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EVALUATION OF MULTI-WALLED CARBON NANOTUBES PERFORMANCE IN ADSORPTION AND DESORPTION OF HEXAVALENT CHROMIUM

In this study, the removal of hexavalent chromium from aqueous solutions using multi-walled carbon nanotubes (MWCNTs) has been investigated as a function of adsorbent dosage, initial Cr(VI) concentration, initial pH, contact time and temperature. Low pH, low initial concentrations of Cr(VI), increasing contact time and high temperature were found as optimal conditions. A comparison of kinetics models applied to the adsorption of Cr(VI) ions on the MWCNTs was evaluated for the pseudo first-order, the pseudo second-order, and Elovich kinetics models, respectively. The pseudo second-order kinetics model was found to correlate with the experimental data well. Equilibrium isotherms were measured experimentally and results show that data were fitted well by the BET model. Thermodynamic parameters were estimated and the results suggest that the adsorption process is spontaneous, physical and endothermic. The reversibility of Cr(VI) adsorption onto MWCNTs by desorption process and the effect of operating factors such as regeneration solution characteristics, contact time and temperature on this process was investigated. Results show that MWCNTs are effective Cr(VI) adsorbents and can be reused through many cycles of regeneration without any high decreasing in their performance.

Keywords: hexavalent chromium, adsorption isotherms, adsorption kinetics, thermodynamic parameters, desorption.

Chromium is an element of 6th group in the latest IUPAC Periodic Table, exists in both hexavalent and trivalent forms. Due to its high solubility, hexavalent form is more toxic than trivalent and requires more concern [1]. Strong exposure of Cr(VI) causes cancer in the digestive tract and lungs [2] and may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [3]. Water pollution by chromium ions is a considerable concern, as this metal has found widespread use in metal finishing, leather tanning, electroplating, nuclear power plant, textile industries, and chromate preparation [4]. Cr(VI) concentrations in industrial wastewater range from 0.5 to 270000 mg/L. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [5]. It is therefore, essential to remove Cr(VI) from wastewater before disposal.

Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and adsorption. Except adsorption, other processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent and energy requirements or generation of toxic sludge or other waste products that require disposal [6, 7]. Adsorption is an effective and versatile method for removing chromium particularly when combined with appropriate regeneration steps. This solves the problems of sludge disposal and renders the system more economically viable, especially if low cost adsorbents are used [8].

Several adsorbents which have been studied for adsorption of metal ions such as activated carbon [9, 10], fly ash [11,12], peat [13], sewage sludge ash [14], zeolite [15], biomaterials [16,17], recycled alum sludge [18], manganese oxides [19], peanut hulls [20], kaolinite [21] and resins [22]. However, these adsorbents suffer from low adsorption capacities or removal efficiencies of the metal ions. Therefore, researchers carried out investigation for new promising adsorbents.

Carbon nanotubes are a relatively new form of carbon first reported by Iijima in 1991. Studies on this new material has shown high adsorption capacity and removal efficiency of various pollutants [23]. The environmental applications of carbon nanotubes that have been investigated thus far include studies on the storage of gases like hydrogen as well as the removal of metal ions and organic contaminants [24].

Recently multi-walled carbon nanotubes (MWCNTs) have also been used as adsorbent in raw or modified form. Removal of Ni, Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} using raw MWCNTs [25-27] and also elimination of Sr(II), Eu(III) and Ni(II) via adsorption on modified MWCNTs can be mentioned as the most important studies done before [28-30]. Di *et al.* have also shown that ceria nanoparticles supported on aligned carbon nanotubes are effective in the removal of Cr(VI) [31].

Although the MWCNTs possess large sorption capacity of heavy metal, the very high unit cost when compared to the other commercially available adsorbents restricts their potential use for environmental protection applications. Thus, testing the reversibility of heavy metal ion adsorption with MWCNTs to diminish their replacement cost is needed before practical use of MWCNTs in water treatment [32].

In recent years, chromium removal using carbon nanotubes has been studied in some cases but most of investigations have had some deficiencies. For example, Di's research, despite of its significant findings, did not include kinetics, thermodynamics and desorption process studies [31]. Probes carried out by Pillay *et al.* and Hu *et al.* were also not complete because they have not studied the desorption process in detail [33,34].

The present investigation deals with the application of MWCNTs in the removal of chromium(VI) from aqueous solutions. The removal amount of Cr(VI) was measured in different effective conditions such as: adsorbent dosage, initial Cr(VI) concentration, solution pH, contact time and temperature. Adsorption kinetics, equilibrium isotherm and thermodynamic parameters of the process were also studied. In addition, the reversibility of Cr(VI) adsorption by multi-walled carbon nanotubes (MWCNTs) and effects of

different parameters on the amount of Cr(VI) desorbed, was investigated by desorption process to evaluate repeated availability performance of the adsorbent in water treatment.

Theoretical part

Modeling of adsorption kinetics

The study of adsorption kinetics is significant as it provides valuable insights into the pathways and the mechanism of the process. Several kinetics models are used to explain the mechanism of the adsorption processes. In this study, pseudo-first order (Eq. (1)), pseudo-second order (Eq. (2)) and Elovich (Eq. (3)) rate equations are used and compared with experimental data. These three models are expressed as below:

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303}t \tag{1}$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{3}$$

where q_e is the Cr(VI) uptake at equilibrium (mg/g), q is the uptake at any time (mg/g), K_1 is pseudo-first order adsorption rate constant (1/h), K_2 is the pseudo-second order rate constant (g/(mg h)) and α (mg/(g h)) and β (g/mg) are the Elovich model constants. The linear regression determination coefficient value shows that which model can justify the experimental data [35,36].

The Cr(VI) uptake, q, the amount of solute adsorbed per unit weight of adsorbent (mg/g), was calculated by the simple mass balance method as:

$$q = \frac{(c_0 - c_t)V}{m_s} \tag{4}$$

where c_0 and c_t are the Cr(VI) concentrations (mg/l) initially and at a given time t, respectively, V the volume of the Cr(VI) solutions (l) and m_s is the weight of adsorbent (g).

The removal percentage of Cr(VI) ions (*R%*) in solution was calculated using:

$$R = 100\frac{(c_0 - c_t)}{c_0} \tag{5}$$

Modeling of adsorption isotherm

To examine the relationship between solute adsorbed (q_e) and the aqueous concentration (c_e) at equilibrium, several isotherm models are widely employed. Here, two-parametric (such as Langmuir,

Freundlich and Temkin) and three-parametric models (such as BET and Sips) are defined, and their equations and parameters are represented in Table 1.

For two-parameter isotherms, the accuracy of the fit of an isotherm model to experimental equilibrium data was typically assessed based on the magnitude of the coefficient of determination for the linear regression. The isotherm giving an R^2 value closest to unity was deemed to provide the best fit.

