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Removal of chromium (VI) from aqueous solutions using activated carbon prepared from crofton weed

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ABSTRACT

Activated carbon from crofton weed (ACCW) was evaluated for its ability to remove Cr(VI) from aqueous solutions. Batch experiments were used to examine kinetics, adsorption isotherm, pH effect, and thermodynamic parameters. Adsorption data for Cr(VI) uptake by ACCW were analyzed according to Langmuir and Freundlich adsorption models. Thermodynamic parameters for the adsorption system were determinated at 293, 303, and 313 K ($\Delta H^\circ = 15.02\,\text{kJ mol}^{-1}$; $\Delta G^\circ = -0.76$ to $-2.91\,\text{kJ mol}^{-1}$, and $\Delta S^\circ = 53.85\,\text{J K}^{-1}\,\text{mol}^{-1}$). The ΔG° values obtained were negative, indicating that the adsorption of Cr(VI) on the surface of ACCW was a spontaneous adsorption process. The kinetics of this process was described very well by a pseudo-second-order rate equation. These results show that the ACCW could be considered as a potential adsorbent for Cr(VI) in aqueous solutions.

Keywords: Chromium(VI); Activated carbon; Adsorption; Isotherms; Thermodynamics; Crofton weed

1. Introduction

Heavy metals removal from industrial wastewater has become an important issue because of environmental concerns. Unlike the organic pollutants, which are often bio-degraded, metal ions do not degrade into harmless end products. To meet environmental regulations, effluents or water contaminated with heavy metal ions must be treated before discharge. Among the heavy metal ions, Cr(VI) holds a distinct position due to its high toxic nature to biological systems. Chromium is used in a variety of industrial applications; hence, large quantities of chromium are discharged into the environment. Sources of chromium waste leading to water pollution includes electroplating, leather tanning, wood preservations, and manufacturing of dye, paint, and paper [1]. In aqueous phase, chromium mostly exists in two stable oxidation states as Cr(III) and Cr(VI) [2]. Cr(III) is relatively innocuous and is an essential trace element for living organisms. Cr(VI) is known to be highly mobile in soil and aquatic system and is also 500 times more toxic, mutagenic, and carcinogenic than Cr(III) [3]. Its toxicity includes cancer as well as kidney, liver, and gastric damages [4]. Due to the severe toxicity of Cr (VI), the World Health Organization has set the maximum contaminant concentration level for Cr(VI) in domestic water supplies as $0.05\,\text{mg L}^{-1}$ [5].

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There are various methods to treat Cr(VI)-contaminated water, such as electrochemical precipitation, ion exchange, adsorption, coprecipitation, solvent extraction, reduction, emulsion per traction technology, and membrane filtration [6–12]. Among all, the adsorption process has been effectively used for the removal of organic as well as inorganic compounds from wastewater because of its simplicity and safety [13,14]. Adsorption by activated carbon is the best and most frequently used method, particularly in treating low concentrations of wastewater streams to meet stringent treatment levels. However, the use of commercial activated carbons based on relatively expensive starting materials is unjustified for most pollution control applications. It is, therefore, very critical to examine the feasibility of using cheaper raw materials to prepare activated carbon. For this purpose, many materials such as, bamboo, rice husk, rubber-wood sawdust, oil palm shell, coir pith, olive stone, coconut shell and sugarcane bagasse were studied [15–22].

Crofton weed (Eupatorium adenophorum spreng) invaded China in the 1940s from Burma and is now widespread in southwest China, damaging native ecosystems and causing great economic losses. Lot of attention has been paid to control this weed. So far, several methods have been developed, including manual, chemical, and biological control methods. But due to some disadvantages, these methods have not become practical till now. Compared with the challenge of control methods, the utilization of the weed gives more potential benefits. The chemical composition of crofton weed is akin to hard wood which is mainly composed of lignin and cellulose. Hence, the conversion of crofton weed into activated carbon is desirable and practicable. The aim of the present study was to investigate and explore the feasibility of crofton weed activated carbon for the removal of Cr (VI) from aqueous solutions. To the best of our knowledge, this material was never used before for this application.

The influence of several operating parameters for the adsorption of chromium (VI), such as contact time, temperature, pH, and adsorbent dose, was investigated in batch mode. The kinetic data were fitted to different models and the isotherm equilibrium data were fitted to Langmuir and Freundlich models.

