Removal of chromium ions through adsorption onto activated carbon: equilibrium study

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Abstract

The equilibrium studies for dichromate anion adsorption from aqueous solution on commercial activated carbon (CAC) were carried out under different conditions of the initial concentrations (0.02 to 0.4 mg mL^{-1}), the adsorbent amount (0.2 g to 1 g), the adsorbent size and the initial solution pH, at room temperature. Dichromate anion removal was favoured by a smaller initial concentration (0.02 mg mL^{-1}), a smaller size of the adsorbent ($d < 1$ mm), as well as by a higher amount of CAC (2 g) used in the lab studies. The experiments performed over a pH range between 2.2 and 6.1 under the present study reveal that the maxima adsorption capacity of anion is at about pH 2.2 and it decrease above pH 3. The equilibrium data have been fitted by using Langmuir and Freundlich adsorption models. The values of the constants obtained using these two models proved contradictory. Based on these values, we concluded that the Freundlich adsorption isotherm is more suitable for describing the equilibrium data than the Langmuir one.
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Keywords: anionic adsorption; commercial activated carbon; Freundlich isotherm, Langmuir isotherm.

Introduction

The presence of dichromate anions is an important environmental problem. It is considered one of the main pollutants in surface waters, since, even at low concentrations, it is harmful to both plants and animals and human health. Even if chromium has a carcinogen potential, it is widely used in electroplating, leather tanning, metal finishing, chromate preparation, the paint and textile industries

(Rani et al., 2010). Chromium is present in natural systems either in the + 3 or + 6 oxidation state, and it has a low allowable limit for industrial wastewaters before its discharge into aquatic systems (Reyes-Gutierrez et al., 2009). The mobility and transport form of chromium depends on its physico-chemical properties and on the co-presence of other chemical species in natural systems. Chromium speciation is pH dependent, with $Cr_2O_7^{2-}$ present in acidic media, and CrO_4^{2-} present at pH values above 7. At a pH higher than 5, the fraction of the $Cr_2O_7^{2-}$ species decreases rapidly with the increase in pH value (Popuri et al., 2007).

Over the last years, special emphasis has been placed on the preparation of different adsorbent materials. The adsorption process of hexavalent chromium has been studied extensively, using low-cost/natural ad-sorbents such as: *Acacia* bark (Rani et al., 2010), tamarind fruit shells (Popuri et al., 2007), rice husk (Bishnoi et al., 2004), tea-leaves waste (Mozumder et al., 2008), lignin (Demirbas, 2005) etc. Commercial activated carbon (CAC) remains, however, a cheaper material, with good results in the adsorption of cations/anions or dye/conventional chemi-cals. The preparation of CACs from a wide range of low-cost materials has been reported in the literature by several researchers (Kannan and Murugavel, 2008, Milenkovic et al., 2009, Ninkovic et al., 2010, Suteu et al., 2011).

The objective of the present paper was to study the adsorption ability of commercial activated carbon – CAC (the sample was initially used in aquarium-like pellets with a specific surface area of 890 $m^2 \cdot g^{-1}$) for dichromate anions from an aqueous solution, under conditions of different initial concentrations, pH values and sizes of the adsorbent. The equilibrium isotherm data were fitted against the Langmuir and Freundlich equations, and the values of the adsorption constants were determined.

Materials and methods

1. Chemicals

The solutions to be tested were obtained by diluting a stock solution of potassium dichromate until reaching the desired concentrations. The stock solution was obtained by dissolving a suitable amount of potassium dichromate (Merck) in bidistilled water, so as to obtain a 1 mg $Cr_2O_7^{2-}$ mL^{-1} solution. The initial solutions desired were prepared by diluting different volumes of stock solution (1, 2, 5, 10, 15 and 20 mL) until reaching exactly 50 mL of solution, therefore the initial anionic solutions varied between 0.02 and 0.4 mg·mL^{-1}. All the chemicals were analytical grade and the solutions were prepared using bidistilled water.

