Removal of Cr(VI) from aqueous solution by a commercial carbon black

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ABSTRACT

Hexavalent chromium is classified as a human carcinogen of high carcinogenic hazard according to the US EPA. Therefore, batch adsorption experiments aiming at Cr(VI) removal from an aqueous solution were carried out using a commercial carbon black (CB) as an adsorbent. The CB was characterized by the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda, scanning electron microscopy with energy dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy methods. Various parameters were tested, including adsorbent dose, solution pH, contact time, initial metal concentration, and temperature, so as to determine their relation to the adsorption yield. The results showed that an initial solution of pH 2.4 was most favorable for the Cr(VI) removal. The equilibrium data were analyzed by the Freundlich, Langmuir, and Temkin isotherm models. The equilibrium data best fitted according to the Freundlich isotherm model. The CB maximum adsorption capacity was found at 33.22 mg/g, thus proved to be promisingly efficient in comparison to other low-cost adsorbents. The thermodynamic parameters yielded by this study showed that the Cr(VI) adsorption on the CB was the spontaneous exothermic process.

Keywords: Adsorption; Carbon black; Cr(VI); Desorption; Equilibrium; Thermodynamics

1. Introduction

Carbon black (CB) is extrinsic carbonaceous component formed in the gaseous phase by the thermal decomposition of hydrocarbons. Several types of CB exist, such as furnace black, channel black, lamp black, thermal black, and acetylene black. These terms refer to the relevant manufacturing processes which essentially involve decomposition either of liquid or gaseous hydrocarbons at elevated temperatures and reduced oxygen content. Nowadays, its worldwide annual production mostly refers to the furnace black process by which hydrocarbons are partially combusted and immediately quenched with water. Various technologies use CB, e.g. as a reinforcing filler in rubber (approximately 80%), as a black pigment in coatings, inks, and toners, as an electrically conductive agent in plastics, and as a catalyst support in the proton exchange membrane fuel cells [1].

The list of potentially toxic elements commonly includes arsenic, chromium, copper, lead, mercury, cadmium, nickel, and zinc. Some of them could be assimilated, stored, and concentrated by humans, resulting in numerous health problems. Among them, chromium is widely used in all sorts of industries. Taking into account the total chrome ore production, some 90% is used in metallurgical industries for the

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steel, alloy, and nonferrous alloy production, whereas the rest is equally used in refractory (iron and steel, cement, glass, ceramics, and machinery) and chemical (leather tanning, plating, wood preservation, and pigment) industries [2,3].

Chromium is commonly found in oxidation states 0, III, and VI. Cr(VI) species are known as toxic and carcinogenic, causing health problems, e.g. liver damage, pulmonary congestions, vomiting, and severe diarrhea, whereas less toxic Cr(III) form can be readily precipitated out of solution in the form of $Cr(OH)_3$ [3]. The latter is essential for human nutrition (especially for the maintenance of glucose metabolism), and is relatively immobile, thus being innocuous. Quite contrarily, Cr(VI) which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) poses significantly higher levels of toxicity. Accordingly, governments are urged to impose very restrictive regulations for chromium species. Hereby, in Croatia, the upper limit for the discharge of Cr(VI) into wastewater is 0.1 mg/L [4].

Since the Cr(VI) pollution has been increasingly recognized, major advances have been made by the scientific community as to how to protect the general population from its exposure. Herewith, countless treatment technologies have been developed to remove chromium from water and wastewater. The most often used are precipitation processes, including the hydroxide, sulfide, carbonate, and phosphate precipitation. Their disadvantage is the production of sludge which is a solid waste, while its disposal poses a serious problem. Ion exchange is considered a better alternative method. However, it is not economically appropriate due to high operational costs. The adsorption process has been studied as one of the most commonly adopted method due to its low initial costs, the simplicity of its design, the operation easiness, and finally its resistance to toxic substances. Hereby, it is regarded as one of the most efficient methods for the removal of toxic and nonbiodegradable compounds such as heavy metals [2,3]. More precisely, it is one of the preferred methods for the Cr(VI) removal from aqueous solutions owing to its efficiency as well as its low cost [3,5–10]. Activated carbon is commonly used as a highly efficient adsorbent due to its large surface area, microporous structure, high adsorption capacity, etc. However, its use is limited due to its high cost and low selectivity.

Following the literature survey, it has been learned that a commercial CB had not been used as an adsorbent for the Cr(VI) removal from aqueous solutions. The aim of this work was to determine the Cr(VI) removal from synthetic aqueous solutions using the commercial CB as a nonconventional adsorbent. The

examined parameters, possibly influencing the adsorption process, were as follows: adsorbent dose, contact time, concentration of adsorbate, temperature, and pH solution.