2. Materials and methods

2.1. Materials and analytical method

All chemicals and reagents used in this work are of analytical grade. In all experiments, deionized water was used for preparation, dilution, and analytical purposes of solutions. The stock solution (1,000 mg L^{-1}) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) in 1,000 mL of deionized water. Other working solutions with different concentrations were obtained by successive dilution.

The concentration of Cr(VI) was analyzed by spectrophotometer (UV-1201 model) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm [23]. Before determination of the concentration of Cr(VI) in the adsorption medium, Cr^{3+} and Cr^{2+} were converted to Cr(VI) using $KMnO_4$. The amount of Cr(VI) absorbed by adsorbent (q) in the sorption system was calculated using the mass balance:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where V is the solution volume (L), W is the amount of adsorbent (g), and C_0 and C_e are the initial and equilibrium metal concentrations (mg L^{-1}), respectively.

2.2. Preparation of adsorbent

The crofton weed was collected from the campus of Kunming Metallurgy College, Yunnan, China and was washed with deionized water three to four times to remove dirt and dust. The washed weed stems were cut into 10–20 mm pieces and dried in an oven at 105°C for one day. Then the dried stems were grounded and sieved to 20–50 mesh particles. This powder was immersed in 40 wt% $ZnCl_2$ solution for 18 h. After that, the slurry was subjected to vacuum drying at 550°C for 15 min in microwave muffle furnace. The product was washed sequentially with 0.5 mol/L HCl and deionized water to remove residual $ZnCl_2$ and other minerals, and then dried at 110°C to reach the activated carbon form. The carbon was grounded and screened through different mesh sizes and stored in a closed bottle to use in future adsorption studies.

2.3. Effect of contact time

The contact time of adsorbent with adsorbate is of great importance in adsorption since contact time depends on the nature of the system used. Adsorption experiments for Cr(VI) on Activated carbon from crofton weed (ACCW) were carried out as follows: to each 0.2 g of the ACCW sample, 100 mL of solution containing 50 mg L^{-1} of Cr(VI) was added. The samples were shaken at room temperature for periods ranging from 5 min to 1.5 h, and then centrifuged and 5 mL portions of liquid phases were measured.

2.4. Effect of pH

Effect of initial solution pH on adsorption was determined by mixing 0.2 g of ACCW with 100 mL of solution containing Cr(VI) concentration of $100\,\mathrm{mg\,L^{-1}}$ at temperature of 20 ± 1℃ and various pH values ranging from 1 to 12. Solution pH was adjusted with 1 M HCl and NaOH solutions. The mixture was shaken for 1 h and the solution was filtered and analyzed.

2.5. Effect of adsorbent amount

Under optimum conditions of shaking time and pH, the effect of adsorbent dosage on the removal of Cr(VI) at $C_0 = 100\,\mathrm{mg\,L^{-1}}$ was also studied by shaking 100 mL of metal solution with 0.1–0.6 g of adsorbent.

2.6. The adsorption isotherms

The adsorption isotherms were studied by varying the concentration of Cr(VI) solutions with a fixed dose of adsorbent. To investigate the sorption isotherms, two models, Langmuir and Freundlich isotherm equations were applied [24,25]. The linearized isotherm equations are expressed as the following:

Langmuir:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \tag{2}$$

Freundlich:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{3}$$

where C_e is the equilibrium liquid phase concentration ($\mathrm{mg\,L^{-1}}$); q_e is the amount of sorbent adsorbed per unit weight ($\mathrm{mg\,g^{-1}}$); and Q_0 and b are the Langmuir constants related to the sorption capacity and the rate of adsorption, respectively. The K and $1/n$ are Freundlich constants. The values of K and $1/n$ roughly correspond to the adsorption capacity and the heterogeneity factor representing the deviation from linearity of adsorption, respectively.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [26], also known as the separation factor, given by Eq. (4):

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where b (L/mg) is the Langmuir constant and C_0 ($\mathrm{mg\,L^{-1}}$) is the initial highest concentration of metal ion. The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

2.7. Thermodynamic studies

Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated from the following equations [27,28]:

$$K_c = \frac{C_{Ae}}{C_e} \tag{5}$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of Cr(VI) ion (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, and C_e is the equilibrium concentration ($\mathrm{mg\,L^{-1}}$) of the Cr(VI) ion in the solution. R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in Kelvin). The Gibbs free energy change is related to enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by Eq. (7).