Three parametric isotherms require an error function assessment, in order to evaluate the fit of the isotherm to the experimental results. In this study, three different non-linear error functions were examined and in each case the isotherm parameters were determined by minimizing the respective error function using the *solver* add-in with Microsoft's spreadsheet, Excel (Microsoft, 2007). The error functions employed were as follows:

1.   The sum of the absolute errors (SAE):

$$SAE = \sum \left| q_{cal} - q_{exp} \right| \qquad (6)$$

2.   The average relative error (ARE):

$$ARE = \frac{100}{x} \sum \left| \frac{q_{cal} - q_{exp}}{q_{exp}} \right| \qquad (7)$$

3.   A composite fractional error function ($HYBRID$):

$$HYBRID = \frac{100}{p - x} \sum \left(\frac{(q_{cal} - q_{exp})^2}{q_{exp}} \right) \qquad (8)$$

As each of the error criteria is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. Hence, in order to try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results was adopted producing a so-called "sum of the normalized errors" for each parameter set for each isotherm. The calculation method for the 'sum of the normalized errors' was as follows:

a)   select one isotherm and one error function and determine the isotherm parameters that minimize that error function for that isotherm to produce the isotherm parameter set for that error function;

b)   determine the values for all the other error functions for that isotherm parameter set;

c)   calculate all other parameter sets and all their associated error function values for that isotherm;

d)   select each error measure in turn and ratio the value of that error measure for a given parameter set to the largest value of that error from all the parameter sets for that isotherm;

e)   sum all these normalized errors for each parameter set.

The parameter set thus providing the smallest normalized error sum can be considered to be optimal for that isotherm [37,38].

EXPERIMENTAL

Materials

MWCNTs, obtained by chemical vapor deposition method, were purchased from the Research Institute of Petroleum Industry (RIPI), Iran, and had a purity of >95%. The stock solution of Cr (VI) was made by dissolving a known amount of $K_2Cr_2O_7$ (analytical grade) in a known volume of double distilled water. Solutions of 0.1 M H_2SO_4 and 0.1 M NaOH were used for pH adjustment.

Table 1. Adsorption isotherm models

Equation type	Model	Model equation	Model parameters	Description and assumptions
Two parametric	Langmuir	$\dfrac{c_e}{q_e} = \dfrac{1}{K_L q_{m1}} + \dfrac{c_e}{q_{m1}}$	K_L, q_{m1}	Valid for monolayer adsorption onto a surface containing a finite number of identical sites (Freundlich, 1906).
	Freundlich	$\ln q_e = \ln K_f + \dfrac{1}{n} \ln c_e$	K_f, n	An empirical equation describing sorption onto heterogeneous surface.
				Assumes that the surface sites of the adsorbent have a spectrum of different binding energies (Zeldowitsch, 1934).
	Temkin	$q_e = B_1 \ln K_T + B_1 \ln c_e$	B_1, K_T	Assumes that the fall in the heat of sorption is linear rather than logarithmic (Aharoni and Sparks, 1991).
Three parametric	Sips	$q_e = \dfrac{q_{m2} A c_e^c}{1 + A c_e^c}$	A, c, q_{m2}	Assumes that the rates of adsorption and desorption are proportional to $(1-\theta)^2$ and θ^2, respectively, where θ is the fractional surface coverage (Sips, 1948).
	BET	$q_e = \dfrac{q_{m3} k c_1 c_e}{(1 - k c_e)(1 + k(c_1 - 1) c_e)}$	k, c_1, q_{m3}	Adsorption occurs on one or more layer and in each layer obeys Langmuir model (Brunauer and Emmat 1938).

Experimental procedure

Adsorption experiments were conducted in 250 ml Erlenmeyer flasks containing known Cr(VI) synthetic solutions. Known quantities of the adsorbents were added to the solutions. The carbon nanotubes were dispersed perfectly in the solution using an ultrasonic bath. The removal percentage was measured at three temperatures (17, 27 and 37 °C) as the contents of the flasks were shaken at 190 rpm until equilibrium state is achieved. The suspension was filtered through a 0.2 μm Biofil syringe filter and the filtrate was analyzed to evaluate the concentration of Cr(VI) metal in the solution. Metal analysis was carried out by using a Cary 50 model UV-visible spectrophotometer. Some Cr(VI) samples were also analyzed using an atomic adsorption spectrometer (SpectraAA 220 model) in order to be sure about the amounts shown by UV-visible spectrophotometer and to find out if any hexavalent chromium reduced to trivalent form.

The solution pH, CNT dosage and initial concentration of Cr(VI) in the experiments were varied from 1 to 10, 0.02 to 0.15 g/l and 20 to 80 mg/l, respectively, to study the effect of these parameters on the removal percent.

The adsorption isotherm experiments were conducted at constant temperature of 17, 27 and 37 °C for the adsorbent dosage varying from 0.02 to 0.1 g. The contact time effect on Cr (VI) removal and the kinetics study were also done at 17, 27 and 37 °C. The samples were taken and analyzed at regular intervals.

To evaluate the reversibility of Cr(VI) adsorption and adsorbent regeneration, 100 mg of adsorbent were added into 100 ml of Cr(VI) solution with initial concentration of 40 (mg/l). As the adsorption reached equilibrium, the amount of Cr(VI) adsorbed onto adsorbent (q) was measured and then the solution was filtered using a 0.22 μm S&S membrane filter to recover the adsorbent. The adsorbents were added into 100 ml of water, NaOH and HNO$_3$ solutions in order to determine the effect of pH of regeneration solution on desorption process. The regeneration solution strength, contact time and temperature were verified from 0.03 to 0.5 M, 4 to 192 h and 15 to 35 °C, respectively, to study the effect of these parameters on the recovery and regeneration amount. The sorption/desorption process was repeated for 10 cycles.

RESULTS AND DISCUSSION

Adsorbent characterization

Figure 1 shows two different resolutions of the TEM image of the MWCNTs with ca. 10 nm *i.d.* and 20nm *o.d.*, and hundreds of nm long. As the image shows the nanotubes are curved. X-ray diffraction (XRD) is a technique that yields the atomic structure of materials. Figure 2 shows the XRD pattern of the MWCNTs sample and revealed the presence of two peaks at 25.8 and 42.8° corresponding to the interlayer spacing of the nanotube and (002) and (100) reflection of carbon atoms [39]. Using BET surface area measurements, the specific surface area of MWCNTs was found to be 102.5 m^2 g^{-1}.

Evaluation of UV-visible spectrophotometer performance

In order to assess the accuracy of UV-visible spectrophotometer output, some chromium solutions were analyzed using atomic adsorption spectrometer. Results of both analyses are represented in Figure 3. According to this figure, the concentration of Cr(VI) measured by UV-visible spectrophotometer was the same as the amount declared by atomic adsorption
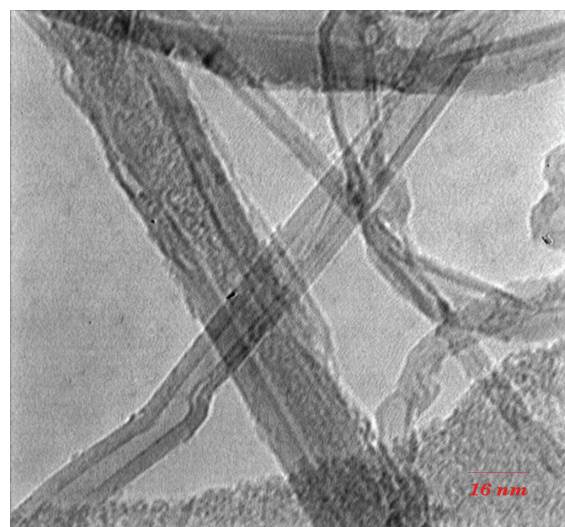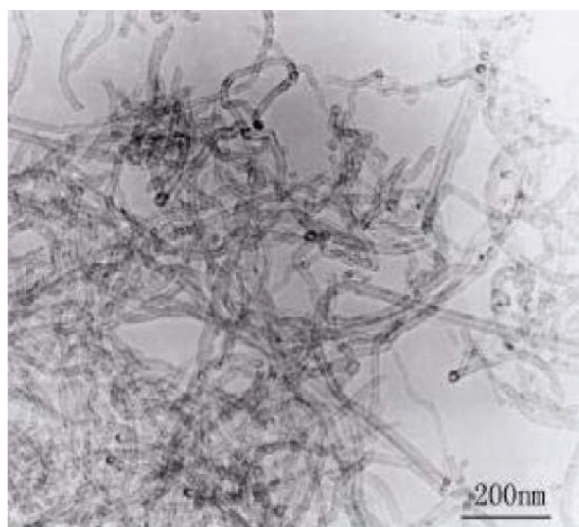

