Sorption Equilibrium of Hexavalent Chromium on Granular Activated Carbon

M. Gheju, A. Miulescu

"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Bd. V. Parvan Nr. 6, Et. 4, 1900, Timisoara, Romania, e-mail: marius.gheju@chim.upt.ro

Abstract: This study investigated, in batch studies, the removal of Cr(VI) from aqueous solutions, by adsorption on commercially granular activated carbon (GAC) Nobrac CG 700. The influence of pH on the efficiency of the Cr(VI) adsorption process was evaluated at 25° C, over the pH range of 1 - 3. Sorption data have been interpreted in terms of Langmuir and Freundlich isotherm equations, and their constants were evaluated. The results show that the adsorption capacity and the adsorption intensity increased with the decrease of pH. Although the determined values of ΔG^0_{298} indicate the spontaneous and exothermic nature of the adsorption process over the entire studied pH range, Cr(VI) adsorption was thermodinamically less favored under very strong acidic conditions (pH = 1.10).

Keywords: Hexavalent chromium, heavy metals, activated carbon, adsorption.

1. Introduction

Chromium is an important metal, which is used in a variety of industrial applications (e.g. textile dying, tanneries, metallurgy, metal electroplating, wood preserving, preparation of chromate compounds); hence, large quantities of chromium have been discharged into the environment due to accidental releases or inadequate precautionary measures [1]. Oxidation states of chromium range from –4 to +6, but only the +3 and +6 states are stable under most natural environments [1,2]. Hexavalent chromium (Cr(VI)) is the most stable form under oxidizing conditions, whereas trivalent chromium (Cr(III)) is the most stable form under reducing conditions. In aqueous systems chromium usually exists in both trivalent and hexavalent forms, which are characterized by different toxicity and chemical behavior. Cr(VI) is known to be toxic to all living organisms, and a well-established human carcinogen by the inhalation route of exposure, having a significant solubility and mobility [3-5]. For a long time, there was some controversy as to whether Cr(VI) should be considered a carcinogen also by the oral route. While some authors doubt that Cr(VI) would be carcinogenic by the oral route, especially because Cr(VI) can be converted to the less toxic form of Cr(III) in the human body [6], other authors believe that Cr(VI) should be regarded as carcinogenic by the oral route, based on evidence that Cr(VI) can be transported to all organs and tissues of the body [7]. Only recently it was proved that Cr(VI) is carcinogenic also by the oral route of exposure [8], being therefore a possible human carcinogen when ingested with water. Cr(III), on the other hand, is less toxic and less mobile, because it readily precipitates as $Cr(OH)_3$ [9] or as mixed Fe(III)-Cr(III) (oxy)hydroxides [10,11] under alkaline or even slightly acidic conditions. Although trivalent chromium is considered an essential nutrient for the human body [12] and the toxicity of trivalent chromium is 500 to 1000 times less to a living cell than hexavalent

chromium [13], exposure to excessive doses of Cr(III), for long periods of time, may also cause some adverse health effects [14,15]. Thus, removal of chromium, and especially of Cr(VI), is an essential pollution abatement process that should be applied to all industrial effluents that contain this contaminant, prior to discharge them in to the natural water bodies.

Several methods are available for the decontamination of waters polluted with Cr(VI) compounds. These include: reduction followed by chemical precipitation, adsorption, electrokinetic remediation, membrane separation processes, bioremediation. The objective of this work was to determine the efficiency of Nobrac CG 700 granular activated carbon (GAC) to remove hexavalent chromium from simulated Cr(VI) contaminated samples. Adsorption experimental data was fitted to Freundlich and Langmuir adsorption isotherm equations, over the pH range of 1 - 3.

2. Materials and Methods

Hexavalent chromium stock solution (10 g/L) was prepared by dissolving 28.29 g of AR grade $K_2Cr_2O_7$ in 1000 ml of distilled deionised water. Standard solutions of the desired initial Cr(VI) concentration (10 mg/L) were prepared by diluting the stock solution.

