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Study on the adsorption isotherms of chromium (VI) by means of carbon nano tubes from aqueous solutions

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Abstract

Background: The presence of heavy metals in the environment especially in water supplies have caused many concerns because of their toxicity and non-degradability. Hexavalent Chromium (Cr) is one of the most toxic metals which is used in many industries, so it is essential to remove it from industrial wastewater. In this study, we made a comparison between different adsorption isotherms in the chromium (VI) removal process using carbon nano tubes from aqueous solutions.

Methods: This experimental study used atomic absorption spectrophotometry. To determine the adsorption isotherms, a synthetic sample with defined concentration of Cr (VI) was prepared and different doses of adsorbent were added to it. The effect of initial Cr concentration, pH, adsorbent dose, and reaction time on removal of Cr was investigated. Temperature and mix rate were steady during a defined time. At the end, Cr (VI) concentration measured and adsorbents equality capacities were calculated via formulas and graphs. Data analysis were performed using descriptive statistics.

Results: Adsorption capacities (q_e) increased with increasing of initial Cr concentration, and reaction time decreased with increasing adsorbent dose and pH. Correlation coefficients for Langmuir, and Freundlich isotherms in oxidized Multi-Walled Carbon Nano Tubes (MWCNTs) were 0.93, 0.874, and 0.714 and in oxidized Single-Walled Carbon Nano Tubes (SWCNTs) were 0.904, 0.868, and 0.711 respectively.

Conclusion: Chromium ions adsorption in carbon nano tubes is accordant to Langmuir isotherm model, and MWCNTs have more cc than SWCNTs. Carbon nano tubes are effective adsorbents in removal of Cr (VI) from aqueous solutions.

Keywords: Adsorption isotherm, Carbon nano tubes, Hexavalent chromium

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Introduction

Waters have been polluted with heavy metals due to rapid growth of industries. Discharging wastewater from various industries like electro plating, leather tanning, glass, acid mine drainage, and ceramic enters hexavalent Chromium (Cr) which is a very toxic and harmful metal in to water supplies (1). Cr does not exist in water naturally (2). There are multiple states of Cr including (III) and (VI) forms as the most common (3,4). Cr (VI) is a toxic metal, whereas Cr (III) is almost non-toxic (5). Researches on human and animals revealed the carcinogenic effects of Cr (VI) (6). United States Environmental Protection Agency (USEPA) listed Cr (VI) as one of the most critical pollutants. Based on World Health Organization (WHO) recommendations, 0.05 ppm of Cr in water was assumed as the maximum permissible level (7). The acceptable amount of Cr based on Institute of Standards and Industrial Research of Iran (ISIRI) directions is 0.05 (8). Cr (VI) in concentrations more than 50 has irreversible effects on kidney and liver, can cause skin and lung cancer, and also can bring allergic problems (9). As Cr (VI) is a rare and expensive metal, its recovery is important (10). There are several methods for chromium removal, such as chemical precipitation, ion exchange resin, reverse osmosis and electro dialysis, although a favorable removal does not occur in any of the (11). Common removal processes, such as chemical precipitation has low performance, and advanced methods are costly and need expert operators (12). Another removal method is adsorption defined as an effective way. It does not need special equipment, ions recovery can be done easily, and adsorbents reuse is possible (13). One of the most effective adsorbents that can be used in this process is active carbon, but its preparation and revival has a high expense (14). In recent years, the use of nano technology especially carbon nano tubes for environmental pollutants removal has been developed (15). Nano filtration is one of the most important applications in nano technology scope. Studies in China showed reduction in cardiovascular diseases and cancer after long-term consumption of water treated by nano filters (16). In this article, we focused on the adsorption isotherms of Cr as one of the secondary purposes in our study on the Cr removal process by use of carbon nano tubes from aqueous solutions. So we do not report our study results about the effect of initial Cr concentration, pH, adsorbent dose and reaction time on removal of chromium by carbon nano tubes here.