2. Adsorption equilibrium

In the present paper, a large-grained (4x8 mesh) sample of activated carbon was used (with a specific surface area 890 $m^2 \cdot g^{-1}$). The sample in question was washed with doubly-distilled water in order to remove any impurity or powder of activated carbon, and then dried for 8h at a temperature of 105°C. The material was later ground and sieved so as to obtain three classes of particle sizes, namely $d > 3$ mm, $d < 2$ mm, and $d < 1$ mm, respectively. Equilibrium studies were carried out by placing different masses (1 or 2 g) of CAC in contact with 50 mL of anion solution of different initial concentrations (0.02 to 0.4 mg·mL^{-1}). Before mixing the solutions with the adsorbent, the pH values were established, the experiments being conducted at an initial pH of 3.8. The flasks were shaken at 150 rpm for 1h, at room temperature (24±1°C). After filtration, the supernatant solutions were photometrically analyzed using an MPM 1500 microprocessor photometer, at 445 nm. The anion concentrations in the solution were determined before and after the adsorption process. The calibration curve was devised using the dichromate solution, and it was very reproducible and linear throughout the entire concentration range used in the present paper.

The percentage of dichromate anion removal ($R\%$) by CAC has been calculated by using the equation:

$$R\% = \frac{c_0 - c_e}{c_0} \cdot 100 \tag{1}$$

where c_0 and c_e are the initial and equilibrium concentrations in the solution, respectively.

The amount of adsorbed anion at equilibrium, q_e (mg·g^{-1}), was calculated using (Eq. 2):

$$q_e = \frac{(c_0 - c_e) \cdot V}{m} \tag{2}$$

where V (mL) is the volume of the solution, and m (g) is the mass of dry adsorbent used in the experiment.

3. Effect of contact time

Former experiments were carried out in order to study the influence of contact time on the adsorption process (Rani et al., 2010, Bishnoi et al., 2004). Thus, a known quantity of sorbent (1 g, $d > 3$ mm) was placed in contact with 100 mL of anion solution of 0.4 mg·mL^{-1}, and shaken at room temperature, for a given amount of recorded time (10, 30, 60, 120, 180 and 240 min., respectively). The anion concentrations and the value of adsorption q_t (mg·g^{-1}) at time t were similarly calculated.

4. Effect of adsorbent dosage

In order to investigate the effect of the adsorbent mass on the adsorption process, different amounts of CAC (0.2 g to 1 g) have been used by contacting them with 50 mL of anionic solution of different initial concentrations (see above). The samples were shaken at 150 rpm, for 1h, at room temperature (24±1ºC). For studying this effect has been used the same experimental set up as described above.

5. Effect of pH

The effect of pH on dichromate anion adsorption has been analyzed over the pH range from 2 to 6, at room temperature. In the present study, 100 mL of dichromate anion solution of 0.4 mg·mL^{-1} were placed in Erlenmeyer flacks and 1 g of CAC ($d < 1$mm)

was added. The values of the pH were initially adjusted with droplets of 0.1M HCl or 0.1M NaOH, so that the pH values of the initial solutions in the conical flasks were 2.2, 2.7, 3.1, 4.0, 5.1 and 6.1, respectively. The values of pH measurements have been performed by using a digital pH-meter (Hanna Instruments). The experimental procedure described above was followed once more.

Results and discussion

1. Effect of contact time

A separate experiment was carried out with a maximum initial concentration of $Cr_2O_7^{2-}$ (0.4 mg·mL^{-1}), at 24°C, and it was discovered that the contact time necessary to reach the equilibrium is of about 60 min. Figure 1 shows the influence of the contact time on the adsorption of Cr(VI), indicating that the percentage of anion removal by the adsorbent increased initially, but, after about 60 min., almost a constant value has been obtained.

