Hexavalent chromium removal from aqueous solutions by use of extruded activated carbon. Sorption kinetic studies

MARIUS GHEJU
Faculty of Industrial Chemistry and Environmental Engineering
“Politehnica” University of Timisoara
Bd. V. Parvan Nr. 6, Et. 4, 300223 Timisoara
ROMANIA
marius.gheju@chim.upt.ro

MARIA MATEESCU
Faculty of Industrial Chemistry and Environmental Engineering
“Politehnica” University of Timisoara
ROMANIA

Abstract: In the present work, commercial extruded activated carbon (EAC) Norit Row 0.8 Supra was used to remove Cr(VI) from artificially contaminated waters. Batch adsorption experiments were conducted to evaluate the kinetics of adsorption process over the pH range of 1.0 - 6.2. The results revealed that rate of Cr(VI) adsorption on EAC increased with decreasing solution pH. The main cause of higher Cr(VI) adsorption rate at low pH was the presence of more positively-charged surface groups under acidic conditions than under circumneutral pH. However, the speciation of Cr(VI) anionic species in aqueous solutions seem also to have an important role on Cr(VI) adsorption. The experimental data was analyzed using the pseudo first and pseudo second-order kinetic models. It was found that adsorption of Cr(VI) on EAC fitted well to the pseudo first-order kinetic model over the pH range of 1.0 - 3.1, while the pseudo second-order kinetic model provided the best match for the experimental data over the pH range of 4.0 - 6.2.

Key-Words: Hexavalent chromium; adsorption; extruded activated carbon; kinetics.

1 Introduction
Chromium is an important heavy metal that is used in various industries (e.g. textile dyeing, tanneries, metallurgy, metal plating, wood preserving, production of inorganic chemicals and pigments); thus, large quantities of chromium have been discharged into the environment either with industrial effluents, or due to accidental releases [1,2]. Chromium can exist in natural environments in two stable oxidation states: (+III) and (+VI), which are characterized by different toxicity and chemical behavior. Cr(VI) is present as highly soluble and mobile oxyanions of chromate (CrO$_4^{2-}$) and bichromate (HCrO$_4^{-}$), known to be toxic to humans, animals, plants and microorganisms; moreover, it has a well-established carcinogenic effect by the inhalation and oral route of exposure [3-7]; in contrast, Cr(III) is up to 1000 times less toxic than Cr(VI) and readily precipitates under alkaline or even slightly acidic conditions as Cr(OH)$_3$ [8], or as mixed Fe(III)-Cr(III) (oxy)hydroxides (Cr$_3$Fe$_{14}$(OH)$_{22}$, Cr$_7$Fe$_{14}$(OOH)$_{22}$) [9-11]. Due to the high toxicity and mobility of Cr(VI), the treatment of industrial effluents contaminated with this pollutant is essential before discharging them to the natural water bodies. Several methods are available for the decontamination of wastewaters polluted with Cr(VI), including reduction followed by chemical precipitation, adsorption, membrane separation processes, electrokinetic remediation, bioremediation. The conventional method for removing Cr(VI) from wastewater is based on its reduction to Cr(III), using chemical reductants such as Fe(0), FeSO$_4$, Na$_2$SO$_3$, NaHSO$_3$, SO$_2$, Na$_2$S$_2$O$_3$, and Na$_2$S$_2$O$_5$, followed by a chemical precipitation process [12]. Even though the effectiveness of these procedures has been proved, they present some inconveniences, such as incomplete metal removal, producing of toxic sludge or other waste products, expensive equipment and reagents, regular monitoring system, energy requirements [13]. The use of activated carbons for removing various contaminants from wastewater has received a great attention for decades, because of their high surface area, highly porous character and relative low-cost [14]. The objective of this study was to explore the kinetics of Cr(VI) adsorption on extruded activated carbon (EAC) Norit Row 0.8 Supra over the pH
range of 1.0 - 6.2. The adsorption experimental data was tested for a number of two kinetic equations and the rate coefficients were determined.