Methods

In this experimental study, we used chemical materials, produced by German Merck Company. Oxidized carbon nano tubes were purchased from Research Institute of Petroleum Industry (RIPI). The unknown Cr (VI) concentration measured by atomic absorption T80+ UV/VIS spectrophotometer. To have an adequate mixing, rotomix shaker made by Iranian Behdad Company was applied. Three different concentrations of Cr (0.5, 1, and 2) were prepared and the effect of three different pH (3, 5, and 7) and three different masses of carbon nano tubes (0.4, 0.8, and 1) during the adsorption process were investigated. Because of the low removal percentage in pH=7, tests continued in pH= 3 and 5. To find the effect of contact time, three different times (30, 60, and 120 minutes) were selected. A discontinuous method was used to determine the pollutant adsorption isotherm. First, a synthetic sample with a defined Cr (VI) concentration was prepared. We solved $K_2Cr_2O_7$ in deionized water to prepare Cr (VI) solution. After that, different doses of adsorbent were added to sample. This container mixed for 24 hours in a condition that temperature and mix rate were steady at 20 and 120 rpm, respectively. A vacuum pump and a 0.45 μ filter were used to separate the sample from adsorbent. Then Cr concentration in liquid phase was measured, and adsorbents equality capacities were calculated by use of formulas and graphs.

Langmuir equation:

$Qe = \theta.b.Ce/1+(b.Ce)$

Ce: It shows the concentration in equality conditions (mg/l)

Qe: It introduces the amount of adsorbate on one unit of adsorbent weight in equality conditions (mg/g)

θ & b: These are Langmuir constants related to maximum adsorption and adsorption energy, respectively.

Freundlich equation:

$Qe=K.Ce^{1/n}$

K: It is an index for adsorption capacity

1/n: It demonstrates the adsorption intensity.

Data analysis were performed using descriptive statistics.

Results

Figures 1A and 1B show Langmuir adsorption isotherm for Cr (VI) ion. As seen in the figures, Cr (VI) adsorption by carbon nano tubes is adjusted to Langmuir isotherm. With respect to other figures, Cr (VI) adsorption does not follow Freundlich isotherm (Figures 1C and 1D). Constants of isotherms are placed in Table 1. As shown in

