

i. film-diffusion controlled process, in which the rate equation is

$$\ln(1 - F) = -kt \quad (3)$$

ii. particle-diffusion controlled process, with the equation as

$$\ln(1 - F^2) = -kt \quad (4)$$

iii. Shrinking core model

$$3 - 3(1 - F)^{2/3} - 2F = kt \quad (5)$$

In all the above equations, F is the fractional approach to equilibrium, which is defined as

$$F = \frac{[Cr]_{c,t}}{[Cr]_{c,e}} \quad (6)$$

whereas k is the corresponding rate constant.

2.4 Modeling of adsorption isotherms

Both the Langmuir and Freundlich approaches had been used to model the experimental data, being both widely used in the modeling of adsorption or ion exchange processes [20].

The Langmuir model is valid for monolayer adsorption onto a surface containing a limited number of identical sites. The equation in its linear form describing this model is

$$\frac{1}{[Cr]_{c,e}} = \frac{1}{[Cr]_{c,m}} + \frac{1}{b[Cr]_{c,m}} \frac{1}{[Cr]_{s,e}} \quad (7)$$

where b is a constant related to the model, $[Cr]_{c,m}$ is the maximum metal uptake in the carbon nanotubes and $[Cr]_{s,e}$ is the equilibrium chromium(VI) concentration in the solution.

The Freundlich model is an empirical expression describing adsorption onto heterogeneous surfaces, having the adsorbent surface sites with a variation of binding energies. In this case, the equation also in its linear form is

$$\ln[Cr]_{c,e} = \ln k_f + \frac{1}{n} \ln[Cr]_{s,e} \quad (8)$$

where k_f and n are parameters related to the Freundlich model.

3. Results and discussion

3.1 Effect of stirring speed

Adsorption of chromium(VI) from aqueous solution to MWCNTs as a function of the stirring speed at $\text{pH } 1 \pm 0.1$ is shown in **Figure 1**. The adsorption of chromium(VI) increases with increasing stirring speed, though from 1000 min^{-1} no significant

Figure 1.
Influence of stirring speed on the percentage of chromium(VI) adsorption at the equilibrium. Aqueous solution: 0.01 g/L Cr(VI). MWCNTs dosage: 1 g/L. Temperature: 20°C. Time: 2 h.

changes are encountered in metal adsorption specially at the longer contact times. These results shown that from 1000 min⁻¹, the thickness of the aqueous diffusion layer and the aqueous resistance to mass transfer were minimized, and the diffusion contribution of the aqueous species to the adsorption process is assumed to be constant.

3.2 Effect of temperature

The relationship between chromium(VI) adsorption and the temperature is also studied using aqueous solutions containing 0.01 g/L Cr(VI) at pH 4 ± 0.1 and adsorbent dosage of 1 g/L. **Table 2** shows the variation of log D_{Cr} vs. T, over the range of temperatures used, where D (the distribution coefficient) was calculated as

$$D = \frac{[Cr]_{c,e}}{[Cr]_{s,e}} \tag{9}$$

where [Cr]_{c,e} and [Cr]_{s,e} being the chromium concentrations in the nanotubes and in the aqueous solution at equilibrium. There is a decrease of chromium adsorption with the increase of temperature. One explanation of these results is to consider the nature of the species with the temperature as predicted by the Bjerrum equation. Accordingly, the estimated change of enthalpy is -14 kJ/mol, and the adsorption process is therefore exothermic.

Temperature	% adsorption	D (L/g)	Log D
20°C	44	0.79	-0.10
40°C	36	0.56	-0.25
60°C	28	0.39	-0.41

Stirring speed: 1000 min⁻¹. Time: 2 h.

Table 2.
Influence of temperature on chromium(VI) adsorption onto the MWCNTs.

The kinetic adsorption data were simulated with the two models shown in Eqs. (1) and (2), representing the pseudo-first- and pseudo-second-order models, respectively. The results are listed in **Table 3**. From the values of r^2 , the kinetic adsorption of chromium(VI) at the temperatures of 20 and 60°C can be fitted by the pseudo-second-order model.