2 Problem Formulation
A stock Cr(VI) solution having a concentration of 1 g/L was prepared by dissolving 2.829 g of K₂Cr₂O₇ in 1 L of distilled deionized water; then, the solution of desired experimental concentration (2 mg/L) was obtained by appropriate dilution. The pH of the solution was set before adsorption by adding small amounts of concentrated H₂SO₄ or NaOH. Kinetic adsorption experiments were carried out in a 1.5 L Berzelius flask by introducing 1 g of EAC into 1000 mL Cr(VI) solution. The solution was continuously and vigorously (200 rpm) mixed using an overhead Heidolph stirrer, under a constant temperature (20 °C). Samples were periodically extracted for Cr(VI) analysis and filtered immediately for the removal EAC particles; the residual Cr(VI) concentration in the filtrate was determined by the diphenylcarbazide method at 540 nm [15], using a Jasco V 530 spectrophotometer. All chemicals used were of analytical grade. The conformity between experimental data and the kinetic model was expressed by the correlation coefficient R²; the model that successfully describes the kinetics of the Cr(VI) adsorption is the one that has the highest R² value; then, the slope and intercept of these lines were used for determining the rate coefficients and equilibrium adsorption capacity.

3 Problem Solution
3.1. Effect of the adsorbent dose
The effect of the EAC dose on the adsorption process was studied by treating 1000 mL of 2 mg/L Cr(VI) solution (pH 2.1) with 0.25 - 1.25 g of adsorbent for 40 min. It is shown in Fig. 1 that residual concentration of Cr(VI) decreased gradually with increasing concentration of EAC. Since Cr(VI) was completely removed from the solution at EAC doses starting from 1 g/L upwards, this value was considered as optimum dose and used for the following experiments.

3.2. Effect of pH
It is known that pH of the aqueous solution is a parameter that significantly affects the adsorption of ionic species on solid adsorbents. The effect of pH variation on Cr(VI) removal kinetics was studied at pH values of 1.0, 2.1, 3.1, 4.0, 5.1 and 6.2.

Fig. 2 depicts the experimental results of pH influence on the adsorption of Cr(VI). It can be seen that rate of Cr(VI) adsorption on EAC significantly decreases with increasing pH. Moreover, the adsorption process proceeds in two steps: a first rapid stage at the beginning of the adsorption, followed by a second one, less rapid. It is important to point out that, by increasing the pH from 5.1 to 6.2, only a small decrease of Cr(VI) adsorption rate was noticed. The effect of pH can be explained by considering the decrease of the number of positively charged adsorption centers for anionic chromium species, with decreasing concentration of hydronium ions in solution [16]. This phenomenon may be also be ascribed to the speciation of Cr(VI) in aqueous solutions; it is known that hexavalent chromium exists mainly as oxyanions of bichromate (pH < 6.5) and of chromate (pH > 6.5) [17]. Therefore, with
increasing pH, the abundance of HCrO$_4^-$ decreases, while that of CrO$_4^{2-}$ increases. This means that, with increasing pH, increasingly more anionic chromium species need two positively-charged centers for the adsorption process.

### 3.3. Study of reaction order

The kinetics of Cr(VI) adsorption on the EAC was analyzed using the pseudo first-order and pseudo second-order models. The linearized forms of the two kinetic models can be expressed in the form of Eqs. 1 (pseudo first-order) and 2 (pseudo second-order) [18]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$  \hspace{0.5cm} (1)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{0.5cm} (2)

where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_t$ is the adsorption capacity at time $t$ (mg/g), $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the pseudo first-order and, respectively, pseudo second-order adsorption rate coefficients. $q_e$ and $q_t$ were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M}$$  \hspace{0.5cm} (3)

$$q_t = \frac{(C_0 - C_t)V}{M}$$  \hspace{0.5cm} (4)

where $M$ is the mass of EAC 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 $\log(q_e - q_t)$ vs. $t$ (pseudo first-order), a straight line should be obtained, which allows computation of $k_1$ and $q_e$ from the slope and intercept of the plot, respectively. Similarly, the plot of $t/q_t$ vs. $t$ (pseudo second-order) enables the $k_2$ and $q_e$ to be determined from intercept and the slope of the plot, respectively. The statistical fits of the experimental data to equations (1) and (2) and the parameters of the two kinetic models are given in Table 1 and 2, respectively.