After a 1h-long experiment, no significant change in the removal percentage was observed, and the equilibrium between adsorbent and adsorbate was achieved under working conditions. The same conclusion was found in the literature (Rani et al., 2010). Other researchers discovered that a long contact time (more than 1h) of Cr(VI) with activated rice husk resulted in the desorption of the anion (Bishnoi et al., 2004).
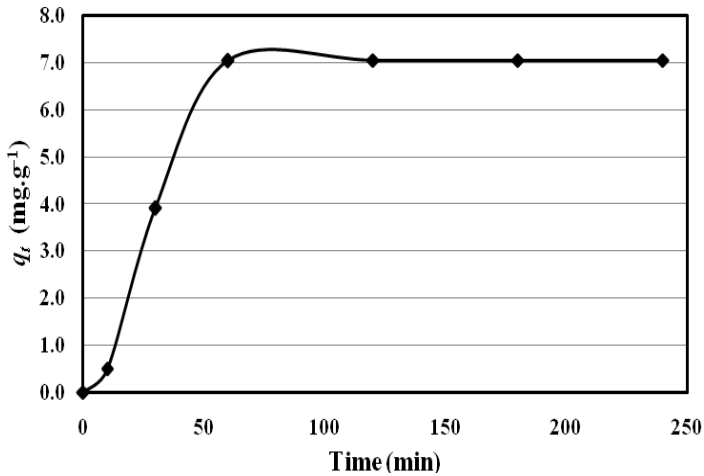
Fig. 1 Effect of time contact on the adsorption of the dichromate anion. Conditions: $c_0 = 0.4$ mg·mL^{-1}, CAC dose = 1 g (d >3 mm), 24°C

2. Effect of adsorbent dosage

In order to investigate the influence of the adsorbent amount on anion adsorption, a series of experiments were carried out using different masses of CAC and different dichromate concentrations. The results showed that for the smallest size of CAC ($d <$ 1 mm) the best yield of the process are attained. Figure 2 illustrates how the increase in adsorbent amount led to an increase in anion adsorption on CAC, from 55.74% to 83.14%, for an initial solution of 0.02 mg·mL^{-1}. This can be attributed to the increase in adsorbent surface area, as well as to more adsorption sites being available as a result of the greater adsorbent amount.
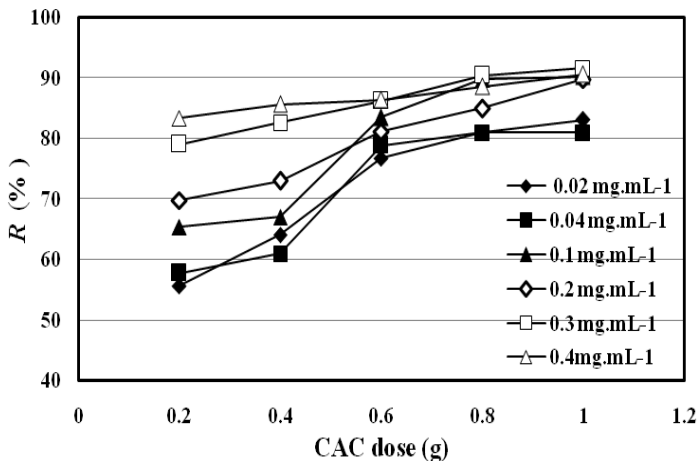

Fig. 2 Effects of adsorbent dosage ($d < 1$mm) on the percentage of dichromate anion removal. Conditions: 50 mL initial solution, $c_0 = 0.02 \div 0.4$ mg·mL^{-1}

The maximum removal percentage was obtained for 1 g of CAC with a 0.3 mg·mL^{-1} anion solution (91.71%). It is also noteworthy that after the contact of 0.6 g CAC with 50 mL anion solution, there is no significant change in the anion removal percentage. This may be explained by the fact that, above this optimum amount of CAC, the adsorbent-adsorbate equilibrium was attained under working conditions (contact time = 1h, 24°C).

3. Effect of the initial concentration

efficiency of the dichromate adsorption process was examined by plotting the anion removal percentage against different initial concentrations (Fig. 3). It was, thus, observed that the removal process is favoured by small anion concentrations (0.02 mg·mL^{-1}) and smaller diameters (less than 1 mm) of CAC. As expected, the anion removal percentage increased along with the initial adsorbent amount. For 1 g of CAC (d >3 mm) used in the experiment, the percentage varied from 36.17% to 41.69%, while for 2 g of CAC (d >3 mm), the percentage varied from 58.17% to 70.50%, respectively.

Further observations proved that the percentage of dichromate removal increases with the increase of CAC concentrations. For the same amount of adsorbent, when the anion concentration increases there is a decrease in the removal percentage of dichromate, maybe due to the accumulation of anion on the surface. The observation is in good agreements with other literature data (Ekpete et al., 2010).

