Optimization and Modeling of Hexavalent Chromium Removal From Aqueous Solution Via Adsorption on Multiwalled Carbon Nanotubes

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Abstract: Hexavalent chromium and its derivatives are potential pollutant due to their mortal affects. Therefore, it is essential to remove these components from wastewaters before disposal. Adsorption can be effective and versatile method for removing of hexavalent chromium. In this article, removal of hexavalent chromium via adsorption on multiwalled carbon nanotubes was investigated as a function of adsorbent dosage, initial solution pH, initial Cr(VI) concentrations, contact time and temperature. The batch experiments were conducted at 3 different temperatures (17, 27 and 37ºC) and shows that Cr(VI) removal obeys pseudo-second order rate equation. Rate constant (K) values in 3 temperatures, pre-exponential factor and adsorption activation energy (E) was also obtained. The sorption data fitted well with Freundlich isotherm adsorption model. Thermodynamic parameters such as Gibbs free energy (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) for Cr(VI) adsorption were estimated and Results suggest that the adsorption process is a spontaneous and endothermic.

Key words: Adsorption, adsorption isotherm, adsorption kinetics, hexavalent chromium, multiwalled carbon nanotubes, thermodynamic parameters

INTRODUCTION

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain and hence in the human body. 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 (Kowalski, 1994). Chromium is an element of 6th group in the latest IUPAC Periodic Table, exists in both hexavalent and trivalent forms. Hexavalent form is more toxic than trivalent and requires more concern (Mohanty et al., 2005). Strong exposure of Cr(VI) causes cancer in the digestive tract and lungs (Kaufaman et al., 1970) and may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage (Browning, 1969). Cr(VI) concentrations in industrial wastewater range from 0.5 to 270.000 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 (Koby, 2004). 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 (Aksu et al., 2002; Baran et al., 2007). 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 (Yavuz et al., 2006).

Several adsorbents which have been studied for adsorption of metal ions such as activated carbon (Sekar et al., 2004; Rao et al., 2006), fly ash (Ayala et al., 1998; Weng et al., 2004), peat (Ho and Mc-Kay, 1999), sewage sludge ash (Pan et al., 2003), zeolite (Biskup and Subotic, 2004), biomaterials (Li et al., 2004; Ekmekyapar et al., 2006), recycled alum sludge (Chu, 1999), manganese oxides (Sublet et al., 2003), peanut hulls (Brown et al., 2000), kaolinite (Arias et al., 2002) and resins (Diniz et al., 2005). 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 (1991). Studies on this new
material has shown high adsorption capacity and removal efficiency of various pollutants (Dai, 2002). 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 (Li et al., 2002). Recently multi-walled carbon nanotubes (MWCNTs) have also been used as adsorbents for the removal of Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ (Li et al., 2003; Lu, 2006). Di et al. (2006) have also shown that ceria nanoparticles supported on aligned carbon nanotubes are effective in the removal of Cr(VI) (Di et al., 2006).

The present investigation deals with the application of multiwalled carbon nanotube in the removal of Chromium (VI) from aqueous solutions. The removal amount of Cr(VI) was determined on the basis of different effective parameters such as: adsorbent dosage, initial Cr(VI) concentration, solution pH, contact time and temperature. Adsorption kinetic, equilibrium isotherm and thermodynamic parameters of the process were also investigated.

**METHODOLOGY**

MWCNTs, obtained by chemical vapor deposition method, were purchased from 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 K₂Cr₂O₇ (analytical grade) in a known volume of double distilled water. Solutions of 0.1M H₂SO₄ and 0.1M NaOH were used for pH adjustment.

**Batch adsorption experiments:** 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 is measured at three temperature (17, 27 and 37ºC) as the flasks content is 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.

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 main parameter on the removal percent.

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

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 follow equation:

\[
q = \frac{(C_0 - C_t)V}{m_s}
\]

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 Eq. (2):

\[
R\% = \frac{C_0 - C_t}{C_o} \times 100
\]

All the experiments were conducted at Instrumental Analysis Laboratory of International Center for Science, High Technology and Environmental science during the Autumn of 2010.