2. Methods

2.1. Preparation and characterization of the adsorbent

A commercial CB is regularly produced by the oil furnace process in Croatia. It is based on the partial combustion of a highly aromatic hydrocarbon fraction. The raw materials were the aromatic oil derivatives produced by the secondary petroleum refining processes. The CB is formed in the furnace by partial oxidation and cracking of the oil feedstock at 1,573–1,673 K, and is transferred by the gas flow to a heat exchanger and a quench cooler, where the temperature is reduced to about 473 K.

The CB samples were grounded and sieved to the particle size ≤0.1 mm.

The fourier transform infrared spectroscopy (FTIR) analysis was used to identify the surface functional groups of the CB sample in the range from 4,000 to 650 cm^{-1} by the Spectrum One FTIR spectrometer, Perkin–Elmer (UK). Sample was characterized in its basic form without any preparation, using the attenuated total reflectance chamber.

The surface area properties were determined by the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) methods using the Micromeritics ASAP 2000 (USA) adsorption instrument. The average pore diameter was calculated using the equation:

$$d = \frac{4 \cdot V_p}{S_p} \tag{1}$$

where V_p is specific volume, and S_p is specific surface area. Pore size distribution of the CB was calculated by the BJH method. Prior the analysis, the CB sample was heated at a temperature of 323 K, and evacuated under the pressure of 666.5×10^{-3} Pa in order to remove any contaminants as well as moisture possibly present on its surface.

The surface morphology of the CB samples was examined using the scanning electron microscope (SEM) Tescan Vega TS 5136 MM (Czech Republic) with the Bruker energy-dispersive spectrometer (EDS) by point analysis.

2.2. Adsorption experiments

The stock solutions were prepared by dissolving 2.8 g of $K_2Cr_2O_7$ (Merck, Germany) in 1 L deionized

water, thus obtaining a concentration of 1,000 mg/L. Standard solutions of the required Cr(VI) concentrations were prepared by the appropriate dilutions.

The batch adsorption experiments were carried out using 100 mL conical flasks containing 50 mL of the test solutions at the desired initial chromium concentrations (50–250 mg/L). Throughout the experiment, the contact time was varied from 5 to 120 min. In order to assess the influence of an adsorbent dose on the adsorption process, the fixed initial chromium concentrations (200 mg/L) were stirred for 75 min with the different CB quantities (2.5, 5, 10, 20, and 25 g/L) at pH 2.4.

The effect of pH on the Cr(VI) adsorption was studied at different pH values (2.4; 3.5; 5.0), with the optimum dose and the initial Cr(VI) concentrations of 200 mg/L at 293 K. The pH of the solution was adjusted to its appropriate value and maintained constant throughout the experiment, using either 0.1 mol/L HCl (Carlo Erba, Italy) or 0.1 mol/L NaOH (Carlo Erba, Italy).

Adsorption isotherm studies were carried out with different initial concentrations of Cr(VI) ions, from 50 to 250 mg/L, at pH 2.4 and the adsorbent dose level of 5 g/L. The time required for reaching the equilibrium condition was estimated at regular intervals till it was achieved (75 min). Following the reaction period, the suspensions were filtered through a Whatman filter paper No. 44, and the supernatant was analyzed for the Cr(VI) concentration. The violet color, resulting from the reaction between the Cr(VI) ions and 1,2-diphenylcarbazide (Prolabo, G. Britain) in acidic medium, was measured using the Camspec M-107, Jencons (UK) spectrophotometer at 540 nm.

The effect of the solution temperature on the adsorption process was studied by determining the adsorption isotherms at three different temperatures (293, 313, and 333 K).

All the reagents used in the study were of analytical grade.

2.3. Desorption experiment

Following the adsorption experiments with 200 mg/L of Cr(VI) ion solution, the metal ion loaded onto the CB was separated by filtration. The CB was washed with deionized water to remove any unadsorbed chromium ions. The spent CB was mixed with 50 mL of 0.1 mol/L and 0.3 mol/L HCl solution for 75 min. The desorbed chromium ions were estimated as described above. The regenerated adsorbent sample was reused in the next cycle of the adsorption experiment. The Cr(VI) recovery was defined as the percentage ratio of the equilibrium adsorption capacity of the regenerated adsorbent to the one of the untapped adsorbent. The adsorption–desorption experiments were conducted for three cycles [11].

3. Results and discussion

3.1. Characterization of the adsorbent

The basic properties of the commercial CB are presented in Table 1. It is a carbonaceous material with the high content of carbon (>98%), sulphur (1%), and ash (0.27%). Fundamentally important features of adsorbents are their porosity and commonly a high surface area. Hereby, their most important characteristics relate to the total pore volumes, pore size distribution, and the specific surface area. The value of the CB's BET surface area was found to be $S_{BET} = 107.29$ m^2/g. This value could be explained by its fine-grained particle size as well as its porous nature. The total pore volume (1.7–300 nm) was calculated at the relative pressure close to the saturation in the adsorption branch, yielding $V_p = 743 \times 10^{-3}$ cm^2/g. The average pore diameter was $d = 16.99$ nm. According to the IUPAC, the pores of the porous material are classified in three groups: micropores (width $d < 2$ nm), mesopores (2 nm $< d < 50$ nm), and macropores ($d > 50$ nm). Above the 50 nm pore radius, the pore surfaces are difficult to distinguish in properties from an external surface. The obtained results show that the CB may be considered as a mesoporous material [12].