3.3 Effect of pH

The pH of the aqueous solution may be one of the most decisive parameters controlling the adsorption process. The influence of pH on the adsorption of chromium(VI) is investigated at pH values ranging from 1 to 13. **Figure 2** shows that the maximum adsorption of the metal occurs at pH 4, and decreases either at more acidic and at alkaline pH values, these mean that HCrO_4^- species (which is predominant at this range of initial chromium(VI) concentration and pH values below 6) is adsorbed onto the MWCNTs better than CrO_4^{2-} species, which is predominant at alkaline pH values. Furthermore, **Table 4** presented data about the adsorption of 0.005 g/L chromium(VI) at pH values of 1 and 4; it is also observed how the percentage of metal adsorption is greatly dependent on the pH of the aqueous solution, decreasing as the pH shifts to more acidic values.

3.4 Effect of carbon nanotubes dosage

It is apparent that the amount of adsorbent used in the removal of a given solute from aqueous solutions is critical for the practical application of such system. Thus, adsorption of chromium(VI) as a function of MWCNT dosages at $\text{pH } 4 \pm 0.1$ is shown in **Figure 3**. The percentage of metal adsorption increases with the MWCNT dosage increasing, i.e. near 90% chromium(VI) is adsorbed at the adsorbent dosage of 10 g/L and this value down until 44% when the adsorbent dose is 1 g/L. These results are consistent with the fact that the increase of the adsorbent dosage results in the increase of the active sites in which the metal can be adsorbed, thus increasing the percentage of metal adsorbed or eliminated from the aqueous solution.

The data of the amount of chromium(VI) adsorbed on the MWCNTs (mg/g) and the metal concentration remaining in solution (mg/L) are fitted to the Langmuir and Freundlich models represented by Eqs. (7) and (8), respectively. The relative parameters obtained from the fit are listed in **Table 5**. The experimental data are well described by both models, indicating that the chromium(VI) uptake onto the MWCNTs is homogeneous and multilayer in nature. However, a singular fact of the Langmuir model can be described by the dimensionless separation factor, defined as

$$R = \frac{1}{1 + b [\text{Cr}]_{s,0}} \tag{10}$$

		20°C	60°C
Pseudo-first order	$k_1 \text{ (min}^{-1}\text{)}$	0.057	0.056
	r^2	0.9493	0.9856
Pseudo-second order	$k_2 \text{ (g/min mg)}$	0.16	0.034
	r^2	0.9992	0.9983

Table 3.
Constants for the kinetic adsorption of chromium(VI) to MWCNTs using different adsorption models.

Figure 2.
Influence of the pH on chromium(VI) adsorption. Experimental conditions as in Figure 1.

pH ± 0.1	% adsorption
1	19.5
2	80.7
3	91.1
4	99.5

MWCNTs dosage: 10 g/L. Temperature: 20°C. Time: 2 h.

Table 4.
Influence of pH on chromium(VI) adsorption onto the MWCNTs.

where $[Cr]_{s,0}$ is the initial metal concentration in the solution and b is the Langmuir constant. The value of R indicates if the adsorption is unfavorable ($R > 1$), linear ($R = 1$), favorable ($0 < R < 1$) or irreversible ($R = 0$). The value of R in this investigation was found to be 0.82, indicating that the adsorption of chromium(VI) is favorable.

3.5 Effect of metal concentration

The various adsorptions of chromium(VI) on MWCNTs as a function of initial metal concentration at $pH\ 4 \pm 0.1$ are shown in Figure 4. The adsorption percentage of chromium(VI) decreases with initial metal concentration increasing.

The rate law governing the metal adsorption was investigated using the three models depicted in Eqs. (3)–(5), and the results from these fits were summarized in Table 6. It can be seen that within the particle-diffusion controlled model, the chromium(VI) adsorption onto the MWCNTs was better explained.

3.6 Comparison with other adsorbent-anion exchangers

The adsorption capacity, in terms of percentage of adsorption, found in this investigation was compared with the results obtained using other potential adsorbent-anion exchangers for Cr(VI). The results obtained from this set of

Figure 3.
Influence of MWCNTs dosage on chromium(VI) adsorption. Aqueous solution: 0.01 g/L Cr(VI) at pH 4.
Temperature: 20°C. Time: 2 h.

	b (L/mg)	[Cr] _{e,m} (mg/g)	r ²	ln k _f	1/n	r ²
Langmuir	0.021	37	0.9950			
Freundlich				-0.28	0.94	0.9952

Table 5.
Langmuir and Freundlich constants.

Figure 4.
Influence of initial chromium(VI) concentration on metal adsorption. MWCNTs dosage: 10 g/L.
Temperature: 20°C.