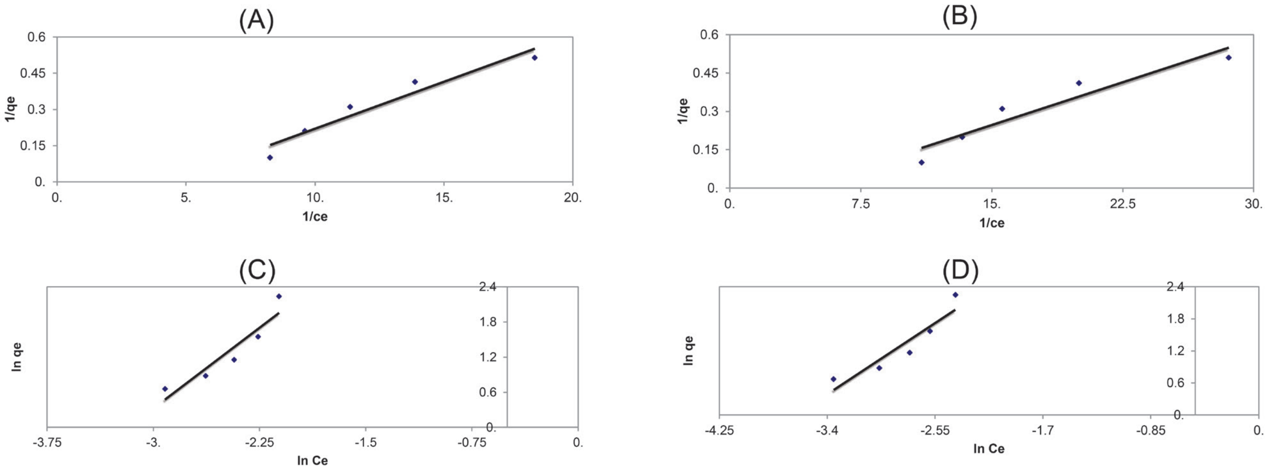

Figure 1. A) Langmuir isotherm for Cr adsorption by different masses of MWCNTs; pH= 3; pollutant= 2 mg/l. B) Langmuir isotherm for Cr adsorption by different masses of SWCNTs; pH= 3; pollutant= 2 mg/l. C) Freundlich isotherm for Cr adsorption by different masses of MWCNTs; pH= 3; pollutant= 2 mg/l. D) Freundlich isotherm for Cr adsorption by different masses of SWCNTs; pH=3; pollutant= 2 mg/l

Table 1. Constants of isotherms

Type of adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m	b	R_2	n	k_f	R_2
SWCNTs	44.64	0.251	0.9045	0.174	4.77	0.8686
MWCNTs	25.64	0.228	0.9309	0.171	6.27	0.8747

SWCNTs= Single-Walled Carbon Nano Tubes; MWCNTs= Multi-Walled Carbon Nano Tubes

Table 2. The effect of adsorbent dose on Cr (VI) remained concentration (C_e), adsorption capacity (q_e), and removal percentage (r_e) by use of carbon nano tubes in time= 120 minutes, pH= 3, and initial Cr concentration= 2

Adsorbent dose (g/l)	Adsorbent types					
	MWCNTs			SWCNTs		
	C_e	R_e	q_e	C_e	R_e	q_e
0.4	0.501	74.95	3.74	0.422	78.9	3.94
0.8	0.412	79.4	1.98	0.334	83.3	2.08
1	0.351	82.45	1.65	0.222	88.9	1.778

SWCNTs= Single-Walled Carbon Nano Tubes; MWCNTs= Multi-Walled Carbon Nano Tubes

Table 2, in the solution of 2 Cr with an increase in adsorption mass, removal percentage (r_e) increased, and adsorption capacity (q_e) decreased. As you can see, adsorption capacities for 0.4 and 1 of adsorption masses, for Single-Walled Carbon Nano Tubes (SWCNTs) in time= 120 minutes and in pH=3 are 3.94 and 1.78 respectively and in the same condition for Multi-Walled Carbon Nano Tubes (MWCNTs) are 3.74, and 1.65 respectively. Table 3 shows the effect of initial Cr concentration on adsorption by carbon nano tubes. According to Table 3, when Cr concentration increased from 0.5 to 2, removal efficiency decreased and adsorption capacity increased. According to the results on Table 4, there is a direct relation between contact time and adsorption capacity and between contact time and removal percentage. The amount of q_e and r_e were calculated to gain a better understanding of the role of pH data earned from analyzed experiments in a defined time and initial Cr concentration. These findings are presented in Table 5.

Discussion

The relationship between adsorbed Cr (VI) and its concentration in solution under equilibrium conditions is described by isotherm models. In one study, bone char used as an adsorbent for Cr (VI) adsorption. The researchers found that adsorption process is done better in acidic pH and follows Langmuir (=0.98) and Freundlich (=0.99) isotherm models (17). Cr (VI) removal by using sulfonated lignite showed maximum adsorption in low pH, and data were well analyzed with Langmuir isotherm (18). Various adsorbents for Cr removal were applied in the acidic conditions which showed the predominant

Table 3. The effect of initial Cr concentration on q_e, r_e, and C_e in adsorbent dose= 1 g/l, time= 120 minutes, pH= 3

Initial Cr concentration mg/l	Adsorbent types					
	MWCNTs			SWCNTs		
	C_e	R_e	q_e	C_e	R_e	q_e
0.5	0.023	95.4	0.477	0.009	98.2	0.49
1	0.113	88.7	0.887	0.071	92.9	0.93
2	0.351	82.5	1.65	0.222	88.9	1.778