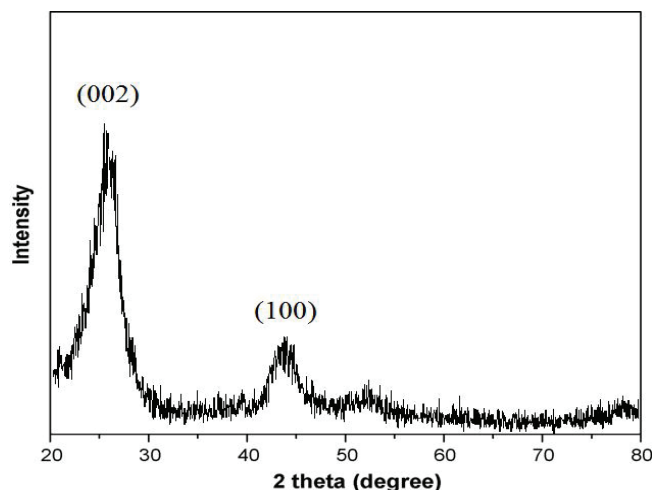Figure 1. TEM Images of MWCNTs (with two different resolutions, 200 and 16 nm).

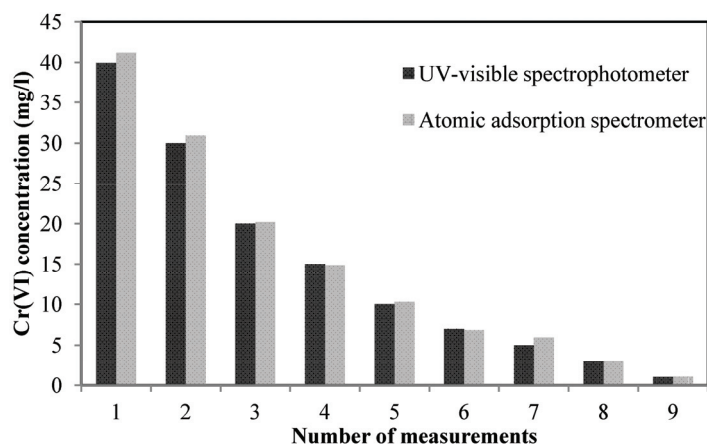Figure 2. XRD Pattern of MWCNTs.

Figure 3. Comparison of the Cr(VI) measurement by UV-visible spectrophotemeter and atomic adsorption spectrometer.

spectrometer especially at low concentrations. This accordance shows that all the chromium available in the solution is in hexavalent form and UV-visible spectrophotometer is an accurate instrument for hexavalent chromium analysis.

Effect of adsorbent dosage

The effect of MWCNTs dosage on the removal of Cr(VI) is shown in Figure 4, where it can be seen that initially the percentage removal increases very sharply with the increase in adsorbent dosage which could be due to the availability of more sorption sites. The increase in adsorbent dosage from 0.02 to 0.1 g resulted in an increase from 40 to 95% in removal of Cr(VI) ions. Beyond a certain value (0.1 g), the percentage removal reaches almost a constant value (about 95%). This value is used as the optimum value of MWCNTs for further experiments.

Effect of initial Cr(VI) concentration

The initial concentration of Cr(VI) provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases. Figure 5 shows that when the initial Cr(VI) ion concentration increased from 20 to 80 mg/L, Cr(VI) removal decreased from 95 to 40% and the uptake capacity of MWCNTs increased. The decreasing in removal percent was due to the saturation of the sorption sites on adsorbents. In addition, the increase in uptake capacity of MWCNTs with the increase of Cr(VI) ion concentration is due to higher availability of Cr(VI) ions in the solution, for the adsorption.

Effect of initial pH

The pH value of the solution is another important factor that controls the sorption of Cr(VI). Figure 6 shows the extent of removal of Cr(VI) as a function of pH, and it shows that at lower pH, the Cr(VI) removal efficiency was higher and at higher pH the removal reduced considerably. The best removal efficiency was achieved at pH 1-2.
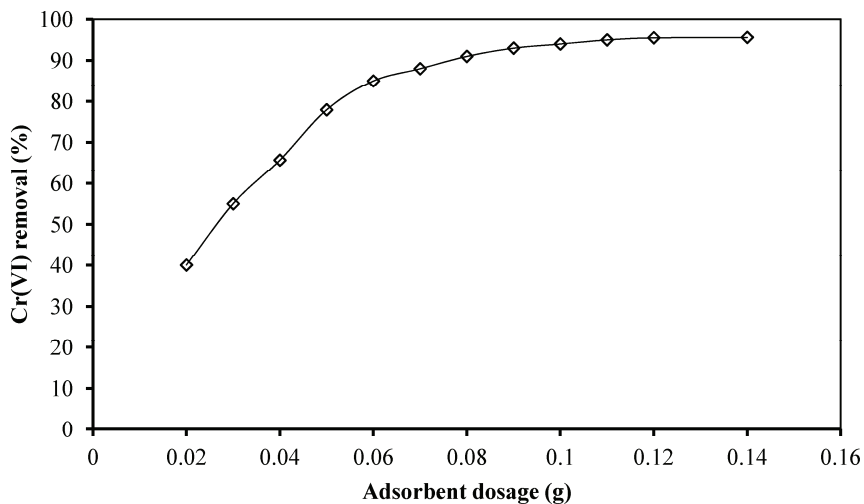
Figure 4. Effect of adsorbent dosage on Cr(VI) removal (at 27 °C, pH 2, c_0 = 20 mg/l and 96 h).
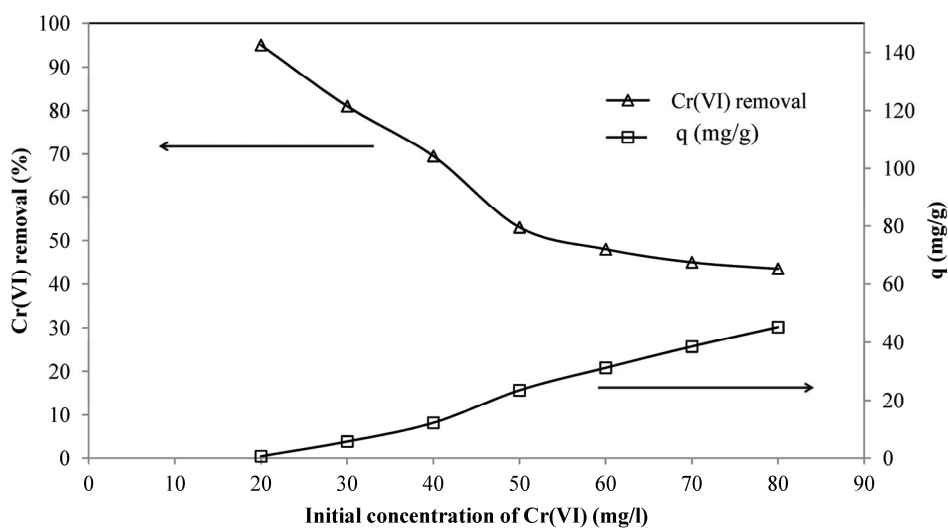