**Modeling:**

**Modeling of adsorption kinetic:** The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetics models are used to explain the mechanism of the adsorption processes. A simple pseudo-first order equation is given by Lagergren equation:

\[
\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t
\]

where, \(q_e\) is the Cr(VI) uptake at equilibrium (mg/g), \(q\) is the uptake at any time (t) and \(k_1\) is first order adsorption rate constant. On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as:

\[
\frac{t}{q} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} t
\]

where, \(k_2\) is the pseudo-second order rate constant (g/mg.min) (Di et al., 2006). The linear regression correlation coefficient value shows that which model can justify the experimental data.

**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, of which the Langmuir and
Freundlich equations are most widely used. According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site. Thus, the Langmuir model is given by the following equation:

\[
\frac{C}{q} = \frac{1}{bQ_0} + \frac{C}{Q_0}
\]

(5)

where, \(Q_0\) and \(b\) are the Langmuir model parameters. \(C\) is the equilibrium solution concentration (mg/L), \(q\) is the Cr(VI) uptake at the equilibrium (mg/g) (Sharma and Bhattacharyya, 2004).

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and is given by the following equation (Oguz, 2005):

\[
\log q = \log k + \left(\frac{1}{n}\right) \log C
\]

(6)

where, \(q\) is the Cr(VI) uptake (mg/g), \(C\) is the equilibrium concentration of the Cr(VI) solution (mg/L) and \(k\) and \(n\) are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively.

RESULTS AND DISCUSSION

**Adsorbent characterization:** Figure 1 shows the TEM image of the MWCNTs with ca. 10 nm i.d. and 30 nm o.d., and hundreds of nm long. As the image shows the nanotubes are curved. Figure 2 shows the XRD pattern of the MWCNTs structure. The most intense peaks of MWCNTs correspond to the (002) and (100) reflections. Using BET surface area measurements, the specific surface area of MWCNT was 102.5 m²/g.

**Effect of adsorbent dosage:** The amount of CNT dosage used in the removal of Cr(VI) is critical for the application of the adsorbent in Cr(VI) elimination. Effect of this parameter on the removal percent is investigated experimentally and the results presented in Fig. 3. The results are shown that Cr(VI) removal increases rapidly with increase in the dose of MWCNTs due to the greater availability of the adsorbent (Fig. 2). The increase in adsorbent dosage resulted in an increase from 40 to 97% in adsorption of Cr(VI) ions.

**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 4 shows that when the initial Cr(VI) ion concentration increased from 20 to 80 mg/L, Cr(VI) removal decreased from 100 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 5 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. With decreasing in pH the amount of Cr(VI) removal increased. Which the best removal efficiency achieved optimum pH 1-2.

The reason for the high removal percent of chromium at lower pH range was explained below. The Cr(VI) exists in different forms such as HCrO$_4^-$, Cr$_2$O$_7^{2-}$, 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 at only 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 (Aksu, 2001; Hamadi et al., 2001).

**Effect of contact time and temperature:** Figure 6 Shows the effect of contact time and temperature on the adsorption of Cr(VI) at 17, 27 and 37ºC by MWCNTs. Temperature has two main effects on the adsorption process. An increasing 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. Results shows that the amount of Cr(VI) adsorbed increased with increase in contact time and temperature.

**Kinetic of adsorption:** In order to find the best model correlate the adsorption process, the kinetic models (Eq. 3 and 4) are used with regression of the experimental data. Results are presented in Fig. 7 and 8. The calculated parameter of the models (rate constant) and correlation coefficient (R$^2$) are reported in Table 1. As seen in Table 1, the value of R$^2$ calculated from pseudo-second order kinetic is near 1 and higher than pseudo-first order kinetic model. These results indicate that the adsorption of Cr(VI) on the MWCNTs follows pseudo-second order kinetics. 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 in different temperature. The activation energy was obtained using Arrhenius equation (Sarin and Pant, 2006):

$$K_2 = K_0 \exp \left( - \frac{E}{RT} \right)$$

(7)
Table 1: The adsorption kinetic model rate constants at different temperatures

<table>
<thead>
<tr>
<th>Model</th>
<th>290 K</th>
<th>300 K</th>
<th>310K</th>
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</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>R²</td>
<td>0.926</td>
<td>0.952</td>
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<tr>
<td></td>
<td>k₁ (1/1 h)</td>
<td>0.0161</td>
<td>0.0173</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>R²</td>
<td>0.995</td>
<td>0.998</td>
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<tr>
<td></td>
<td>k₂ (g/mg.h)</td>
<td>0.011</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 2: Isotherm model constants and correlation coefficients for adsorption of Cr(VI) on MWCNTs