The FTIR analysis provides the information on the surface chemistry of the examined samples. The FTIR spectra of the CB are shown in Fig. 1. The CB sample exhibited some characteristic peaks, at wavenumbers of 2,357 and 2,324 cm^{-1}, which were ascribed to the carbonyl groups in R–(C=O)–R′. The peak at 2,100 cm^{-1} was attributed to the stretching vibrations of C=C. The amounts of functional groups, such as hydroxyl, carbonyl, and carboxylic groups resulted in the increased surface cation exchange and complexation capacities of the CB [13,14].

The CB surface, prior and following the Cr(VI) adsorption was examined using the SEM-EDS (Figs. 2

Table 1
The properties of the commercial CB

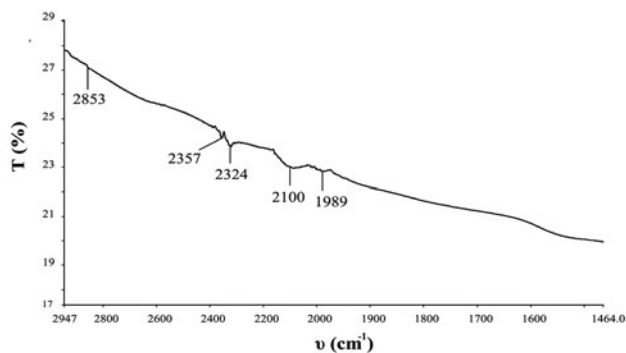| Property	Value	Unit	Test method
Heating loss	0.57	%	ISO 1126
Iodine number	119	mg/g	ISO 1304
Ash content	0.27	%	ISO 1125
Sulfur content	1.0	%	DIN 51400
Density	340	kg/m^3	ISO 1306
pH value	9.2		ASTM D 1512
Tint strength	116	% ITRB	ISO 5435

Fig. 1. FTIR spectra of the CB.

and 3). Fig. 2(a) shows the SEM image of the CB surface with clearly visible, mostly rounded particles, but of different sizes. Aggregates formed by coalescence of elemental particles. Fusion of aggregates by the Van der Waals forces resulted in the formation of the new structures-agglomerates, as previously described in the literature [1,14]. The changes caused by the Cr(VI) adsorption in the form of accumulations and deposits are shown in Fig. 2(b). Fig. 3 shows the EDS spectra. Following the Cr(VI) adsorption, it was evident that the surfaces contained Cr (Fig. 3(b)).

3.2. Effect of adsorbent dose

The adsorbent dose is a parameter which determines the capacity of the adsorbent for a given initial
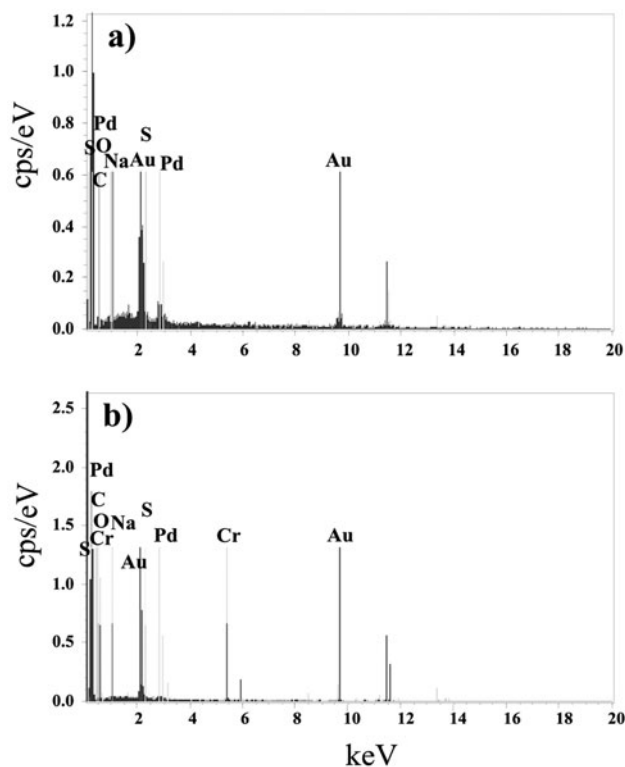

Fig. 3. EDS spectra of the CB: (a) prior, and (b) following the Cr(VI) adsorption; $c_i = 50$ mg/L.

