

Kinetics of Hexavalent Chromium Adsorption 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: The kinetics of Cr(VI) adsorption on granular activated carbon (GAC) Nobrac CG 700 was investigated in batch system, over the pH range of 1.10 – 4.05, at 24° C. The effect of pH was observed and experimental data has been interpreted in terms of zero-order, first-order, second-order, pseudo first-order and pseudo second-order integrated kinetic models. It was noticed that Cr(VI) adsorption rates decreased significantly with increasing pH. Moreover, at pH = 4.05 and higher, the adsorption process was found to be negligibly slow; therefore, all further kinetic interpretations were performed only for the pH range of 1.10 – 3.06. The adsorption process proceeds in two stages: high adsorption rates were observed within the first time interval, whereas a strong decrease in the Cr(VI) adsorption occurs in the second one. The results obtained indicate pseudo second-order kinetics for the first time interval, and zero-order kinetics for the second time interval. The rate coefficients were determined for both stages of the adsorption process.

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

1. Introduction

The production of heavy metals increased rapidly since the industrial revolution. As a result, pollution of water bodies with heavy metals becomes a major environmental problem of the modern world. Therefore, in last decades, the presence of heavy metals in aquatic ecosystems has received widespread attention due to their potential human health risks and harmful effect to living organisms. Chromium is an important heavy metal that has numerous industrial applications; the major industries that may contribute to water pollution by chromium are: mining, metallurgy, leather tanning, wood preserving, textile dyeing, metal electroplating, production of inorganic chemicals and pigments. The effluents of these industries contain Cr(VI) or/and Cr(III), at concentrations ranging from tenths to hundreds of milligrams/liter. Hence, large quantities of chromium have been discharged into the natural waters either with this effluents, or due to accidental releases [1,2].

Chromium can exist in natural environments in two stable oxidation states: (+III) and (+VI), with differing solubility, mobility and toxicity [3,4]. Cr(VI) is present as highly soluble dichromate or chromate anions, known to be toxic to all living organisms, and to have a well-established carcinogen effect by the inhalation and oral route of exposure. The main concern about Cr(VI) compounds is associated with their mobility, which can easily lead to the contamination of both surface and groundwaters [4-9]. Cr(III), on the other hand, is present mainly as relatively insoluble, immobile and non-toxic hydroxides and oxides [10,11]. Although trivalent chromium is considered an essential nutrient for the human body [12,13] and the toxicity of trivalent chromium is 500 to 1000 times less to a living cell than hexavalent chromium [14], Cr(III) could

also be a concern if, under certain conditions, it would be converted to the hazardous Cr(VI).

The treatment of chromium, and especially of Cr(VI) contaminated wastewaters is essential before discharging them to the natural water bodies. In recent years, many attempts have been made to reduce the presence of Cr(VI) in water. Several methods were used to remove Cr(VI) from industrial wastewater. These include: reduction followed by chemical precipitation, adsorption, electrochemical treatment, liquid membrane separation, reverse osmosis, ion exchange, bioremediation [15].

The objective of this study was to explore the kinetics of Cr(VI) adsorption on granular activated carbon, over the pH range of 1.10 – 4.05. The adsorption experimental data was tested for a number of five kinetic equations and the rate coefficients were determined.

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, 19.23×10^{-5} M (10 mg/L), were prepared by diluting the stock solution.

Kinetic batch experiments were performed, at 24 °C, using a 1-L flask open to the atmosphere, containing 500 ml of the standard solution. To remove traces of chromium, the flask was soaked in 1 N HCl before each experiment, and washed with distilled deionised water thereafter. The pH of the standard solution was adjusted prior to the kinetic experiments by small addition of H_2SO_4 98%. The initial Cr(VI) concentration, the mixing speed (200 rpm) and the amount of Nobrac CG 700 GAC (0.5 g) were held constant throughout the study. The flask contents were mixed

continuously with a overhead stirrer having a glas stirring shaft.

Aliquots were periodically extracted for Cr(VI) analysis and filtered immediately for the removal GAC particles. Cr(VI) concentration in the filtered supernatant was measured by the 1,5-diphenylcarbazide colorimetric method. The purple color was fully developed after 15 min and the sample solutions were transferred to a Jasco V 530 spectrophotometer; the absorbance of the color was measured at 540 nm in a 1 cm long glass cell [16]. The pH of solutions was measured using an Inolab pH-meter.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the rate of Cr(VI) adsorption on Nobrac CG 700 GAC is presented in figure 1. From this figure it appears that, over the pH range of 1.10 – 4.05, the rate of Cr(VI) adsorption significantly decreased with increasing pH. This observation can lead to the conclusion that the adsorbent has a pH dependent charged surface; as the hydronium ions concentration increases, the majority of adsorbent surface will be positively charged, according to equation (1):



Therefore, the adsorption rate of Cr(VI) negatively charged species, which take place according to equation (2), will increase with the decrease of pH.