Figure 5. Effect of initial Cr(VI) concentration on Cr(VI) removal and adsorption capacity (q) (at 27 °C, pH 2, X = 0.1 g and 96 h).
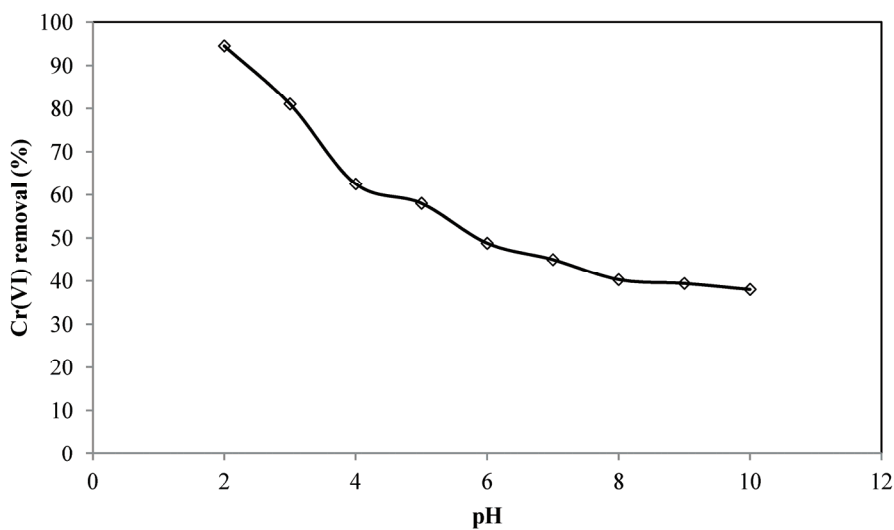

Figure 6. Effect of initial pH on Cr(VI) removal (at 27 °C, c_0 = 20 mg/l, X = 0.1 g and 96 h).

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This can be explained by two reasons. First, The Cr(VI) exists in different forms such as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} in aqueous solution and the stability of these forms is dependent on the pH of the system. The active form of Cr(VI) adsorbed on the adsorbent is $HCrO_4^-$. This form is stable only at a lower pH range, which leads to high removal of chromium. But the concentration of this form decreases when there is an increase in pH. Hence, chromium removal at higher pH decreases. Secondly, at lower pH range, the adsorbent is exposed to acidic environment. Acidic environment begets some modifications on adsorbent surface by oxidizing some useless parts. Chen and Wang reported that functional groups such as -OH, -COOH and -COO⁻ present on the surfaces of oxidized MWCNTs treated with nitric acid or sulfuric acid (Figure 7) [29,30].

The Fourier transform infrared spectroscopy (FTIR) of oxidized MWCNTs is shown in Figure 8. The peak at 3326 cm⁻¹ is attributed to the stretching vibration of O-H band. The peak at 1721cm⁻¹ is attributed to the vibration of -COOH band, whereas the peaks at 1600 and 1381 cm⁻¹ are attributed to the asymmetric and symmetric -COO⁻ stretching [11]. These groups participate in Cr(VI) adsorption to MWCNTs and improve its capacity by activation adsorbent surface especially some disordered, disjointed or malformed parts of the surface that can not get involved in adsorption process.
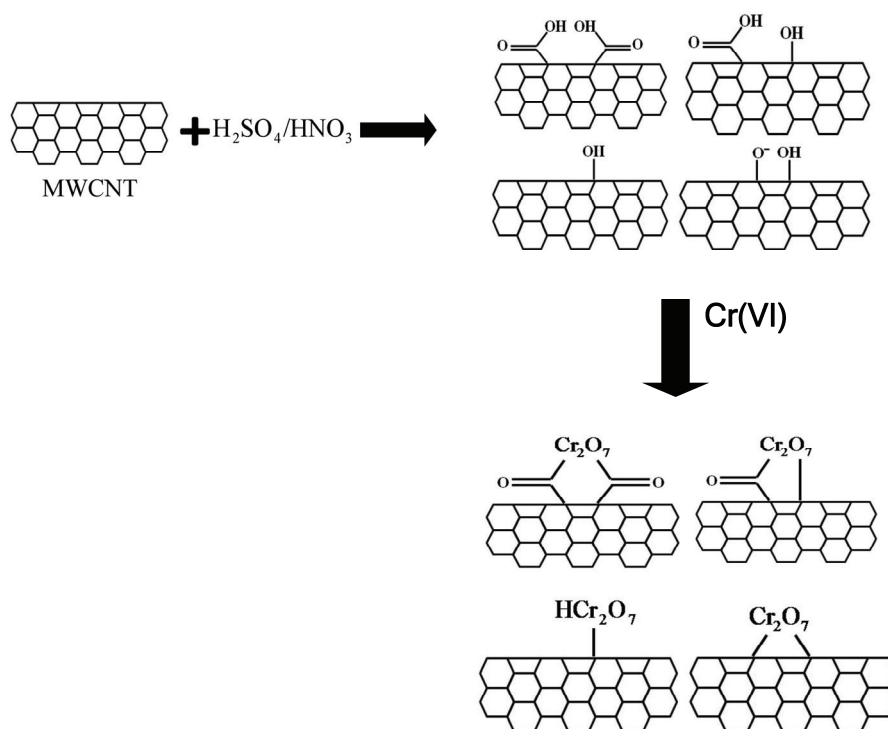
Effect of contact time and temperature

Figure 9 shows the effect of contact time and temperature on the adsorption of Cr(VI) at 17, 27 and 37 °C by MWCNTs. Temperature has two main effects on the adsorption process. An increase in temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and within the adsorbent. It could be the result of decreasing solution viscosity. Furthermore, changing the temperature will modify the equilibrium capacity of the adsorbent for a particular adsorbate.

For the contact time, removal efficiency increased with an increasing in contact time before equilibrium is reached and after equilibrium removal efficiency would be constant. The results show that the amount of Cr(VI) adsorbed increased with increase in contact time and temperature.