concentration of the adsorbate. The effect of the adsorption concentration on the Cr(VI) removal for the initial concentrations of 200 mg/L is shown in Fig. 4.
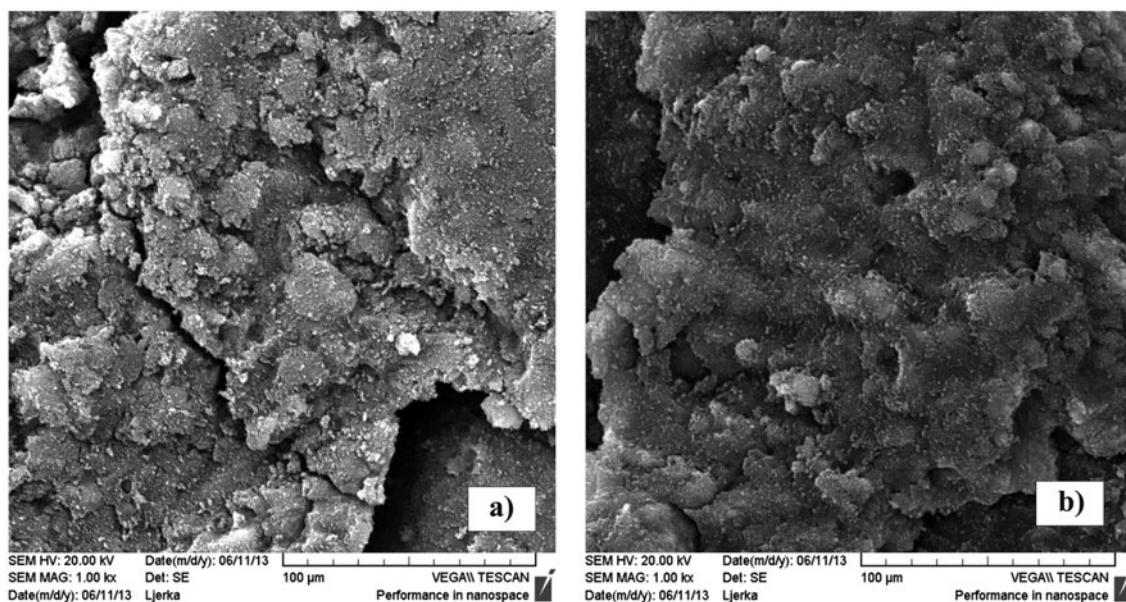

Fig. 2. SEM of the CB surface: (a) prior, and (b) following the Cr(VI) adsorption; $c_i = 50$ mg/L.
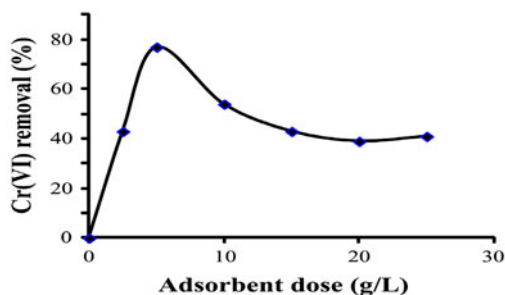
Fig. 4. Effect of the adsorbent dose on the Cr(VI) removal: $c_i = 200$ mg/L, pH 2.4, contact time 75 min, 293 K.

Fig. 5. Effect of pH on the Cr(VI) removal: $c_i = 200$ mg/L, adsorbent dose 5 g/L, contact time 75 min, 293 K.

The removal efficiency (%) of the chromium ions was calculated as follows:

$$\text{Removal} (\%) = [(c_i - c_t)/c_i] \cdot 100 \tag{2}$$

where c_i is the initial concentration of Cr(VI) in the solution (mg/L), and c_t is the concentration of Cr(VI) in the solution at time t.

The Cr(VI) removal efficiency increased from 2.5 to 5.0 g/L of the adsorbent concentration; a further increase of the concentration (from 10 to 25 g/L) had no obvious effect on the Cr(VI) removal. The increased adsorbent concentration resulted in a larger CB surface area as well as more adsorption sites available for the adsorption process, whereas the Cr(VI) ions were mostly adsorbed as the concentration was 5 g/L. The decreased Cr(VI) removal at a higher adsorbent dose may be attributed to the competition of the Cr(VI) ions for the available adsorption sites [7]. Further agglomeration of the CB particles resulted in a decrease of the total adsorbent surface area available for the Cr(VI) ions, and in an increase of the diffusion path length which might be another reason for the decreased Cr(VI) removal. Therefore, 5 g/L of the adsorbent dose was chosen for the consecutive investigations in the study.

3.3. Effect of pH on the adsorption and possible mechanisms of the adsorption

The pH value is important parameter that strongly influences the adsorption of metals onto the solid–liquid interface. The solution pH would affect both the aqueous chemistry and the adsorbent surface binding sites. Fig. 5 shows the effect of pH on the Cr(VI) removal by the commercial CB adsorbent. The maximum adsorption of the chromium ions (77%) occurred at the pH 2.4. The obtained results demonstrate that the Cr(VI) removal depends on the proton concentration.
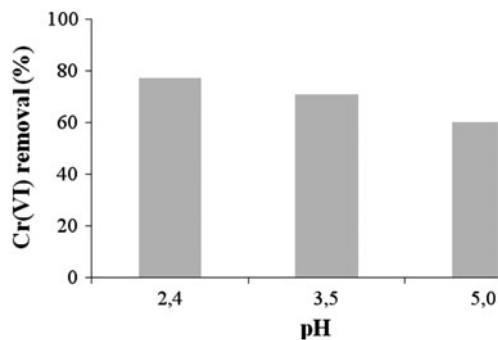
The higher the proton concentration, the higher the efficiency of the Cr(VI) removal. The decreases in the percentage adsorptions at higher pH values can be attributed due to the competitiveness of the chromium oxyanions and OH$^-$ ions in the solution. Such a dependence was also observed in other studies [6,7,15,16].