Because at pH = 4.05 and higher (data not shown) the adsorption process was found to be negligibly slow, all further kinetic interpretations were performed only for the pH range of 1.10 – 3.06.

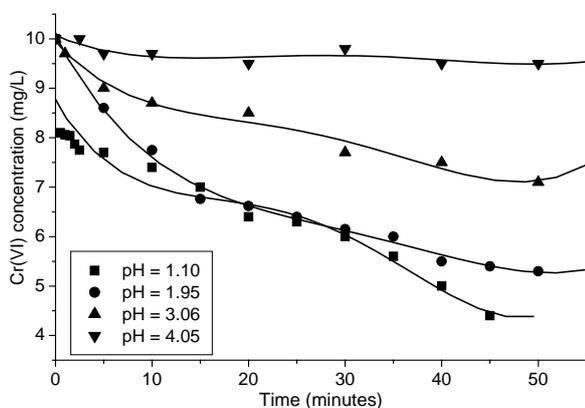


Figure1. Cr(VI) concentration vs. time, at different Cr(VI) solution pH

From figure 1 it can also be seen that the adsorption process proceeds in two stages. High adsorption rates are observed within the first time interval, whereas a strong decrease in the Cr(VI) adsorption occurs in the second one. The initial rapid adsorption is due to the availability of the positively charged functional groups of the GAC adsorbent. The subsequent slower adsorption can be attributed to changes in GAC surface reactivity, due to continuous diminishing of the number of positively charged functional groups throughout the adsorption experiment. The results are in agreement with similar literature reports [17], which also reported two stages adsorption of Cr(VI) on activated carbon.

3.2. Study of reaction order

The kinetics of Cr(VI) adsorption on Nobrac CG 700 GAC was evaluated by the integral method, using zero-order (eq.1) [18], first-order (eq.2) [18], second-order (eq.3) [18], pseudo first-order (eq.4) [19] and pseudo second-order (eq.5) [19] integrated kinetic models.

$$C_{Cr(VI)} = C_{Cr(VI)}^0 - k \cdot t \quad (3)$$

$$\ln C_{Cr(VI)} = \ln C_{Cr(VI)}^0 - k \cdot t \quad (4)$$

$$\frac{1}{C_{Cr(VI)}} = \frac{1}{C_{Cr(VI)}^0} + k \cdot t \quad (5)$$

$$\ln(q_e - q_t) = \ln q_e - kt \quad (6)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (7)$$

where $C_{Cr(VI)}$ is the Cr(VI) concentration at time t (M), $C_{Cr(VI)}^0$ is the initial Cr(VI) concentration (M), q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g), q_t is the amount of Cr(VI) adsorbed at time t (mg/g), k is the adsorption rate coefficient, and t is the time (minutes). q_e and q_t were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (8)$$

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (9)$$

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

By plotting $C_{Cr(VI)}$ (zero-order), $\ln C_{Cr(VI)}$ (first-order), $1/C_{Cr(VI)}$ (second-order), $\ln(q_e - q_t)$ (pseudo first-order), and $1/(q_e - q_t)$ (pseudo second-order) vs. time, using the experimental data, a straight line was obtained; subsequently, the line equation was calculated by regression analysis. The conformity between experimental data and the kinetic model was expressed by the correlation coefficient R^2 ; the model that successfully describes the kinetics of the Cr(VI) adsorption is the one that has the highest R^2 value.

The regression equations and R^2 values for the integrated kinetic models are presented in tables 1 and 2. The results indicate pseudo second-order kinetics for the adsorption first time interval, and zero-order kinetics for the adsorption second time interval, over the pH range of 1.10 – 3.06, as presented in table 3. Both pseudo second-order and zero-order observed rate coefficients decreased linearly as the pH increased, as shown in table 4 and figures 2, 3. This confirms the fact that the rate of Cr(VI) adsorption increased with decreasing pH.

TABLE 1. Regression equations and R^2 values for first adsorption stage experimental data.