Kinetics of adsorption

The kinetics of adsorption describe the rate and the mechanism of hexavalent chromium adsorption on MWCNTs, which controls the equilibrium time. In order to find the best kinetics model correlate the adsorption process, three kinetics models (Eqs. (1)-(3)) are used with regression of the experimental data. The calculated parameters (rate constants) of the models and determination regression coefficients (R^2) are reported in Table 2. As seen in Table 2, a relatively high R^2 value calculated from the pseudo-second

Figure 7. Schematic diagram of the major mechanism for the adsorption of Cr(VI) on oxidized MWCNTs surfaces.

order kinetics model, indicates that this model successfully describes the kinetics of Cr(VI) adsorption. Figure 10 shows this comparison.

The activation energy of the adsorption process is a criterion of the rate functionality with temperature and it can be calculated using the rate constant amounts at different temperatures. The activation energy was obtained using the Arrhenius Equation [40]:

$$k_2 = k_0 \exp(-E/RT) \tag{9}$$

where k_2 is the pseudo-second order adsorption rate constant (g/(mg h)), k_0 is the temperature-independent factor (g/(mg h)), E is the sorption activation energy (kJ/mol), R is the universal gas constant

(8.314 J/mol K) and T is the solution temperature (K). The Arrhenius plot of rate constant with temperature using data reported in Table 1 was shown in Figure 11. The activation energy and pre-exponential factor were determined to be 50.07 kJ/mol and 403.4 g/(mg h), respectively.

Adsorption isotherms

The equilibrium studies were conducted at fixed initial concentration of Cr(VI) solutions by varying MWCNTs dosage. The equilibrium data obtained were analyzed in the light of five isotherm models and the results are shown in Table 3 and Figure 12. These results show that the Langmuir model, between two
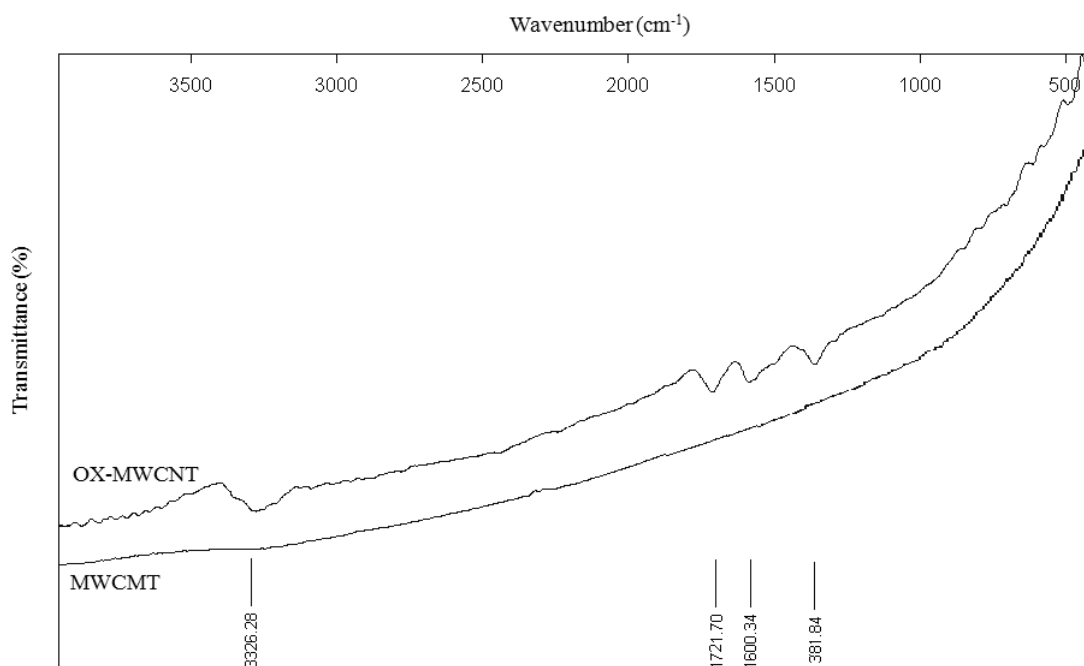

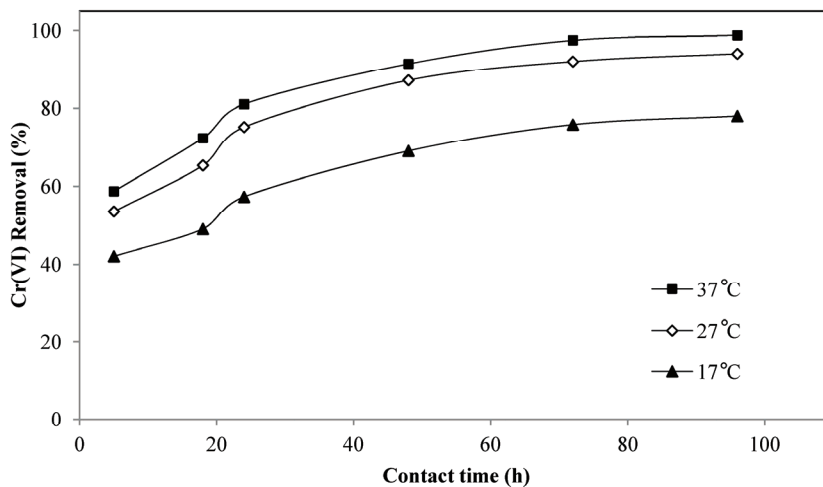Figure 8. FTIR Analysis of raw and oxidized MWCNTs surfaces.

Figure 9. Effect of contact time and temperature on Cr(VI) removal (at c_0 = 20 mg/l and X = 0.1 g).
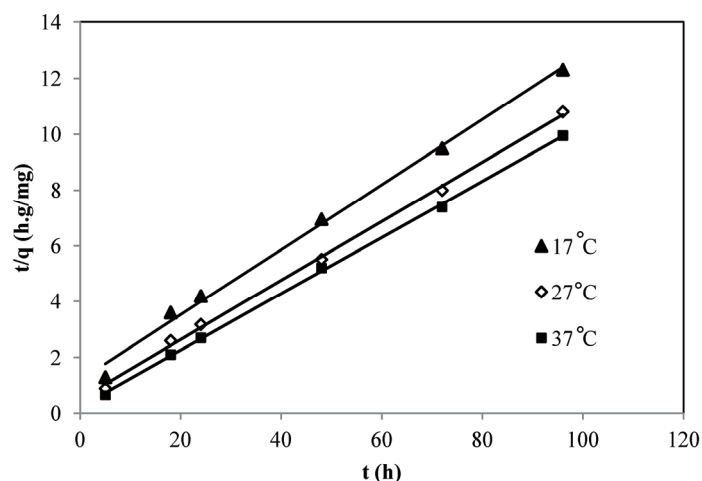
Figure 10. Determination of the rate constant of pseudo-second order adsorption k_2.