Hexavalent chromium exists primarily as the salts of chromic acid (H_2CrO_4), the hydrogen chromate ion ($HCrO_4^-$), and the chromate ion (CrO_4^{2-}) depending on the pH value [2]. The $HCrO_4^-$ predominates at pH values between 1.0 and 6.0, and CrO_4^{2-} at pH above the value around 6.0. Although the oxyanion of dichromate, $Cr_2O_7^{2-}$ was used as the source of Cr(VI) in the solution under pH < 6.0, the Cr(VI) exists in the predominant form of $HCrO_4^-$ with the hydrolysis reaction of $Cr_2O_7^{2-}$ as follows [15]:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow HCrO_4^- \quad pK_3 = 14.56$$

The maximum adsorption at pH 2.4 indicates that the $HCrO_4^-$ form of Cr(VI) was the predominant species at this pH range, thus preferentially adsorbing on the adsorbents.

Good adsorption properties of the adsorbent can be attributed to the presence of the C=O group which can coordinate trace metal ions [11]. Acidic C=O groups play a main role in the chromium removal by the analyzed adsorbent. The hydrophilic character and the adsorption affinity of C=O groups promote the adsorption of chromium ions. The reaction C=O with H$^+$ form the positive hydronium ion, C=OH$^+$. Presumably, the chromium adsorption mechanism might be as follows [5]:

$$CB\text{-}C = O + H^+ \leftrightarrow CB\text{-}C = OH^+$$

$$CB\text{-}C = OH + HCrO_4^- \leftrightarrow CB\text{-}C = OH^+ \cdot HCrO_4^-$$
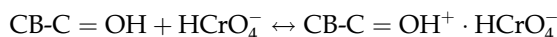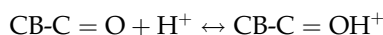
3.4. Adsorption isotherm

In order to assess the maximum adsorption capacity of an adsorbent, it is essential to conduct the isothermal studies. An isotherm, as defined in the literature, is "a functional expression for the variation of adsorption with concentrations of adsorbate in bulk solution at constant temperature" [17]. Commonly, the amount of an adsorbed material per unit weight of an adsorbent increases with increasing concentration, however not in direct proportion.

Fig. 6 shows the adsorption isotherm of the Cr(VI) ions onto the CB at different temperatures. The equilibrium quantity (Δc) of an adsorbate on the CB was calculated as the difference between the initial concentration (c_i) and the concentration achieved at the equilibrium (c_e). The amount of an adsorbate adsorbed per unit mass of an adsorbent at the equilibrium, i.e. the adsorption capacity, q_e was calculated according to the formula:

$$q_e = \frac{\Delta c}{m} \cdot V \tag{3}$$

where q_e is the equilibrium adsorption capacity, mg/g; Δc is the quantity of an adsorbed adsorbate, mg/L; V is the volume of the solution, L; and m is the adsorbent mass, g. It can be seen from Fig. 6 that the adsorption capacities were increased with an increase in initial concentrations, and decreased with a rise in temperature.

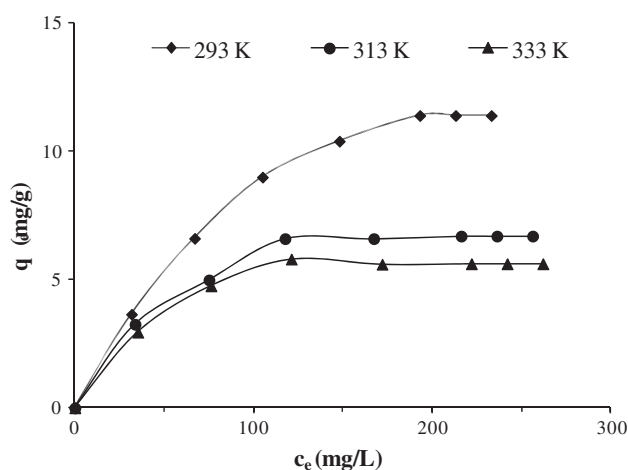The adsorption equilibrium data are formulated according to the specific isotherm model. Equilibrium relationships among adsorbents and adsorbates are described by the adsorption isotherms and characterized by certain constants, the values of which provide the information on the adsorbent capacity and its affinity for a certain adsorbate. The Langmuir and Freundlich isotherm models are frequently used for the description of the Cr(VI) adsorption on various adsorbents.