4. Effect of the pH on dichromate adsorption

The initial pH of the anion solution is an important parameter in the adsorption process. The amount of anion adsorbed onto CAC is higher for pH values between 2.2 and 2.7 and lower for a pH above 3 (Fig. 4). Consequently, adsorption increases along with acidity, and decreases dramatically at pH values above 4, independent of the amount of CAC. The maximum anion adsorption found to be about 83.14% at pH 2.2 and decrease to about 12.16% at pH 6.1. Previous reports on Cr(VI) adsorption by activated carbon showed that anion removal is enhanced in the acidic range, with an optimum value at pH 2, followed by a decrease in adsorption for pH values above 4 (Mozumder et al., 2008).
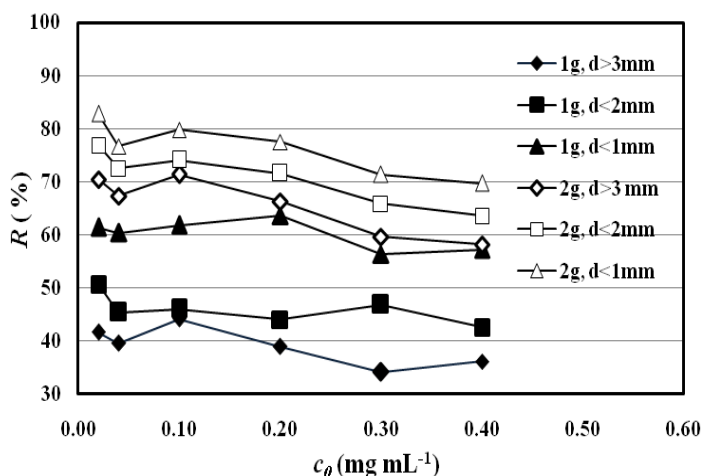

Fig. 3 Effects of initial concentration on the percentage of dichromate anion removal from the initial solution. Conditions: c_0 = 0.02÷0.4 mg·mL^{-1}, CAC dose = 1–2 g, contact time=1h, 24°C
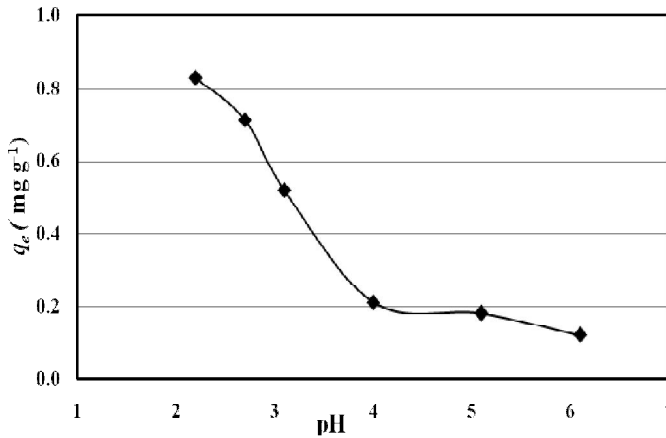
Fig. 4 Effects of the pH on dichromate anion adsorption from solution onto CAC.
Conditions: $c_0 = 0.4$ mg·mL^{-1}, 1 g CAC, diameter < 1mm, contact time=1h, 24°C

Furthermore, the optimum adsorption of Cr(VI) on modified lignin was found to occur at a pH of 2, while, for higher pH values, the positively charged ligands bound the negatively-charged anion (Demirbas, 2005). Other researchers used activated rice husk to adsorb Cr(VI), and they also found that the optimum pH value for adsorption is 2 (Bishnoi et al., 2004).

At low pH values, the surface of CAC is in protonated form, and a stronger attraction for active CAC sites appears for anionic species. Potassium dichromate is totally ionized in solution, and negative ions are attracted to the protonated surface of CAC via electrostatic forces. The fact that the adsorbed amount decreased along with the pH values is attributed to the presence of hydroxyl ions at higher pH values, which prevented the uptake of dichromate ions. At these higher pH values, the deprotonation process starts and OH$^-$ ions compete with dichromate anions on sorption sites, thereby causing decreased adsorption process.

5. Adsorption equilibrium

The adsorption isotherms show the anion distribution between the liquid and solid phases in the equilibrium state. The adsorption isotherm obtained for anion adsorption using different CAC sizes is presented in Figure 5.