### Table 1. Regression equations and correlation coefficients for kinetic experimental data at different initial pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Kinetic model</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
<th>$k_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
<th>$q_{eexp}$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Pseudo first-order</td>
<td>0.196</td>
<td>2.29</td>
<td>0.023</td>
<td>3.62</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Pseudo second-order</td>
<td>0.068</td>
<td>2.15</td>
<td>0.008</td>
<td>3.74</td>
<td>2.00</td>
</tr>
<tr>
<td>3.1</td>
<td>Pseudo first-order</td>
<td>0.036</td>
<td>1.99</td>
<td>0.008</td>
<td>2.96</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Pseudo second-order</td>
<td>0.025</td>
<td>1.24</td>
<td>0.022</td>
<td>1.96</td>
<td>1.70</td>
</tr>
<tr>
<td>5.1</td>
<td>Pseudo first-order</td>
<td>0.017</td>
<td>1.22</td>
<td>0.015</td>
<td>1.36</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>Pseudo second-order</td>
<td>0.017</td>
<td>1.09</td>
<td>0.014</td>
<td>1.75</td>
<td>1.45</td>
</tr>
</tbody>
</table>

It is shown in Table 1 that pseudo first-order kinetic model provided the best match for the experimental data recorded over the pH range of 1.0 - 3.1, since the correlation coefficients for this model are better than for the pseudo second-order model; in contrast, over the pH range of 4.0 - 6.2, adsorption of Cr(VI) fits the best the pseudo-second order model. This conclusion is also suggested by the comparison made in Fig.5 between the predicted equilibrium adsorption capacity ($q_e$) and the experimental determined equilibrium adsorption capacity ($q_{eexp}$); it can be seen that predicted $q_e$ values fits the best the experimental $q_e$ values for the pseudo first-order model over the pH range of 1.0 - 3.1, and for the pseudo second-order model over the pH range of 4.0 - 6.2. Figs. 3 - 5 depict the dependence of adsorption rate coefficients and equilibrium adsorption capacity as a function of pH, showing that rate of Cr(VI) adsorption on EAC continuously decreases with increasing pH; additionally, the results of this study indicate that also the EAC equilibrium adsorption capacity is detrimentally affected by the increase of pH.
Hexavalent chromium has an extremely high toxicity and mobility. Consequently, it should be removed from contaminated wastewaters prior to their discharge into natural waters. Activated carbons are suitable sorbents for the removal of heavy metals from contaminated waters. The kinetics of Cr(VI) adsorption on extruded activated carbon Norit Row 0.8 Supra was studied in batch scale. The rate of Cr(VI) adsorption was found to be strongly dependent on EAC dose and pH: the adsorption rate increases with increasing dose and with decreasing pH. By comparing the $R^2$ correlation coefficients for each linear transformation of the kinetic analysis, it was found that Cr(VI) adsorption followed pseudo first-order kinetics over the pH range of 1.0-3.1, and pseudo second-order kinetics over the pH range of 4.0-6.2. Two main causes were suggested to explain the effect of pH on Cr(VI) adsorption rate: the increase of the number of positively-charged surface groups with increasing pH, and the increase of the abundance of bivalent anionic chromium species ($\text{CrO}_4^{2-}$) with increasing pH. The results of this work suggests that Norit Row 0.8 Supra could represent a suitable absorbent material for the removal of Cr(VI) from contaminated waters.

References:
[6] M.Z. Hauschild, Putrescine (1,4-diaminobutane) as an indicator of pollution-induced stress in...
higher plants: barley and rape stressed with Cr(III) or Cr(VI), *Ecotoxicology and Environmental Safety*, Vol.26, 1993, pp.228-247.