Adsorption batch experiments were carried out at 25° C using 100 mL flasks containing 50 mL of the standard Cr(VI) solution and various amounts of Nobrac CG 700 granular activated carbon. The initial Cr(VI) concentration and the mixing speed were held constant (10 mg/L, 200 rpm) throughout the study. The pH of the Cr(VI) standard solution was adjusted by the small addition of concentrated H_2SO_4. The required amount of Nobrac CG 700 GAC was added to the 50 mL of the standard Cr(VI) solution and the flasks were shaken orbitally continuously, using a GFL 3017 shaker, for 4 hours, in order to reach the sorption equilibrium. After the required contact time, the

supernatant was filtered trough filter paper and analyzed for final Cr(VI) concentration.

Cr(VI) concentration in the filtered supernatant was measured by the 1,5-diphenylcarbazide colorimetric method at 540 nm [16], using a Jasco V 530 spectrophotometer. The pH of solutions was measured using an Inolab pH-meter.

3. Results and Discussion

Two adsorption isotherms, Langmuir and Freundlich, were used in this study for fitting the obtained experimental adsorption data, to estimate the GAC adsorption capacity and the degree of adsorption favorability.

Langmuir adsorption isotherm can be expressed as nonlinearized (1) and linearized form (2) [17,18]:

$$q_e = \frac{Q(b \cdot C_e)}{(1 + b \cdot C_e)} \qquad (1)$$

$$\frac{1}{q_e} = \frac{1}{Qb}\frac{1}{C_e} + \frac{1}{Q} \qquad (2)$$

where Q and b are constants of Langmuir isotherm; Q is the maximum adsorption capacity of the GAC (mg Cr(VI)/g GAC); b a constant related to the free energy of adsorption (L/mg); q_e is the amount of Cr(VI) adsorbed at equilibrium (mg Cr(VI)/g GAC) (3):

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (3)$$

where M is the mass of GAC used in the batch experiments (g); C_e the equilibrium concentration of Cr(VI) (mg/L); C_0 the initial concentration of Cr(VI) (mg/L); V the volume of Cr(VI) solution used in the batch experiments (L).

By plotting $1/q_e$ vs. $1/C_e$ using the experimental data, a straight line should be obtained. The line equation was calculated by regression analysis; $1/Q$ is the intercept and $1/Qb$ the slope of this line.

Similarly, Freundlich adsorption isotherm can also be expressed as nonlinearized (3) and linearized (4) form [17,18]:

$$q_e = C_e^{1/n} \cdot K_f \qquad (3)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where K_f and n are constants of Freundlich isotherm; K_f is a constant related to the maximum adsorption capacity of the adsorbent; $1/n$ a constant which indicates the intensity

of adsorption; q_e has the same signification as in Langmuir isotherm.

By plotting *log q_e* vs. *log C_e* using the experimental data, a straight line should be obtained. The line equation was calculated by regression analysis; *log K_f* is the intercept and *1/n* the slope of this line.

The isotherms for the Cr(VI) adsorption are presented in figures 1 - 9. The obtained results, presented in table 1, showed that the adsorption process fitted better the Freundlich isotherm equation.

TABLE 1. Comparison of Langmuir and Freundlich isotherm constants for Nobrac CG 700 granular activated carbon

pH	Langmuir isotherm constants			Freundlich isotherm constants		
	Q (mg/g)	b (L/mg)	R^2	K_f	1/n	R^2
1.10	14.68	0.45	0.9220	4.52	0.577	0.9526
1.95	8.94	0.72	0.9392	4.08	0.310	0.9750
3.06	4.67	0.64	0.8737	2.41	0.232	0.9322

From the comparison of Langmuir Q constant and and of Freundlich K_f constant it can be seen that the adsorption capacity of NOBRAC GC 700 GAC increased with the decrease of Cr(VI) solution pH. This can be attributed to the fact that the adsorbent is a pH dependent charged surface. As the pH decreases, the number of negatively charged sited diminishes, the majority of adsorbent surface will be positively charged and the adsorption of Cr(VI) negatively charged species will increase [19].