SWCNTs= Single-Walled Carbon Nano Tubes; MWCNTs= Multi-Walled Carbon Nano Tubes

Table 4. The effect of contact time on q_e, r_e, and C_e in adsorbent dose= 0.4 g/l, pH= 3, and initial Cr concentration= 2 mg/l

Time (min)	Adsorbent types					
	MWCNTs			SWCNTs		
	C_e	R_e	q_e	C_e	R_e	q_e
0	2	0	0	2	0	0
30	0.961	51.95	2.6	0.796	60.2	3.01
60	0.797	60.15	3.01	0.591	70.45	3.52
120	0.501	74.95	3.74	0.422	78.9	3.94

SWCNTs= Single-Walled Carbon Nano Tubes; MWCNTs= Multi-Walled Carbon Nano Tubes

Table 5. The effect of pH on q_e, r_e, and C_e in time= 30 minutes and Cr concentration = 2 mg/l

Adsorbent dose (g/l)	pH	Adsorbent types					
		MWCNTs			SWCNTs		
		C_e	R_e	q_e	C_e	R_e	q_e
0.4	5	1.176	41.2	2.06	0.982	50.9	2.54
	3	0.961	51.95	2.6	0.796	60.2	3.01
0.8	5	1.057	47.15	1.18	0.843	57.85	1.44
	3	0.776	61.2	1.53	0.591	70.45	1.76
1	5	0.883	55.85	1.12	0.664	66.8	1.33
	3	0.625	68.75	1.37	0.503	74.85	1.49

SWCNTs= Single-Walled Carbon Nano Tubes; MWCNTs= Multi-Walled Carbon Nano Tubes

sorption for Cr (VI) species. Isotherm data fitted well for both Langmuir and Freundlich models at the lower initial Cr concentration, although the Langmuir isotherm was determined to be the most suitable model over the entire range (19). In our study for Freundlich isotherm, Correlation coefficient with adsorption data is less than 0.9, so adsorption process is not similar to this isotherm. x^2= 0.796 and 0.0025 were gained for Freundlich model and Langmuir model respectively. Because value of x^2 is very low for Langmuir model, it adjusts to adsorption process. In this study, the efficiency of carbon nano tubes as a new adsorbent in removal of Cr (VI) was examined. The results from the study of Hu *et al* (20), and Moradi *et al* (21) on Cr and other heavy metals removal by means of carbon nano tubes have shown that these adsorbents are effective for the removal of heavy metals especially Cr (VI). In the study of Hu *et al* (20), the effect of initial Cr concentration, pH, and temperature on Cr removal were investigated. Their study results showed decreasing removal percentage after pH increase and increasing removal percentage after temperature increase. In our study, removal percentage decreased after Cr concentration increase from 0.5 to 2 mg/l. To cite the cause, we can say that adsorbents have a limited number of active areas, so active areas become saturated quickly by pollutant and the efficiency of removal process goes down in high concentrations. In Ghanizadeh *et al* (17) study, the efficiency of removal process also came down by increasing initial pollutant concentration. In Hu *et al* study (20), you can see a diverse relationship between pH and removal percentage like our study. A good reason for that can be $HCrO_4$ and CrO_4 ions production under these conditions which facilitate adsorption process.

Conclusion
Based on findings adsorption capacities (qe) increased with increasing of initial Cr (VI) concentrations and reaction time and decreased when adsorbent dose and pH increased. According to the results Langmuir isotherm model can better define this adsorption process. Carbon nano tubes are proper adsorbents for the Cr (VI) ion removal from aqueous solutions and MWCNTs have better efficiency than SWCNTs.

Ethical issues
Ethical issues (including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

Competing interests
The authors have declared that no competing interest exists.

Authors' contributions
All authors contributed equally and all authors participated in the data acquisition, analysis and interpretation. All authors critically reviewed, refined and approved the manuscript.

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