Equation		0.005 g/L	0.01 g/L	0.04 g/L
3	k (min ⁻¹)	0.48	0.27	0.26
	r ²	0.9008	0.7710	0.8968
4	k (min ⁻¹)	0.36	0.14	0.15
	r ²	0.9537	0.9739	0.9796
5	k (min ⁻¹)	0.11	0.06	0.06
	r ²	0.9004	0.8767	0.9760

Table 6.
The rate law governing the adsorption of chromium(VI) onto the MWCNTs.

experiments together with the experimental conditions used in the investigation were summarized in **Table 7**.
It can be concluded that, under the present experimental conditions, Dowex 1×8 resin is the most effective to remove hazardous chromium(VI) from near neutral or acidic solutions, whereas MWCNTs presented the worse registers. The above is not a bad conclusion about the use of these MWCNTs as adsorbents for Cr(VI), and not delegitimize the investigation presented in this work, only stated that there are other potential adsorbents-ion echargers that remove Cr(VI) from liquid effluents with a better efficiency.

3.7 Thermodynamics

Besides the data of the change of enthalpy (see Section 3.5) derived for the adsorption process of chromium(VI) onto the carbon nanotubes, a further thermodynamic analysis of the adsorption process can be considered taking into account the next equations:

$$\Delta G^\circ = -RT \ln b \tag{11}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{12}$$

Accordingly with Eq. (11) in which b is the Langmuir constant showed in **Table 5**, it can be obtained that the value of ΔG° is 9 kJ/mol, confirming that the chromium(VI) uptake onto the nanotubes is nonspontaneous.
To calculate ΔS° for the present adsorption system, Eq. (12) is used, obtaining a value of −0.08 kJ/mol K. The negative value for the change of entropy characterizes a decrease disorder of the system when chromium(VI) is adsorbed onto the nanotubes.

Adsorbent-anion exchanger	Active group	pH 1	pH 4
Dowex 1x8	QAS-Cl ⁻ form	89	>99
MWCNTs	None	32	42
ox-MWCNTs	–COOH	68	No data
Activated carbon	None	47	59

Aqueous solution: 0.01 g/L Cr(VI) at different pH values. Solid dosage: 1 g/L. Temperature: 20°C. Stirring speed: 1000 min⁻¹. Time: 1 h.
QAS: quaternary ammonium salt.

Table 7.
Percentage of Cr(VI) adsorption using various adsorbent-anion exchangers.

3.8 Chromium(VI) desorption

In the present investigation, the desorption of chromium(VI) from the metal-loaded carbon nanotubes was studied using hydrazine sulfate solutions as desorbent for the metal, at the same time, in the desorption process, Cr(VI) is reduced to the less hazardous Cr(III) oxidation state, accordingly to

Desorption experiments were carried out with aqueous solutions containing 25–50 g/L of hydrazine sulfate and 2 mg/g Cr(VI)-loaded MWCNTs at a 25 mL/g solution volume/weighed MWCNTs relationship and 20°C. The results from these experiments indicated that:

- i. The variation in the hydrazine sulfate solution concentration has no effect on the reaction yield (95% chromium recovery from loaded nanotubes).
- ii. The equilibrium is reached within 5 min of reaction.
- iii. The desorbed solution contained a chromium(III) concentration near eight times the initial chromium(VI) concentration in the feed solution (0.01 g/L) of the adsorption experiments.

4. Conclusions

The adsorption of chromium(VI) onto the multi-walled carbon nanotubes is dependent on the pH values of the aqueous solution. The adsorption reaches a maximum at pH 4 and decreases at more acidic and alkaline pH values. The adsorption is exothermic ($\Delta H^\circ = -14$ kJ/mol) and nonspontaneous (positive ΔG° valor), whereas at 20–60°C, the adsorption of chromium (VI) onto the nanotubes better fits to the pseudo-second-order model. In the 0.005–0.04 g/L range of chromium(VI) concentrations in the aqueous solution, the metal uptake onto the nanotubes responded well to the particle-diffusion model, and the metal adsorption responded to the Langmuir and Freundlich isotherms, indicating that the adsorption process is homogeneous and multilayer in nature. Chromium(VI) can be desorbed from MWCNTs by the use of hydrazine sulfate solutions, which releases to the aqueous solution chromium in the less hazardous (III) valence state.

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Conflict of interest

The authors declare no conflicts of interest.

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