Table 2. The adsorption kinetics models rate constants at three different temperatures

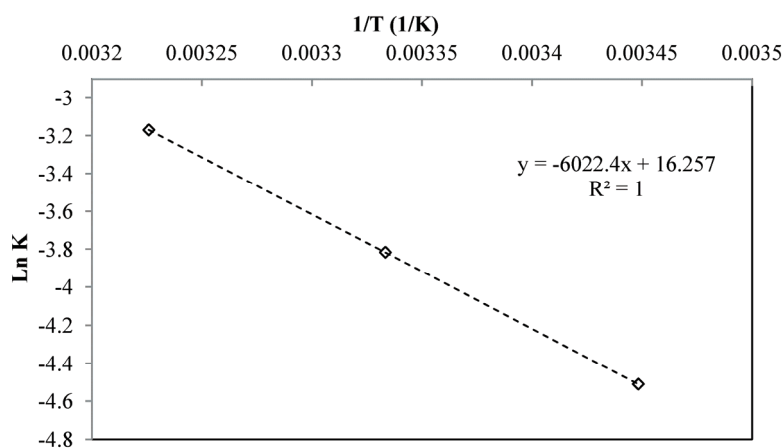| Model	Parameter	Temperature, K		
		290	300	310
Pseudo first order	R^2	0.926	0.952	0.874
	k_1 / h^{-1}	0.0161	0.0173	0.018
Pseudo Second order	R^2	0.995	0.998	0.999
	k_2 / g mg^{-1} h^{-1}	0.011	0.022	0.042
Elovich	R^2	0.976	0.967	0.982
	α / mg g^{-1} h^{-1}	3.58	21.88	8862.3
	β / g mg^{-1}	0.704	0.806	1.434

$$y = -6022.4x + 16.257$$
$$R^2 = 1$$

Figure 11. Determination of the adsorption activation energy, E.

parametric models, and BET model, between three parametric models, have a better fitting than other models and a comparison between determination regressions coefficients (R^2) of Langmuir and BET models shows that the BET model has higher determination regression coefficient and fitting than the Langmuir model. The BET constants were determined using error function assessment and were reported in Table 3. According to equilibrium studies, hexavalent chromium adsorption on MWCNTs can occur in both monolayer and multilayer postures and in each layer obeys the Langmuir model.

Thermodynamic studies

The thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) obtained for the adsorption process were calculated using the following equations:

Table 3. Constant parameters and determination coefficients calculated for different adsorption models

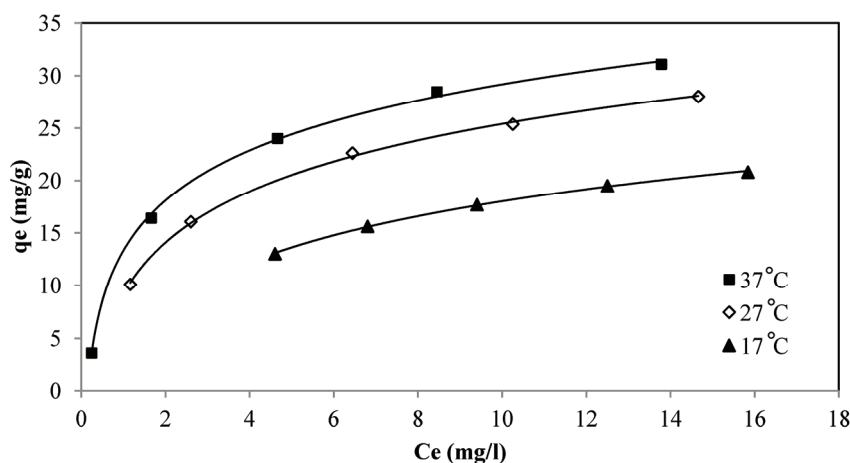| Model	Parameter	Temperature, K		
		290	300	310
Langmuir	q_{m1} / mg g^{-1}	23.6	27.8	31.95
	K_L / l mg^{-1}	0.4	1.2	1.7
	R^2	0.985	0.995	0.995
Freundlich	n	4.95	7.92	9.23
	K_F / mg g^{-1}	11.6	18.65	22.44
	R^2	0.889	0.951	0.955
Temkin	B_1 / mg g^{-1}	3.46	2.75	2.7
	K_T / l mg^{-1}	20.57	864.6	4210.5
	R^2	0.863	0.931	0.931
Sips	Error function	ARE	SAE	SAE
	SNE	2.98	2.96	2.06
	q_{m2} / mg g^{-1}	29	30.1	31.6
	A / l mg^{-1}	0.6	1.6	3.3
	c	0.42	0.42	0.6
	R^2	0.982	0.980	0.986
BET	Error function	HYBRID	HYBRID	SAE
	SNE	1.32	1.11	1.713
	q_{m3} / mg g^{-1}	14.87	21.74	34.9
	k / l mg^{-1}	0.018	0.013	0.018
	c_1	210	425	150.3
	R^2	0.999	0.999	0.999

Figure 12. BET isotherm for adsorption of Cr(VI) on MWCNTs (at pH 2, c_0 = 20 mg/l and 96 h).

$$K_c = \frac{q_e}{c_e} \tag{10}$$

$$\Delta G^o = -RT \ln K_c \tag{11}$$

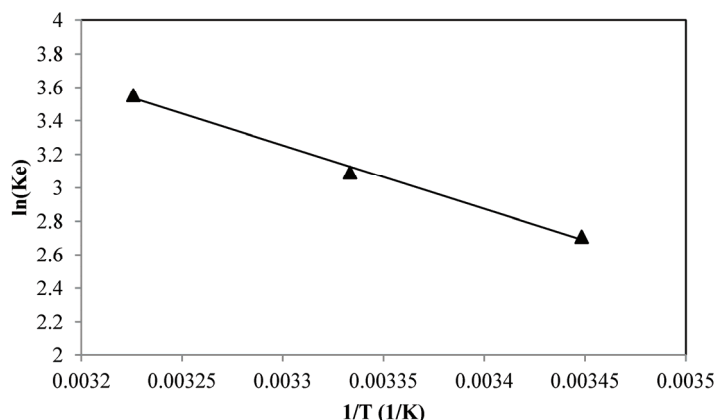$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{12}$$

where K_c is the equilibrium constant, q_e is the Cr(VI) uptake at equilibrium (mg/g) and c_e is Cr(VI) concentration at equilibrium (mg/l). Table 4 shows the calculated values of the thermodynamic parameters for the adsorption of Cr(VI) on MWCNTs. ΔH^o and ΔS^o

were obtained from the slope and intercept of linear plots of ln K_c versus $1/T$ (Figure 13) and the standard Gibbs free energy ΔG^o values (kJ/mol) were calculated from Eq. (11).

The positive value of enthalpy change ΔH^o for the process confirms the endothermic nature of the process, the positive entropy of adsorption ΔS^o reflects the affinity of the adsorbent material toward Cr(VI) and the negative free energy values ΔG^o indicate the feasibility of the process and its spontaneous nature. The amount of ΔG^o (<10 kcal) suggest that the adsorption is physical, and the increase in ΔG^o with

Table 4. Thermodynamic parameters for the adsorption of Cr(VI) on MWCNTs

Temperature, K	ΔG° / kJ mol^{-1}	ΔH° / kJ mol^{-1}	ΔS° / kJ mol^{-1}
290	-4.712	31.5	0.131
300	-7.68		
310	-9.155		

Figure 13. Graphical determination of ΔH° and ΔS°.

increasing temperature shows that the adsorption is more favorable at high temperature [36].