The better adsorption under strong acidic conditions is also confirmed by the analysis of the *1/n* constant. The adsorption process is considered favorable when 0.1 < *1/n* < 1.0. The larger the value of *1/n* (up to 1), the greater the intensity of adsorption [20]; when *1/n* = 0.5 the interparticle diffusion is considered to be the rate limiting step [21]. The larger value of *1/n* observed at pH 1.10 indicates a stronger bond between Cr(VI) and the adsorbent used in this study [20]. Comparison of Langmuir and Freundlich isotherm constants with similar data found in literature for other activated carbons, or for some non-conventional adsorbents (Table 2) shows that NOBRAC GC 700 GAC is not a a very strong adsorbent for hexavalent chromium, even under strong acidic conditions.

Another important characteristic of the Langmuir isotherm is the dimensionless separation parameter R_L, which can predict whether an adsorption system is favorable or unfavorable. R_L is defined as [27]:

$$R_L = \frac{1}{1 + b \cdot C_0} \qquad (5)$$

where C_0 is the initial concentration of the Cr(VI) (mg/L), and b is the Langmuir constant.
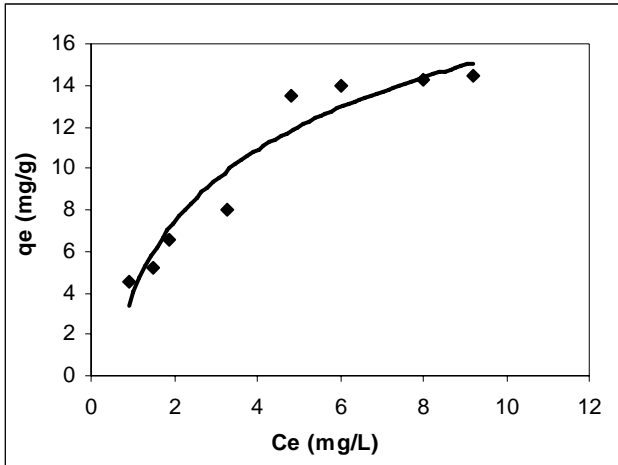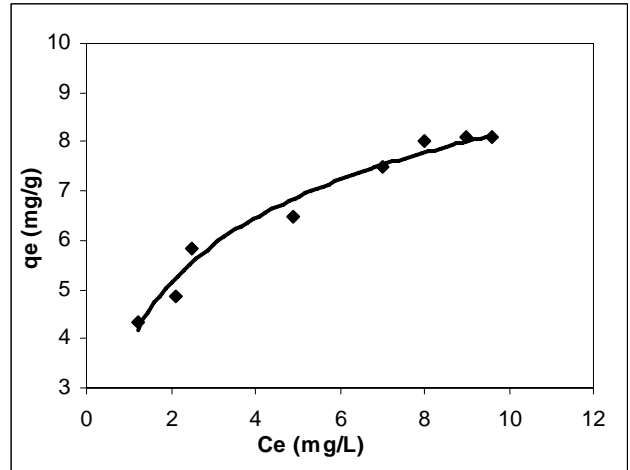
Figure 1. Adsorption isotherm at pH = 1.10

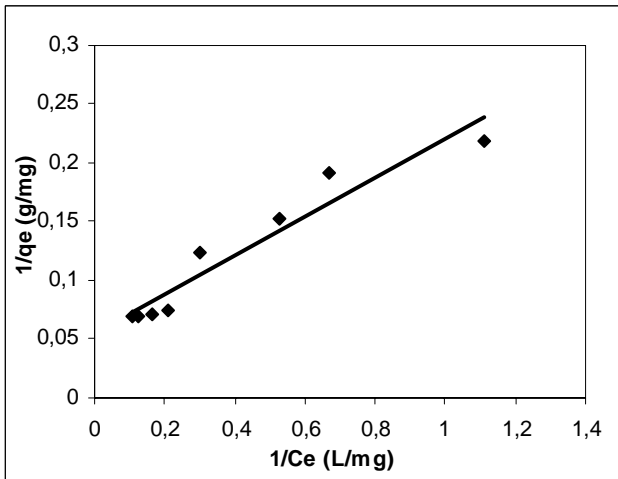Figure 4. Adsorption isotherm at pH = 1.95