The linear least-squares method with linearly transformed isotherms has been widely applied so as to confirm the experimental data and isotherms using correlation coefficients of determination. Several isotherm equations are available and three important isotherms were applied to fit the equilibrium data in this study: the Langmuir, Freundlich, and Temkin isotherms.

The Freundlich isotherm is suitable for the heterogeneous surface [18] and expressed by the following equation [19]:

$$q_e = K_F \cdot c_e^{\frac{1}{n}} \tag{4}$$

where q_e is the equilibrium adsorption capacity, mg/g; c_e is the equilibrium concentration of the adsorbate, mg/L; K_F and n are the Freundlich constants.

The values of K_F and n were calculated from the intercept and slope of the plot of $\ln q_e$ vs. $\ln c_e$, as shown in Fig. 7.

The Langmuir isotherm [20] is applicable to a monomolecular layer adsorption. The theory is based on the assumption that there is a finite number of binding sites that are homogeneously distributed over the adsorbent surface, and once the adsorbate occupies a site, no further adsorption can take place at that site. The equation of the Langmuir isotherm is following:

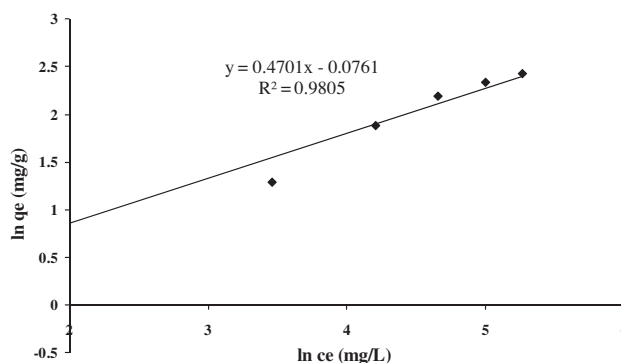Fig. 6. Adsorption isotherm of Cr(VI) onto the CB at different temperatures.

Fig. 7. Linearized Freundlich isotherm for the Cr(VI) adsorption onto the CB.

$$q_e = \frac{q_{\max} K_L c_e}{1 + K_L c_e} \tag{5}$$

where c_e is the equilibrium concentration of the adsorbate, mg/L; q_e is the amount of the adsorbate which is adsorbed per unit mass of the adsorbent at the equilibrium, mg/g; $q_{\max}$ is the theoretical maximum monolayer adsorption capacity of the adsorbent, mg/g; and K_L is the Langmuir isotherm constant related to the adsorption energy, L/mg. The values of K_L and $q_{\max}$ can be determined from the slope and intercept of the linear plot of $1/q_e$ vs. $1/c_e$ (Fig. 8).

Temkin and Pyzhev considered the effects of some indirect adsorbent/adsorbate interactions on the adsorption isotherms, and suggested that due to these interactions, the heat of adsorption of the molecules in the adsorbent surface layer would decrease linearly with coverage. The Temkin isotherm is represented by the linear equation as follows [7]:

$$q_e = B \ln K_t + B \ln c_e \tag{6}$$

where K_t (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy, the constant $B = RT/b$ represents the heat of the adsorption, R is the universal gas constant, T is the absolute temperature, and $1/b$ indicates the adsorption potential of the adsorbent. Both, K_t and B can be determined from a plot q_e vs. $\ln c_e$ (Fig. 9) [7].

The values of isotherm constants and other statistical parameters are given in Table 2, where all the Freundlich parameters, together with the correlation coefficients, R^2, are summarized. The obtained values of $n = 2.1272$ ($1 < n < 3$) indicate that the Cr(VI) adsorption on the CB was favorable [15]. Also, the R^2 values of the Freundlich isotherm was found to be higher (0.9805) than the R^2 values of the Langmuir
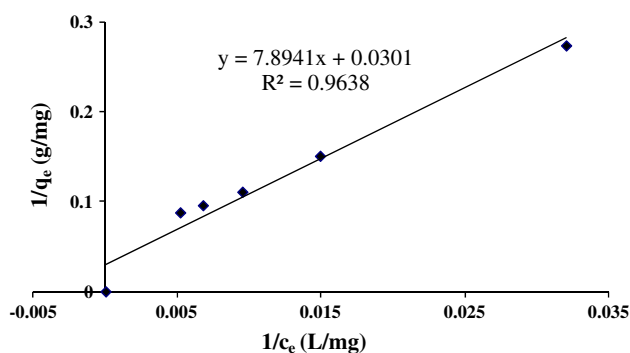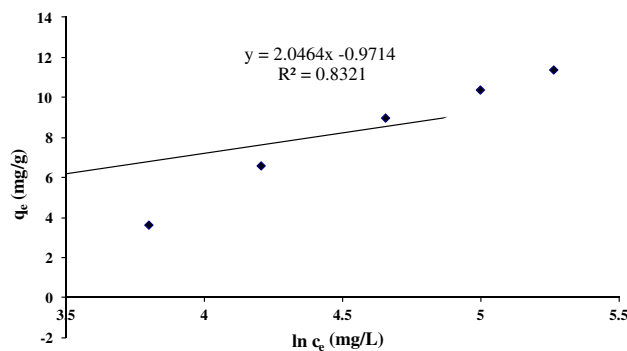
Fig. 9. Linearized Temkin isotherm for the Cr(VI) adsorption onto the CB.