As expected, the amount of anion adsorbed per unit mass of CAC increased with the increase in the initial concentration of the anion, on the one hand, and with the decrease of the initial dose of adsorbent, on the other. This decrease in adsorption can be attributed to the lack of available active sites at high initial concentrations of the $Cr_2O_7^{2-}$ anion and at high initial doses of adsorbent. Activated carbon has a porous structure, with a large internal surface. The same steps in the process of adsorption onto porous materials are presented in the literature: first, the adsorbed species migrates through the solution (diffusion), followed by the movement of the solute from the particle surface into interior sites, and, finally, the adsorbate is adsorbed into the active sites in the interior of the adsorbent particle (Hameed et al., 2007). Similar results to those obtained in the present study have been reported in the literature for the removal of dyes (Hameed et al., 2007, Kannan and Murugavel, 2008) or cations (McKay et al., 1989) onto CAC or other adsorbent materials.
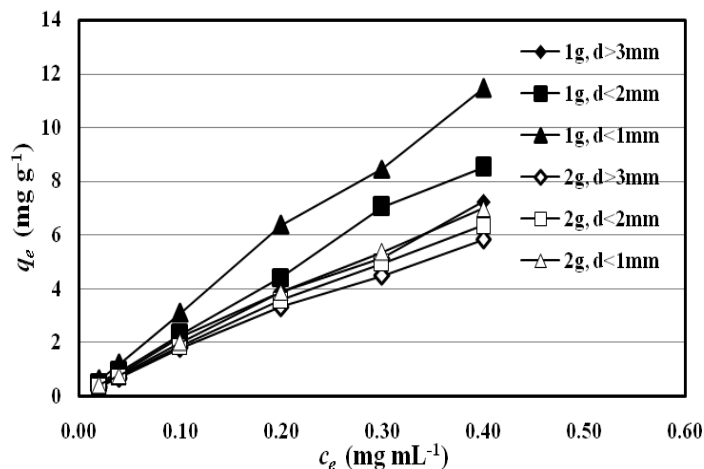
Fig. 5 Equilibrium adsorption isotherm of the dichromate anion on different amounts of CAC. Conditions: $c_0 = 0.02 \div 0.4$ mg·mL^{-1}, contact time=1h, 24°C.

In order to estimate the adsorption abilities of CAC under various conditions, the Langmuir isotherm for monolayer was used. The isotherm theory assumes that adsorption takes places at specific homogeneous sites inside the adsorbent; once an ion occupies a site, no further adsorption takes place at this site, until monolayer saturation is achieved. The Langmuir equation, (Eq. 3) was modeled using the equation below (Isac et al., 1995, McKay et al., 1989):

$$\frac{c_e}{q_e} = \frac{1}{q_{max} \cdot K_L} + \frac{c_e}{q_{max}} \tag{3}$$

where q_e (mg·g^{-1}) = the amount of anion adsorbed at equilibrium per unit mass of CAC, q_{max} (mg·g^{-1}) = the maximum adsorption capacity, K_L (mL·mg^{-1}) = the Langmuir constant related to the energy of adsorption. The plotting of specific adsorption against equilibrium concentration (Fig. 6) rendered the linear isotherm parameters of q_{max} and K_L, which are presented in Table 1.

The Langmuir equation gave a good fit for experimental data on dichromate anion adsorption within the concentration range used in the present study. The significance of q_{max} is that of maximum adsorption capacity of the adsorbent, corresponding to complete monolayer coverage. The values of q_{max} appear to be higher for the dichromate anion in the case of 1 g of CAC (maximum adsorption capacity of 58.82 mg·g^{-1}), compared to that of 2 g CAC (adsorption capacity of 14.02 mg·g^{-1}) used in the experiment.