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

2.8. Adsorption kinetics

Adsorption kinetics is important from the point of view that it controls the efficiency of the process and the models correlate the adsorbate uptake rate with its bulk concentration. Experiments were also performed in order to understand the kinetics of Cr(VI) removal by ACCW. At various time intervals, samples were taken and the concentration was measured. The amount of Cr(VI) adsorbed q_t at time t was determined by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{8}$$

where q_t is the amount of Cr(VI) adsorbed at time t ($\mathrm{mg\,g^{-1}}$), V is the volume of the solution (L), W(g) is the mass of the adsorbent, and C_0 and C_t are the concentrations of the Cr(VI) at initial ($t = 0$) and at time t, respectively.

In order to analyze the sorption rate, the kinetic data were modeled using Lagergren pseudo-first-order and Ho pseudo-second-order equations [29,30].

Lagergren pseudo-first-order:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{9}$$

Ho pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{10}$$

where q_t and q_e are the amounts of Cr(VI) adsorbed (mg g^{-1}) at time t and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 (mg g^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants. The Arrhenius equation for calculating adsorption activation energy is expressed as [31]:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{11}$$

where E_a is the activation energy of adsorption (kJ mol^{-1}); k_2 is the rate constant of pseudo-second-order adsorption (mg g^{-1} min^{-1}); A is the Arrhenius factor; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); and T is the temperature in Kelvin (K).

2.9. Characterization of the sorbents

The morphologies of the activated carbon from crofton weed were characterized by scanning electron microscopy (SEM) (Quanta 200 FEG, FEI Company, USA). The samples were observed at high voltage of 30 kV, 2.5 spot size, and 9.6 mm working distance. The Brunauer-Emmett-Teller (BET) specific surface area of the activated carbon was determined from N_2 adsorption isotherms, measured at 77 K with a Coulter Omnisorp 100 CX apparatus.

3. Results and discussion

3.1. Sorbent characterization

Fig. 1 shows a general SEM micrograph of the ACCW. It has considerable number of heterogeneous pores where there is a good possibility for Cr(VI) to be trapped and adsorbed. The shape of isotherms provides information about the sizes of pores, which are usually divided into micro, meso, and macropores. Fig. 2 illustrates the shape of the N_2 adsorption–desorption isotherm at 77 K for the ACCW. According to the IUPAC classification, the isotherm shown in Fig. 2 is clearly of type IV curve, which is indicative of a solid material rich in mesopores. The BET surface area of ACCW was measured from Fig. 2 and it was found to be 1,184 m^2 g^{-1}. The average pore diameter was found as 3.55 nm. The total pore volume was 1.05 cm^3 g^{-1}. This shows that ACCW is reasonably good for adsorption.

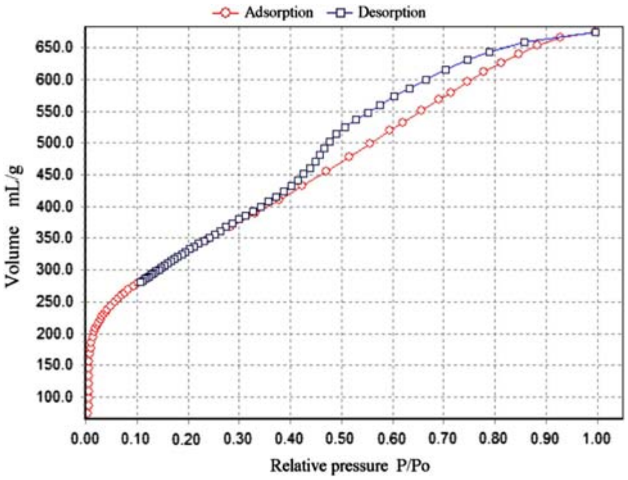

Fig. 2. Nitrogen adsorption–desorption isotherms.