<table>
<thead>
<tr>
<th>Model</th>
<th>290 K</th>
<th>300 K</th>
<th>310 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Q₀ (mg/g)</td>
<td>35.36</td>
<td>41.67</td>
</tr>
<tr>
<td></td>
<td>b (L/mg)</td>
<td>3.76</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.994</td>
<td>0.996</td>
</tr>
<tr>
<td>Freundlich</td>
<td>k</td>
<td>15.6</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>4.6</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Adsorption isotherms: Regression of equilibrium data of the process using both Langmuir and Freundlich models (Eq. 5 and 6) was carried out and shown in Fig. 10 and 11. The regression determination results presented in Table 2, shown that Freundlich isotherm model has a better fitting than Langmuir model. This shows that adsorption occurs on heterogeneous surface.

The Freundlich constants were determined from the slope and intercept of a plot of log Q versus log C and were reported in Table 2. There was a good agreement between experimental and predicted behavior observed from the values of the regression coefficient R² close to 1. Moreover, Kf is large at higher temperatures showing that the adsorption rate also increases with a rise in temperature. The slope “1/n” is less than 1, which is related to a favorable adsorption of chromium ions (McCabe et al., 2001).

Thermodynamic parameters: Thermodynamic parameters of the process such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following:

\[ \Delta G^° = RT \ln K_c \]  

where, Kc is the equilibrium constant, qe is the solid phase concentration at equilibrium (mg/L) and Ce is the equilibrium concentration in solution (mg/L). \( \Delta H^° \) and \( \Delta S^° \) were obtained from the slope and intercept of linear plots of lnKc versus 1/T (Fig. 12) and The standard Gibbs free energy \( \Delta G^° \) values (kJ/mol) were calculated from the Eq. 10. Table 3 shows the calculated values of the thermodynamic parameters for the adsorption of Cr(VI) on MWCNT.

The positive value of enthalpy change \( \Delta H^° \) for the process confirms the endothermic nature of the process, the positive entropy of adsorption \( \Delta S^° \) reflects the affinity of the adsorbent material toward Cr(VI) and the negative free energy values \( \Delta G^° \) indicate the feasibility of the process and its spontaneous nature. The amount of \( \Delta G^° \) (<10 Kcal) suggest that the adsorption is physical an also The increase in \( \Delta G^° \) with increasing temperature shows that the adsorption is more favorable at high temperature (Sharma and Bhattacharyya, 2004).
Table 3: Thermodynamic parameters for the adsorption of Cr(VI) on MWCNTs

<table>
<thead>
<tr>
<th>Temp.(ºK)</th>
<th>ΔGº (KJ/mol)</th>
<th>ΔHº (KJ/mol)</th>
<th>ΔSº (KJ/mol ºK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290 K</td>
<td>-21.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 K</td>
<td>-23.7</td>
<td>52.1</td>
<td>0.257</td>
</tr>
<tr>
<td>310 K</td>
<td>-26.3</td>
<td></td>
<td></td>
</tr>
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</table>

Fig. 11: Freundlich plots for adsorption of Cr(VI) at different temperatures

Fig. 12: Graphical determination of ΔH0 and ΔS0

CONCLUSION

The following major conclusions can be drawn based on the above study:

The removal of Cr(VI) from aqueous solutions strongly depends on the pH of the solution, adsorbent dosage, initial Cr(VI) concentration, temperature and contact time. The maximum adsorption capacity was obtained at pH 2. Increase in the dose of the adsorbent and decrease in the initial concentration of Cr(VI) leads to increase in Cr(VI) adsorption and increase in temperature and contact time increases the Cr(VI) removal.

The adsorption kinetics data were modeled using the pseudo-first order and pseudo-second order kinetics equations. It was shown that the pseudo-second order kinetics described best the sorption kinetics.

The experimental results have been analyzed by Langmuir and Freundlich adsorption isotherms and the results show that the Freundlich isotherms can be fitted well to the equilibrium data. The thermodynamic parameters ΔGº, ΔHº and ΔSº values of Cr(VI) adsorption onto MWCNTs show that the adsorption process is a spontaneous, physical and endothermic.

Thus, the results show that the MWCNTs can be effectively applied for the removal of Cr(VI) from wastewater.

REFERENCES