(0.9638), and Temkin (0.8321) isotherms, thus indicating that the Freundlich model fitted the experimental data better than the other two models. This finding further supports the conclusion that the CB surface was possibly made up of small heterogeneous adsorption patches dissimilar to each other, what is reported elsewhere [10].

To justify the capability of the CB as an effective adsorbent for the Cr(VI) removal, its adsorption capacity was compared with other low-cost adsorbents (Table 3). The results indicate that its maximum adsorption capacity ($q_{\max} = 33.22$ mg/g) obtained in this study compares well with the reported values, either at the similar or same solution pH values.

3.5. Effect of the temperature and calculation of the thermodynamic parameters

The effect of temperature has important implications on the adsorption process. The results of the Cr(VI) adsorption as a function of temperature are presented in Fig. 10. It was found that the adsorption

Fig. 8. Linearized Langmuir isotherm for the Cr(VI) adsorption onto the CB.

Table 2
Isotherm parameters for Cr(VI) adsorption on the CB

Isotherm parameters	Value
Freundlich isotherm	
K_F	0.9267
n	2.1272
R^2	0.9805
Langmuir isotherm	
$q_{\max}$ (mg/g)	33.2223
K_L (L/mg)	0.0038
R^2	0.9638
Temkin isotherm	
K_T	0.6221
B (L/g)	2.0464
R^2	0.8321

Table 3
Comparison of Cr(VI) adsorption capacities of various adsorbents [2]

Adsorbent	pH	q_{max} (mg/g)
Activated sludge	4.5	95.2
Aluminium oxide	4	11.7
Bagasse fly ash	1	259
Blast furnace slag	1	1.45
Brown coal, YK	3	47.83
Carbon, F-400	2	48.5
Cation-exchange resin, IRN77	3.5	35.4
Chitosan	4	154
Diatomite	3	11.55
Granular activated carbon	1	147.1
Hazelnut shell activated carbon	1	170
Hydrous titanium(IV) oxide	2.5	284.4
Olive cake	2	33.4
Red mud	5.2	1.6
Rice husk carbon	2–3	45.6
Sawdust	2	39.7
Wool	2	41.2
Carbon black (in this study)	2.4	33.22

capacity of the CB declined with temperature. This might be due to the desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate, causing its desorption [16,21].

The thermodynamic parameters, free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were estimated according to the Gibbs–Helmholtz relation:

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

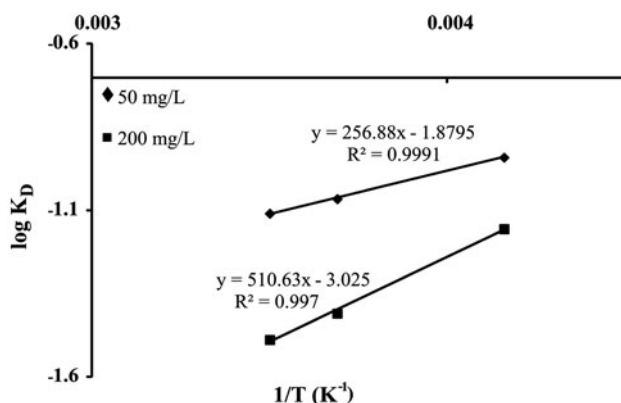The corresponding values of $\Delta H°$ and $\Delta S°$ can be estimated from the relationship between the equilibrium

constant (or the distribution coefficient), and $\Delta H°$ which is defined by the Clausius–Clapeyron equation; this is in fact the thermodynamic basis by which is possible to predict the change of the equilibrium constant with temperature [22]:

$$\log K_D = \Delta S°/2.3R - \Delta H°/2.3RT \tag{8}$$

where K_D is the distribution coefficient (L/g), and R is the gas constant (J/mol K).

The distribution coefficient K_D is defined as follows [23]:

$$K_D = [(c_i - c_e)/c_e] \times V/m \tag{9}$$

where c_i is the initial concentration (mg/L), c_e is the equilibrium concentration (mg/L) of Cr(VI), V is the volume of the solution (L), and m is the adsorbent mass (g).

The Gibb's free energy change of the process is related to the distribution coefficient K_D by the equation:

$$\Delta G° = -RT \ln K_D \tag{10}$$

where K_D is the distribution coefficient (L/g), and R is the gas constant (J/mol K).

A plot of log K_D vs. $1/T$ was linear (Fig. 10). The values of $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept of the plots. The distribution coefficient K_D values decreased with temperature, thus indicating the exothermic nature of the adsorption.