Kinetic models.	Regression equations and R^2 value		
	pH = 1.10	pH = 1.95	pH = 3.06
Zero-order	$y = -1.3166x + 17.612$ $R^2 = 0.5784$	$y = -0.3266x + 18.775$ $R^2 = 0.9389$	$y = -0.245x + 18.958$ $R^2 = 0.922$
First-order	$y = -0.0783x - 8.6485$ $R^2 = 0.597$	$y = -0.0206x - 8.5793$ $R^2 = 0.9524$	$y = -0.0138x - 8.5702$ $R^2 = 0.9303$
Second-order	$y = 465.45x + 5728.1$ $R^2 = 0.6158$	$y = 131.09x + 5310.2$ $R^2 = 0.9629$	$y = 76.733x + 5273$ $R^2 = 0.9366$
Pseudo first-order	$y = -0.1579x + 1.5425$ $R^2 = 0.6147$	$y = -0.0615x + 1.5147$ $R^2 = 0.971$	$y = -0.046x + 1.2138$ $R^2 = 0.9477$
Pseudo second-order	$y = 0.0375x + 0.217$ $R^2 = 0.6595$	$y = 0.0248x + 0.2032$ $R^2 = 0.9868$	$y = 0.0169x + 0.2956$ $R^2 = 0.9674$

TABLE 2. Regression equations and R^2 values for second adsorption stage experimental data.

Kinetic models.	Regression equations and R^2 value		
	pH = 1.10	pH = 1.95	pH = 3.06
Zero-order	$y = -0.1419x + 15.547$ $R^2 = 0.9838$	$y = -0.102x + 14.896$ $R^2 = 0.9599$	$y = -0.0648x + 17.146$ $R^2 = 0.9804$
First-order	$y = -0.0117x - 8.7453$ $R^2 = 0.9744$	$y = -0.009x - 8.7723$ $R^2 = 0.9562$	$y = -0.0045x - 8.658$ $R^2 = 0.9474$
Second-order	$y = 96.881x + 6064.2$ $R^2 = 0.9557$	$y = 80.249x + 6058.3$ $R^2 = 0.9532$	$y = 31.32x + 5662.7$ $R^2 = 0.9612$
Pseudo first-order	$y = -0.0429x + 1.5555$ $R^2 = 0.8943$	$y = -0.1248x + 3.5019$ $R^2 = 0.9072$	$y = -0.0438x + 1.6089$ $R^2 = 0.9785$
Pseudo second-order	$y = 0.0305x - 0.0388$ $R^2 = 0.6975$	$y = 0.4401x - 11.701$ $R^2 = 0.7978$	$y = 0.0805x - 1.7048$ $R^2 = 0.8136$

TABLE 3. Variation of adsorption reaction order as a function of pH and adsorption stage.

pH	Adsorption reaction order	
	First stage	Second stage
1.10	Pseudo second	Zero
1.95	Pseudo second	Zero
3.06	Pseudo second	Zero

TABLE 4. Variation of adsorption rate coefficient as a function of pH and adsorption stage.

pH	Adsorption rate coefficient	
	First stage	Second stage
1.10	0.0375 $\text{g mg}^{-1} \text{min}^{-1}$	0.1419 $\text{mol L}^{-1} \text{min}^{-1}$
1.95	0.0248 $\text{g mg}^{-1} \text{min}^{-1}$	0.1020 $\text{mol L}^{-1} \text{min}^{-1}$
3.06	0.0169 $\text{g mg}^{-1} \text{min}^{-1}$	0.0648 $\text{mol L}^{-1} \text{min}^{-1}$

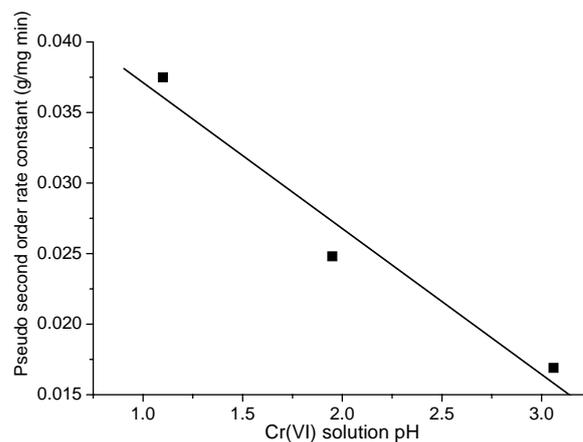


Figure 2. Effect of Cr(VI) solution pH on pseudo second-order adsorption rate coefficient (first adsorption stage)