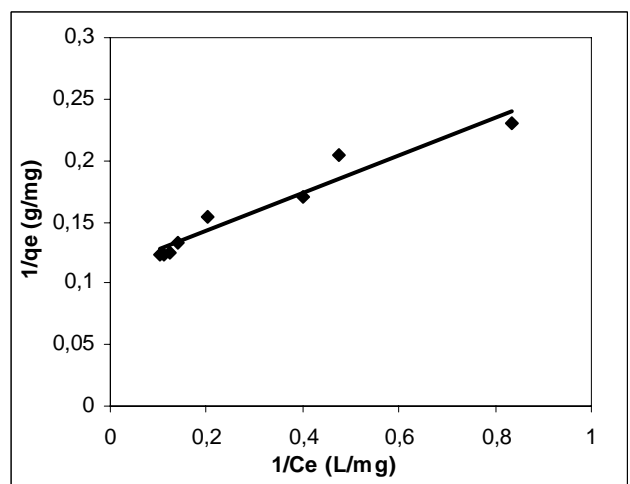Figure 2. Langmuir adsorption isotherm at pH = 1.10

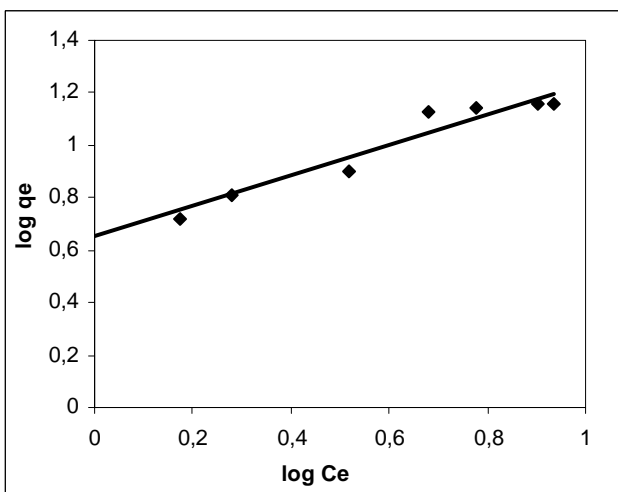Figure 5. Langmuir adsorption isotherm at pH = 1.95

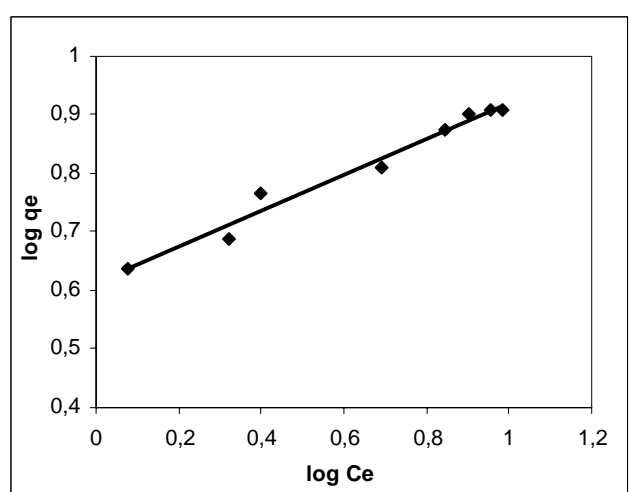Figure 3. Freundlich adsorption isotherm at pH = 1.10