The adsorption coefficient, K_L, which is related to the apparent energy of adsorption for the dichromate anion, is higher for 2 g of CAC (7.88 mg·mL^{-1}), and lower for 1 g of CAC (1.14 mg·mL^{-1}) used in the experiment. Similar conclusions were reported for the adsorption of methylene blue on bamboo-based activated carbon, confirming the homogeneous nature of the bamboo carbon surface, with the formation of a monolayer coverage of dye molecules on this surface (Hameed et al., 2007). Other

authors were reported results for the adsorption of phenol on activated carbon preparated from agriculture products (pumpkin) (Ekpete et al., 2010).
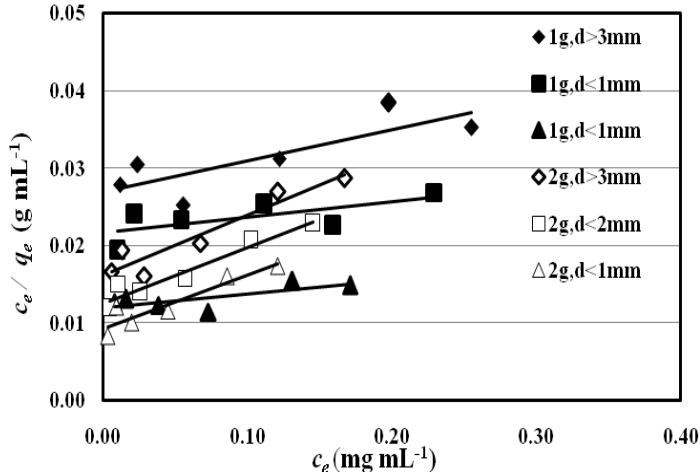

Fig. 6 Langmuir adsorption isotherm of the dichromate anion for different amounts of CAC. Conditions: $c_0 = 0.02 \div 0.4$ mg·mL^{-1}, contact time = 1h, 24°C

The favorability of the adsorption process can be expressed in terms of the dimensionless equilibrium parameter, (Eq. 4) (McKay et al., 1989):

$$R_L = \frac{1}{(1 + K_L \cdot c_0)} \qquad (4)$$

where K_L is the Langmuir constant and c_0 is the highest anion concentration in the solution (mg·mL^{-1}). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The values of R_L for CAC were between 0.241 and 0.724, which means that the adsorbent is suitable for anion adsorption under the conditions used in the present study (Table 1).

Table 1 Equilibrium constants obtained for the adsorption of $Cr_2O_7^{2-}$ onto CAC from the Langmuir equation

CAC dose (g)	Size	q_{max} (mg·g^{-1})	K_L (mg·mL^{-1})	R^2	R_L
	d >3 mm	25.64	1.44	0.659	0.634
1	d <2 mm	50.02	0.95	0.660	0.724
	d <1 mm	58.82	1.14	0.634	0.638
	d >3 mm	12.98	4.89	0.902	0.342
2	d <2 mm	13.88	6.02	0.938	0.294
	d <1 mm	14.02	7.88	0.865	0.241

The Freundlich isotherm model assumes the presence of heterogeneous surfaces, where the energies vary as a function of the surface coverage. The equation is an empirical one, and it is based on sorption on a heterogeneous surface, suggesting that the binding sites are not equivalent. The adsorption data were analyzed using the linearized forms (Eq. 5) of the Freundlich isotherm (Isac et al., 1995, McKay et al., 1989):

$$\lg q_e = \lg K_F + \frac{1}{n} \lg c_e \tag{5}$$

where, q_e (mg·g^{-1}) = the amount of anion adsorbed at equilibrium per unit mass of CAC, K_F [(mg·g^{-1}) (L·mg^{-1})$^{1/n}$] = the Freundlich constant related to adsorption capacity, $(1/n)$ = the intensity of the adsorption.

The values of the Freundlich parameters were obtained based on the graphic representation of *lg c_e vs lg q_e* (Fig. 7). The plot gives straight lines with slope equal with $(1/n)$, which indicates that the adsorption of the dichromate anion follows the Freundlich isotherm. The parameters of the process are provided in Table 2.
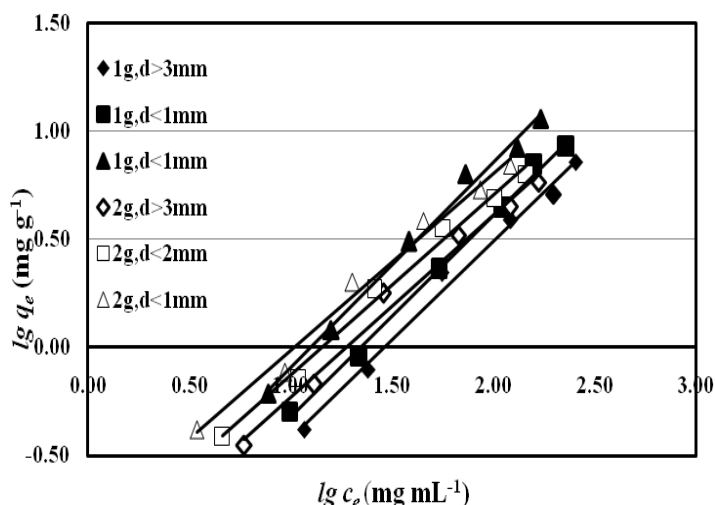