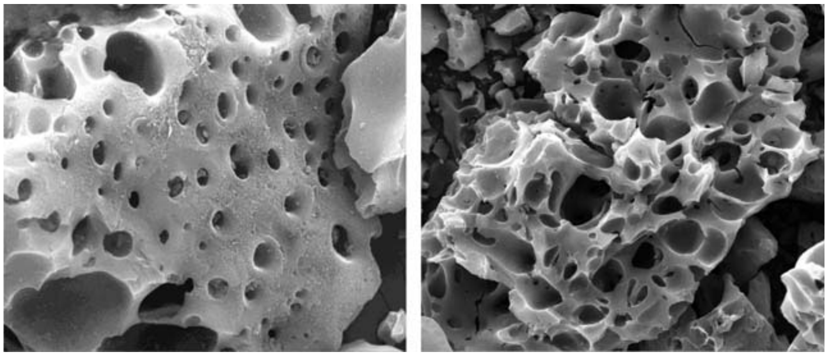

Fig. 1. SEM images of the produced ACCW.

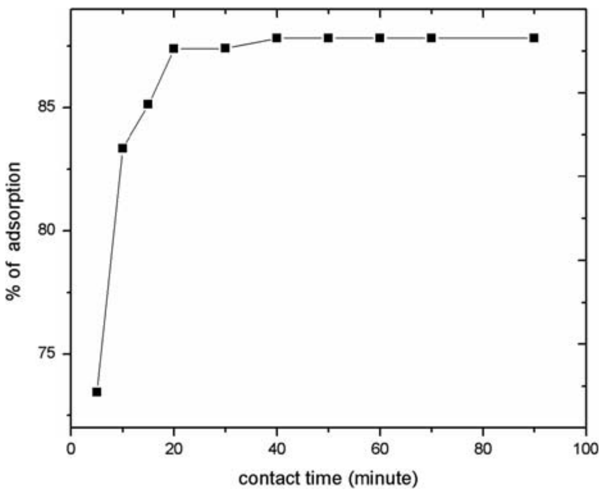

Fig. 3. Adsorption of Cr(VI) ions on ACCW as a function of contact time.

3.2. *Effect of contact time*

The effect of contact time on the adsorption of Cr (VI) is shown in Fig. 3, where it is clear that adsorption of Cr(VI) ions into the ACCW is rather quick and after 40 min the complete adsorption equilibrium between the two phases is obtained. The adsorption of Cr(VI) increased with increasing contact time and attained an optimum at about 40 min for the ACCW. The amount of Cr(VI) ions removed reached a maximum of 87.72%. No further adsorption above the quantity obtained in 40 min of contact time was obtained by placing adsorbent samples in contact with Cr(VI) solutions for 8 h of shaking time. This phenomenon could be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

3.3. *Effect of pH*

Some experiments were carried out to examine the influence of initial pH on the adsorption of Cr(VI) with 100 mg L^{-1} solutions. The results obtained are shown in Fig. 4. Accordingly, when pH was held in the strongly acidic region, preferably below pH = 3, over 94.56% removal was attained. The pH dependence of chromium adsorption can largely be related to the type and ionic state of functional groups present on the adsorbents and chromium speciation in solution [32]. Hexavalent chromium can exist in the solution as CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4, and $Cr_2O_7^{2-}$ which depends on the concentration of the chromium ion and pH of the solution. Cr(VI) exists predominantly as $HCrO_4^-$ in aqueous solution between pH 1.0 and 4.0. The low pH leads to an increase in H^+ ions on the carbon surface which results in strong electrostatic attraction between positively charged ACCW surface and $HCrO_4^-$. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$, while the OH^- ions are increased too. Adsorption of Cr(VI) on the activated carbon was not significant at pH values greater than 8.0 due to dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates. Therefore, with the decrease in solution pH, protonation of groups of ACCW increased favoring more electrostatic attraction of negatively charged Cr(VI) ions yielding high removal of Cr(VI).

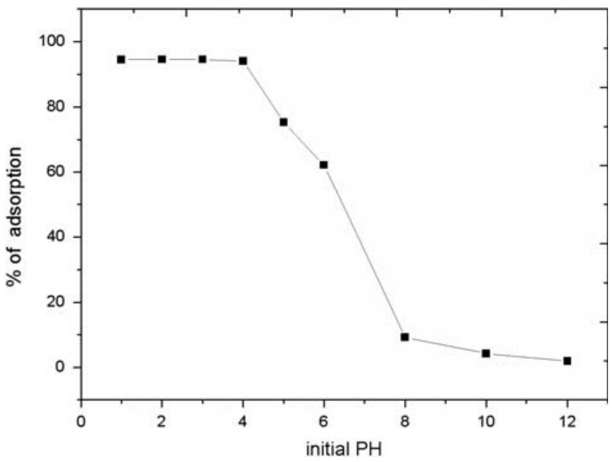

Fig. 4. Influence of initial pH on Cr(VI) ions adsorption.