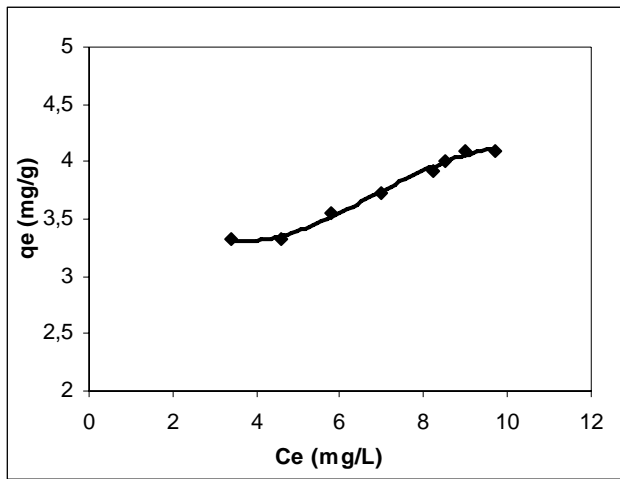Figure 6. Freundlich adsorption isotherm at pH = 1.95
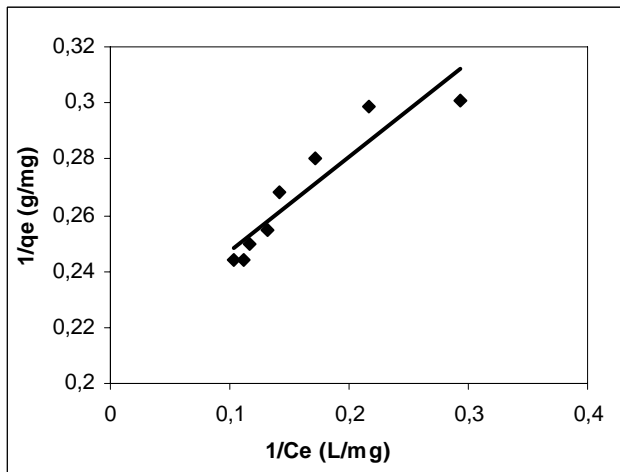
Figure 7. Adsorption isotherm at pH = 3.06
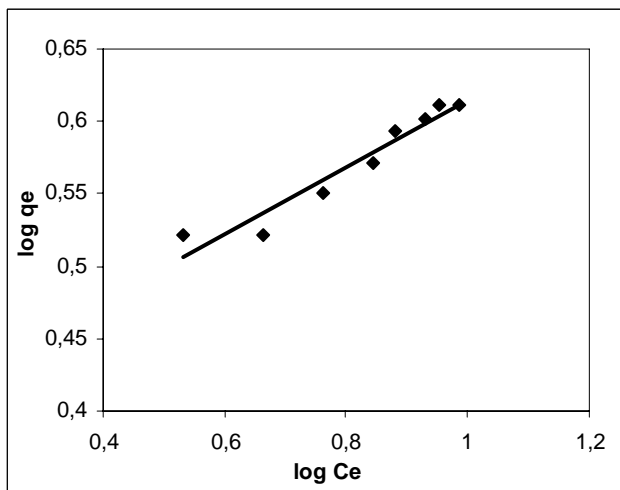

Figure 8. Langmuir adsorption isotherm at pH = 3.06

Figure 9. Freundlich adsorption isotherm at pH = 3.06

TABLE 2. Comparison of Langmuir and Freundlich isotherm constants for different adsorbents

Adsorbent	Langmuir isotherm constants		Freundlich isotherm constants		Source
	Q (mg/g)	b (L/mg)	K_f	1/n	
Wool	41.50	7.15×10^{-3}	2.230	0.435	17
Olive cake	33.44	4.70×10^{-3}	0.489	0.634	17
Sawdust	15.82	9.17×10^{-3}	0.877	0.436	17
Pine needles	21.50	5.44×10^{-3}	0.270	0.694	17
Almond	10.61	5.46×10^{-3}	0.141	0.684	
Coal	6.78	11.50×10^{-3}	0.207	0.595	17
Cactus	7.08	6.13×10^{-3}	0.094	0.704	17
Hazelnut shell, pH 1.0	9.38	20.9	-	-	22
Hazelnut shell, pH 2.0	17.7	20.4	-	-	22
Hazelnut shell, pH 3.0	3.99	240	-	-	22
Hazelnut shell, pH 4.0	2.72	107	-	-	22
Hazelnut shell, pH 5.0	1.21	66.8	-	-	22
Soybean cake	0.28	0.623	0.140	0.200	18
Coal ash, pH 3.5	0.449	74.23	0.519	0.199	23
Coal ash, pH 6.0	0.21	57.16	0.197	0.121	23
Hydrous stannic oxyde	3.48	0.941	1.480	0.312	24
Neem leaves	10	9.73×10^{-2}	1.282	0.483	25
GAC LB830; oxic, pH=4.0	-	-	22.4	0.463	26
GAC LB830; oxic, pH=7.5	-	-	0.04	3.76	26
GAC LB830; anoxic, pH=4.0	-	-	86.3	0.441	26
GAC LB830; anoxic, pH=7.5	-	-	1.19	0.566	26
GAC F400; oxic, pH=4.0	-	-	24.5	0.444	26
GAC F400; oxic, pH=7.5	-	-	0.028	4.031	26
GAC F400; anoxic, pH=4.0	-	-	80.9	0.405	26
GAC F400; anoxic, pH=7.5	-	-	1.25	0.646	26
GAC FS100	69.3	0.151	-	-	20
GAC GA3	101.4	0.143	-	-	20
GAC SH3	69.1	0.108	-	-	20