Desorption results

Desorption experiments were performed to evaluate repeated availability performance of MWCNTs in hexavalent chromium removal. In order to represent these experimental results, "Cr(VI) recovery percentage" is defined as the percentage ratio of the q_e of the regenerated adsorbent to that of the saturated adsorbent. All the results are plotted and expounded further.
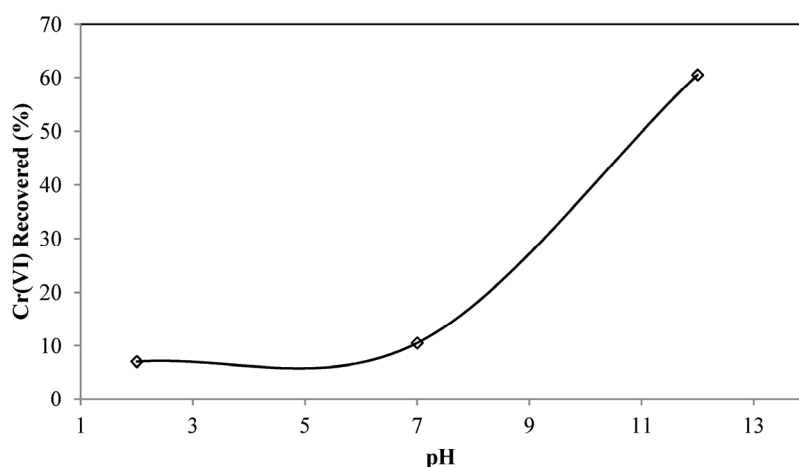
Effect of regeneration solution pH on desorption

In order to find out the effect of regeneration solution pH on desorption process, HNO$_3$ and NaOH

solutions were used as acidic and alkaline environments, respectively, and water was used as neutral environment. Figure 14 shows the recovery percentage of Cr(VI) at these three different pH. According to Figure 14, at higher pH, the recovery of Cr(VI) and regeneration of MWCNTs was higher. OH$^-$ is the main compound lead Cr(VI) being recovered from adsorbent surface. At low and neutral pH, the concentration of OH$^-$ is lower than alkaline solutions, so the Cr(VI) recovery percentage is lower. Therefore, NaOH solution was selected as the regeneration solution for desorption tests.

Effect of regeneration solution strength on desorption

The effect of the strength of regeneration solution (NaOH) on the recovery of Cr(VI) and regene-

Figure 14. Effect of solution pH in desorption of Cr(VI) on MWCNTs (at 27 °C, c_0 = 40 mg/l, X = 0.1 g and 96 h).

ration of MWCNTs is shown in Figure 15. When the strength of regeneration solution increased from 0.03 to 0.2 M, the recovery percentage of Cr(VI) increased rapidly from 19.7 to 61%, due to the higher OH⁻ concentration at higher NaOH solution concentration. After that, from 0.2 to 0.5 M, the recovery percentage was almost constant thus 0.2 M was considered as optimum NaOH concentration for the desorption process.

Effect of contact time on desorption

Figure 16 shows the effect of contact time on recovery percentage of Cr(VI). The results show that desorption efficiency increased with an increasing in contact time before equilibrium is reached and after equilibrium Cr(VI) recovered percentage would be constant. Furthermore, it can be seen that most of the Cr(VI) ions are separated from the adsorbent surface in the first 48 h.

Effect of temperature on desorption

The effect of temperature on the recovery percentage of Cr(VI) is shown in Figure 17. It is obvious from this figure that increasing temperature brings about an increase in recovery of Cr(VI) and regeneration of MWCNTs. Increasing temperature results in the increase of particle movements and this phenolmenon facilitates the detachment of Cr(VI) from the MWCNTs surface. Also, this increase indicates that the desorption process is endothermic.

Number of acceptable successive adsorption/desorption processes

The recovery percentage of Cr(VI) and MWCNTs regeneration under 10 cycles of successive adsorption and desorption processes (i) is presented in Figure 18. This figure shows that as i increased, the recovery percentage Cr(VI) and adsorbent regeneration and also Cr(VI) removal slightly decreased. Thus, it was realized that MWCNTs could be reused for 10
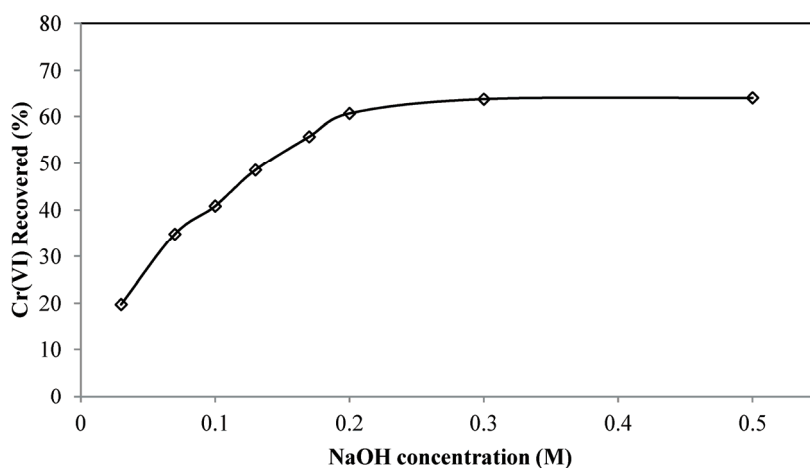

Figure 15. Effect of regeneration solution strength on desorption (at 27 °C, c_0= 40 mg/l, X = 0.1 g and 96 h).