Fig. 7 Freundlich isotherm of dichromate anion adsorption onto different amounts of CAC. Conditions: $c_0 = 0.02 \div 0.4$ mg·mL^{-1}, contact time = 1h, 24°C

The value of K_F can be defined as the adsorption coefficient, and it represents the anion quantity adsorbed onto a unit of CAC at equilibrium concentration. The value of *(1/n)*, ranging between 0 and 1, is a measure of adsorption intensity; the surface of the adsorbent becomes more heterogeneous as its value approaches zero (Hameed et al., 2007). The Freundlich equation gave a very good fit for experimental data of dichromate anion adsorption, in the concentration range used in experiment. The values of K_F show that the adsorption process had better results for the adsorbent with the smallest particle size ($d < 1$ mm), while for the other two groups of CAC, the adsorption coefficient is nearly equal. The values of the *n*

parameter indicate a favorable process for anion adsorption onto CAC. Its values show a proper increasing trend with the increase in specific adsorbent surface, from 1 g to 2 g of CAC.

As can be seen in the Table 2, the Freundlich model yields a somewhat better fit, than Langmuir model. Thus, one can say that the Freundlich model describe better the adsorption process of anion than Langmuir model. The R-squared value (a criterion for good fit) was found to be close to 1, indicating that the Freundlich isotherm is more applicable than the Langmuir isotherm (tabs. 1 and 2), due to a limited set of actual data.

The values obtained for both the q_{max} and K_F constants on the CAC sample used in the experiments of the present study are smaller than those provided in the literature for different classes of activated carbon. However, the present CAC sample needs optimization for a large capacity of adsorption for dichromate anions.

Table 2 Equilibrium constants obtained for $Cr_2O_7^{2-}$ adsorption onto CAC based on the Freundlich equation

CAC dose (g)	Size	K_F [(mg·g^{-1}) (L·mg^{-1})$^{1/n}$]	n	R^2
	$d > 3$ mm	0.046	1.095	0.990
1	$d < 2$ mm	0.056	1.075	0.995
	$d < 1$ mm	0.091	1.053	0.992
	$d > 3$ mm	0.084	1.183	0.985
2	$d < 2$ mm	0.109	1.200	0.992
	$d < 1$ mm	0.147	1.219	0.986

Conclusions

It is evident that the use of commercial activated carbon (CAC) for dichromate anion removal appears to be both a feasible and an attractive technique for the treatment of polluted wastewaters. The advantages of using CAC are the system simplicity and the large effluent concentrations range.

In the present study, the adsorption of the dichromate anion from aqueous solution was investigated using commercial activated carbon (CAC) as adsorbent. The results indicated that the adsorption capacity of the adsorbent was considerably influenced by the initial concentration, pH, size and amount of adsorbent. The results showed that the percentage removal of anion was favored by smaller initial concentration (0.02 mg·mL^{-1}). The percentage removal of dichromate anion from solutions was favored by smallest size of adsorbent ($d < 1$ mm) and also by the amount

of CAC (2 g) used in the experiments. Dichromate anion adsorption was also found to be pH-dependent, since the removal efficiency decreases from pH 2.2 to pH 6.1.

For experimental data, Langmuir and Freundlich models have been used to find out the appropriate mechanism of anionic adsorption. The constant values obtained within these two models showed contradictory results. Thus, the values of q_{max} are higher for the dichromate anion in the case of 1 g of CAC, compared to that of 2 g CAC. The value of K_F showed that the adsorption process rendered better results for an adsorbent with small-sized particles ($d < 1$ mm), while for the other two groups of CAC the adsorption coefficient is nearly equal. Concerning the values the R-squared parameter it can be suggested that Freundlich model is preferable than Langmuir model for dichromate removal in this concentrations domain.

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