In order to have a favorable adsorption the R_L values should fall between 0 and 1. The lower the value of R_L, the more favorable the adsorption. The calculated R_L values, presented in table 3, showed that, over the entire studied pH range, the R_L values fall between 0 and 1, which is indicative of the favorable adsorption of Cr(VI) on NOBRAC GC 700 GAC.

TABLE 3. The dimensionless separation parameter R_L as a function of Cr(VI) solution pH

	pH		
	1.10	1.95	3.06
R_L	0.232	0.122	0.135

However, it can be seen that the adsorption of Cr(VI) was more favorable for pH 1.95 and 3.06 than for pH 1.10. This conclusion is confirmed also by the analysis of *b* Langmuir constant and of the standard Gibbs free adsorption energy. The larger the *b* Langmuir constant, the higher the standard Gibbs free adsorption energy, reflected by a fast increase in adsorption at low concentrations of adsorbate [20].

The standard Gibbs free energy (ΔG^0_{298}) was calculated to evaluate the thermodynamic feasibility of the process. The *b* Langmuir constant was used for estimation of the ΔG^0_{298}, despite the adsorption data fitted somewhat poorly this type of isotherm:

$$\Delta G^o_{298} = -R \cdot T \cdot \ln K \qquad (6)$$

where T is the experimental temperature (K); K is the *b* Langmuir constant (L/mol), at 298 K; R is the ideal gas constant (8.314 J/mol K);

TABLE 4. The standard Gibbs free energy as a function of Cr(VI) solution pH

	pH		
	1.10	1.95	3.06
b (L/mol)	23.40×10^3	37.44×10^3	33.28×10^3
ΔG^0_{298} (kJ/mol)	-24.925	-26.090	- 25.798

The negative ΔG^0_{298} values, reported in table 4, confirm the spontaneous nature and feasibility of the sorption process on Nobrac CG 700 granular activated carbon, over the entire studied pH range. However, the results show that the value of ΔG^0_{298} becomes more negative with decreasing pH from 3.06 to 1.95. At pH 1.10 the ΔG^0_{298} value is less negative than at pH 1.95 and 3.06, which means that that sorption on NOBRAC GC 700 GAC is thermodinamically less favored under very strong acidic conditions.

4. Conclusions

The present work evaluates the use of NOBRAC GC 700 granular activated carbon for the elimination of Cr(VI) from aqueous solutions. The Langmuir and Freundlich models were used to describe the adsorption process, and their isotherm constants were determined from experimental data. From the comparison of the correlation coefficients resulted that the Freundlich model best fit the Cr(VI) adsorption. The adsorption capacity of NOBRAC GC 700 GAC was found to be pH dependant: the lower the pH value, the higher the adsorption capacity. From the comparison of the *1/n* constants resulted that the adsorption intensity also increased with the decrease of pH. The calculated values of the dimensionless separation factor R_L showed that, over the entire studied pH range, the adsorption was favorable. However, the adsorption was more favorable for pH 1.95 and 3.06 than for pH 1.10. Similarly, it was found that, at pH 1.10, the standard Gibbs free energy (ΔG^0_{298}) value was less negative than at pH 1.95 and 3.06, although the determined values of ΔG^0_{298} indicate the spontaneous and exothermic nature of the adsorption process over the entire studied pH range. This means that that sorption on NOBRAC GC 700 GAC is thermodinamically less favored under very strong acidic conditions (pH 1.10). Comparison of Langmuir and Freundlich isotherm constants with similar data found in literature for other adsorbents shows that NOBRAC GC 700 GAC is not a a very strong adsorbent for Cr(VI), even under strong acidic conditions.

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