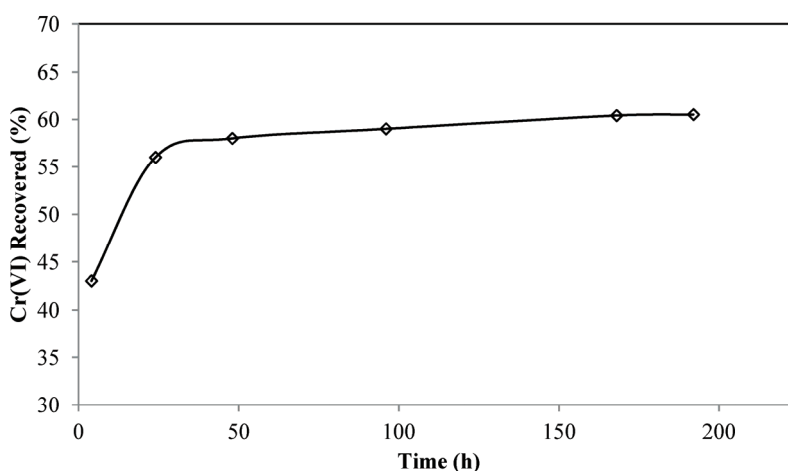Figure 16. Effect of contact time on desorption (at 27 °C, c_0 = 40 mg/l, X = 0.1 g and C_{NaOH} = 0.2 M).
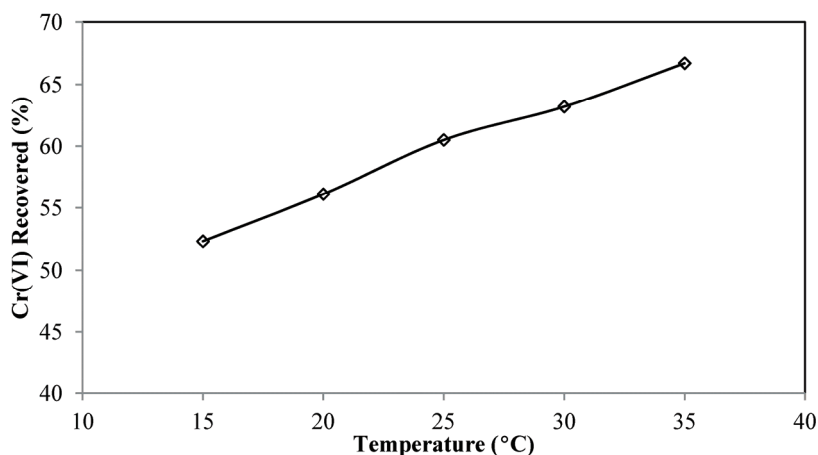
Figure 17. Effect of temperature on desorption (at c_0 = 40 mg/l, X = 0.1 g, C_{NaOH} = 0.2 M and 96 h).
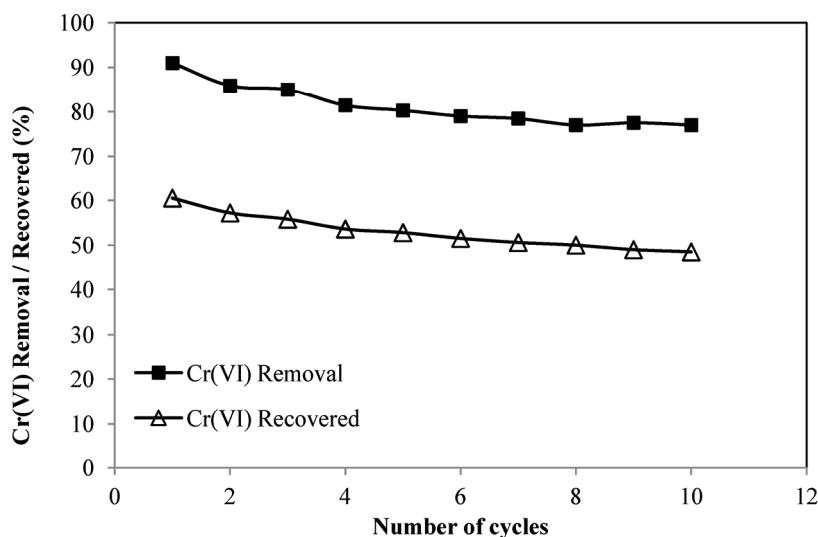

Figure 18. Number of acceptable successive adsorption/desorption processes.

successive adsorption/desorption processes because it had not lost their adsorption/desorption abilities and had preserved their performance.

CONCLUSIONS

In this work hexavalent chromium removal using multi-walled carbon nanotubes was investigated. The following major conclusions can be drawn based on this study:

• The key factors that favor the adsorption of Cr(VI) onto MWCNTs are increasing contact time, high temperature, low pH and low initial concentrations of Cr(VI).

• The kinetic studies showed that pseudo-second order rate equation was able to provide a realistic description of adsorption kinetics of Cr(VI).

• The experimental results have been analyzed by two and three parametric adsorption isotherms. The results showed that the BET model was a better fitting model than others, which means that hexavalent chromium adsorption on MWCNTs can occur in both monolayer and multilayer postures.

• The thermodynamic parameters ΔH^o, ΔS^o and ΔG^o values of Cr(VI) adsorption onto MWCNTs showed that the adsorption process is spontaneous, physical and endothermic.

• Desorption experiments showed that the recovery percentage of Cr(VI) and MWCNTs regeneration strongly depends on regeneration solution pH, regeneration solution strength, contact time and temperature. The maximum desorption capacity was obtained by 0.2 M NaOH used as regeneration solution and increasing temperature and contact time increases the Cr(VI) removal.

• Results of Cr(VI) recycling and adsorbent regeneration showed that after 10 cycles of successive adsorption/desorption process MWCNTs could be re-

generated and reused well without any high decreasing in its performance.

Nomenclature

α Elovich isotherm parameter (mg/g.h);
β Elovich isotherm parameter (g/mg);
A Sips isotherm parameter (l/mg);
B_1 Temkin isotherm parameter (mg/g);
c Sips isotherm parameter;
c_0 Initial Cr(VI) concentration (mg/l);
c_1 BET isotherm parameter;
c_e Cr(VI) concentration at equilibrium (mg/l);
c_t Cr(VI) concentration and at a given time t (mg/l);
E Activation energy (kJ/mol);
i Number of acceptable successive adsorption/desorption processes;
k BET isotherm parameter (l/mg);
K_0 Temperature-independent factor (g/mg h);
K_1 Pseudo-first order adsorption rate constant (1/h);
k_2 Pseudo-second order rate constant (g/mg h);
K_c Equilibrium constant;
K_f Freundlich isotherm parameter (mg/g);
K_L Langmuir isotherm parameter (l/mg);
K_T Temkin isotherm parameter (l/mg);
m_s Weight of Adsorbent (g);
n Freundlich isotherm parameter;
p Number of variations (data);
q Cr(VI) uptake at any time (mg/g);
q_{cal} Calculated q (mg/g);
q_e Cr(VI) uptake at equilibrium (mg/g);
q_{exp} Experimental q (mg/g);
q_{m1} Langmuir isotherm parameter (mg/g);
q_{m2} Sips isotherm parameter (mg/g);
q_{m3} BET isotherm parameter;
R Universal gas constant (J/mol K);
$R\%$ The removal percentage of Cr(VI) ions;
R^2 Statistical linear coefficient of determination (the square of the correlation coefficient, R);
T Temperature (K);
t Time (h);
V Volume of the Cr(VI) solutions (l);
x Number of parameters of isotherm model.

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NAUČNI RAD

PROCENJIVANJE PERFORMANSI VIŠESLOJNIH UGLJENIČNIH NANOCEVI U ADSORPCIJI I DESORPCIJI ŠESTOVALENTNOG HROMA

U ovom radu je istraživano izdvajanje šestovalentnog hroma iz vodenih rastvora pomoću višeslojnih ugljeničnih nanocevi (VUNC) kao funkcija količine adsorbenta, početne koncentracije Cr(VI), početnog pH, kontaktnog vremena i temperature. Mali pH, mala početna koncentracija Cr(VI), povećano kontaktno vreme i visoka temperatura su optimalni uslovi. Izvršeno je poređenje pseudo-prvog, pseudo-drugog i Elovich-evog kinetičkog modela adsorpcije Cr(VI) jona na VUNC. Utvrđeno je da model pseudo-drugog reda dobro koreliše eksperimentalne podatke. Ravnoteže izoterme su određene eksperimentalno, a rezultati pokazuju da BET model dobro fituje podatke. Izračunati su termodinamički parametri, a rezultati ukazuju na to da je proces adsorpcije spontan, fizički i endoterman. Ispitivani su, takođe, reverzibilnost adsorpcije Cr(VI) jona na VUNC i uticaj operativnih fakotra, kao što su karakteristike rastvora za regeneraciju, kontaktno vreme i temperature, na ovaj proces. Rezultati pokazuju da su VUNC efektivni adsorbenti Cr(VI) jona i da mogu biti ponovno korišćene višestrukom regeneracijom bez smanjenja njhovih performansi.

Ključne reči: šestovalentni hrom, adsorpcione izoterme, kinetika adsorpcije, termodinamički parametri, desorpcija.