It can be seen from the calculated values of the thermodynamic parameters (Table 4) that the negative $\Delta H°$ value represents the exothermic nature of the Cr(VI) adsorption onto the CB. Accordingly, the amount of Cr(VI) adsorbed at the equilibrium must decrease with increasing temperature, as $\Delta G°$ decreases with the rise in temperature. This was confirmed by the

Fig. 10. The distribution coefficient K_D for the Cr(VI) adsorption onto the CB as a function of temperature.

Table 4
Thermodynamic parameters for the Cr(VI) adsorption on the CB

Concentration (mg/L)	Temperature (K)	$-\Delta G°$ (kJ/mol)	$-\Delta H°$ (kJ/mol)	$-\Delta S°$ (J/K mol)
50	293	5.25		
	313	6.37	4.91	35.94
	333	7.07		
200	293	6.47		
	313	8.49	9.76	57.84
	333	9.47		

$\Delta G°$ values becoming more negative with the rise in temperature (Table 4). The obtained negative $\Delta S°$ values corresponded to a decrease in the degree of freedom of the adsorbed ions [24].

3.6. Desorption experiment

The desorption studies were carried out so as to understand the regenerative capability of the CB. Metal ions loaded on the CB represent a disposal problem due to their hazardous characteristics. This could be solved to some extent by means of elution methods; they allow the recovery of metal ions back to the solution, whereas the regenerated adsorbents may be recycled and consecutively reused [11,25,26].

The desorption studies of the chromium ions were carried out in three cycles using two (0.1 and 0.3 mol/L) concentrations of HCl solution. During the desorption stage, hydronium ions from HCl may replace Cr ions on the metal-loaded adsorbent. In dilute HCl, the Cr(VI) ions were probably desorbed, resulting in H_2CrO_4 which was stable at pH < 1.0 [27]. Desorption experiments evidence that 0.3 mol/L HCl solution (desorption percentage 65.08%) was more efficient while desorbing the Cr(VI) ions for the CB than 0.1 mol/L HCl solution (desorption percentage 47.06%).

The desorption experiment results showed that the Cr(VI) recovery decreased from 92.20 to 88.06%, following the completion of three cycles.

4. Conclusions

The results of this study demonstrate that the CB proved to be suitable for the Cr(VI) adsorption removal from an aqueous solution. They are summarized as follows:

(1) Optimum adsorbent dose was found to be 5 g/L.
(2) The Cr(VI) removal depended on the hydronium ions in the solution. The maximum adsorption took place at pH 2.4.
(3) The adsorption equilibrium was attained within 75 min.
(4) The experimental Cr(VI) adsorption data were preferably explained using the Freundlich isotherm model which points at the heterogeneous nature of the CB surface adsorption sites.
(5) The thermodynamic parameters implied the spontaneous nature of the process, decreasing with an increase in temperature, what purports an exothermic nature of the Cr(VI) adsorption.
(6) The adsorption capacity of the CB (q_{max} = 33.22 mg/g) regarding the Cr(VI) removal was estimated in comparison with various adsorbents reported in the literature.
(7) The results suggest that the high carbon content (>98%) of the CB, its high surface area (S_{BET} = 107.29 m^2/g) together with a high content of mesopores, and carbonyl functional groups, improve the Cr(VI) removal efficiency from an aqueous solution.
(8) Following the dissolution of Cr(VI) ions in diluted HCl, they were removed from the CB, which could be used several consecutive times.

List of symbols

$1/b$	—	adsorption potential of the adsorbent
B	—	temkin constant
BET	—	Brunauer–Emmett–Teller
BJH	—	Barrett–Joyner–Halenda
CB	—	carbon black
c_e	—	equilibrium concentration of chromium ions in the solution (mg/L)
c_i	—	initial concentration of chromium ions in the solution (mg/L)
c_t	—	concentration of chromium ions in the solution at time t (mg/L)
d	—	pore diameter (nm)
EDS	—	energy dispersive X-ray spectroscopy
FTIR	—	fourier transform infrared spectroscopy
K_D	—	distribution coefficient (L/g)
K_F, n	—	Freundlich constants
K_L	—	Langmuir isotherm constant (L/mg)
K_t	—	equilibrium binding constant corresponding to the maximum binding energy (L/mg)
M	—	adsorbent mass (g)
q_e	—	equilibrium adsorption capacity (mg/g)
q_{max}	—	theoretical maximum adsorption capacity (mg/g)
R	—	universal gas constant (J/mol K)
R^2	—	correlation coefficient
S_{BET}	—	BET surface area (m^2/g)
SEM	—	scanning electron microscopy
T	—	absolute temperature (K)
V	—	volume of the solution (L)
V_p	—	total pore volume (cm^2/g)
Δc	—	quantity of chromium ions adsorbed (mg/L)
ΔG	—	free energy change (kJ/mol)
ΔH	—	enthalpy change (kJ/mol)
ΔS	—	entropy change (J/K mol)

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