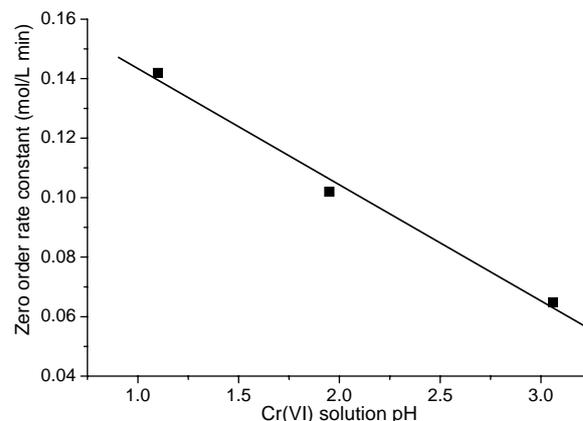


Figure 3. Effect of Cr(VI) solution pH on zero-order adsorption rate coefficient (second adsorption stage)

4. Conclusions

Hexavalent chromium is a strong toxic and carcinogenic agent and it should be removed before disposed to the environment. Its retaining on adsorbent materials seems to be a possible solution. The present work evaluates the kinetics of Cr(VI) adsorption on NOBRAC GC 700 granular activated carbon. Results obtained show that pH significantly affects the rate of Cr(VI) adsorption, with more rapid adsorption occurring at lower pH values. Therefore, it can be concluded that this adsorbent has a pH dependent charged surface. It was noticed that the adsorption process proceeds in two stages, with high adsorption rates within the first time interval, and lower adsorption rates within the second one. Over the pH range of 1.10 – 3.06, the experimental kinetic results, evaluated by the integral method, indicate pseudo second-order kinetics for the first time interval, and zero-order kinetics for the second time interval. The rate coefficients were determined for both stages of the adsorption process.

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REFERENCES

- Barnhart, J., Occurrences, uses and properties of chromium. Regul. Toxicol. Pharmacol. 26 (1), **1997**, s3–s7.
- Gheju, M., Cromul și mediul înconjurător, Editura Politehnica, Timișoara, **2005**.
- Cotton, F.A., Wilkinson, G., Murillo, C.A., Bochmann, M., Advanced inorganic chemistry, John Wiley & Sons, Inc., **1999**.
- Kimbrough, D.E., Cohen, Y., Winer, A.M., A critical assessment of chromium in the environment, Crit. Rev. Environ. Sci., 29, **1999**, p.1-46.
- Bagchi, D., Stohs, S.J., Downs, B.W., Cytotoxicity and oxidative mechanisms of different forms of chromium, Toxicology, 180, **2002**, p.5-22.
- Cieslak-Golonka, M., Toxic and mutagenic effects of chromium(VI). A review, Polyhedron, 15, **1995**, p.3667-3689.
- Cohen, M.D., Kargacin, B., Klein, C.B., Mechanisms of chromium carcinogenicity and toxicity, Crit. Rev. Toxicol., 23, **1993**, p.255-281.
- Costa, M., Toxicity and carcinogenicity of Cr(VI) in animal models and humans, Crit. Rev. Toxicol., 27, **1997**, p. 431-442.
- Chromium in water a cancer suspect, Wat. Condition. Purific. Magazine, 49(7), **2007**, p.18.
- Rai, D., Sass, B.M., Moore, D.A., Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide, Inorg. Chem., 26, **1987**, p.345-349.
- Palmer, C.D., Wittbrodt, P.R., Processes affecting the remediation of chromium-contaminant sites. Environ. Health Persp. 92, **1991**, p.25-40.
- *** Public health goal for chromium in drinking water, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, **1999**.
- Anderson, R.A., Essentiality of chromium in humans, Sci. Total Environ., 86, **1989**, p.75-81.
- Costa, M., Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol. 188, **2002**, p.1-5.
- Gheju, M., Iovi, A., Kinetics of hexavalent chromium reduction by scrap iron, J. Hazard. Mater., 135B (1-3), **2006**, p.66-73.
- APHA, AWWA, WEF, Standard methods for the examination of water and wastewater, 21th Edition, United Book Press, Inc., Baltimore, MdD, **2005**.
- Park, S.J., Jang, Y.S., Pore structure and surface properties of chemically modifies activated carbons for adsorption mechanism and rate of Cr(VI), J. Colloid Interface Sci., 249, **2002**, p.458-463.
- Davidescu, C., Păcurariu, C., Curs de chimie-fizică, Litografia UPT, Timișoara, **1990**.
- Erhan D., Mehmet K., Elif S., Tuncay O., Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water SA, 30, **2004**, p.533-539.