3.4. *Effect of the amount of adsorbent*

The effect of adsorbent dosage on the percentage removal of Cr(VI) has been shown in Fig. 5. It can be seen from the figure that the metal ion removed almost remain unchanged after adsorbent dosage 4 g L^{-1}. Increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. At very low adsorbent concentration, the absorbent surface becomes saturated with the metal ions and the residual metal ions concentration in the solution is large. With an increase in adsorbent dosage, the metal ion removal increases until a certain value is reached; afterwards, the removal efficiency is maintained constant even if the ACCW is added. So, the use of 4 g L^{-1} adsorbent dose is justified for economical purposes.

3.5. *The adsorption isotherm*

Isotherms are represented in Figs. 6 and 7, the Langmuir and Freundlich models, respectively.

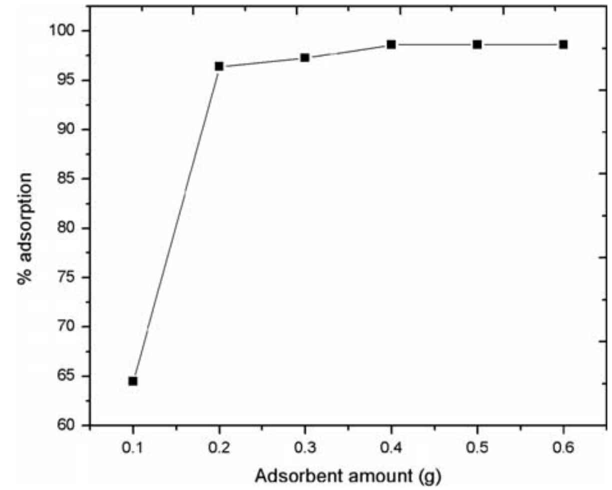

Fig. 5. Dependence of Cr(VI) ions adsorption on the amount of ACCW.

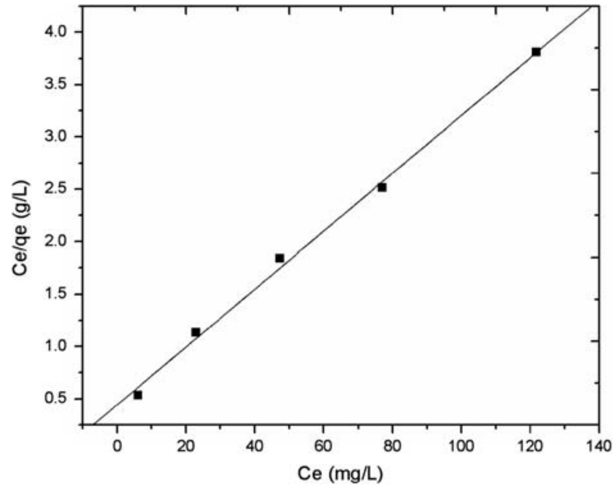

Fig. 6. Langmuir adsorption isotherm for Cr(VI) ions adsorption on ACCW.

Isotherm parameters for the Langmuir and Freundlich models for the ACCW are reported in Table 1. The correlation coefficients (R^2) values were higher for Langmuir isotherm than that of the Freundlich isotherm. The high value of correlation coefficient ($R^2 = 0.9956$) reinforces the fact that Langmuir isotherm is useful to explain the adsorption of Cr(VI) from the solution on the current adsorbent when it follows the monolayer mode, rather than the multilayer mode. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogenous sites on the adsorbent. When a site is occupied by an adsorbate, no further sorption can take place at that site. The values of Q_0 and b, obtained from experimental data, are $36.22\,\mathrm{mg\,g^{-1}}$ and $0.062\,\mathrm{L\,mg^{-1}}$, respectively. The value of R_L in the present investigation is 0.308. Hence, the sorption process was very favorable and the adsorbent employed exhibited a good potential for the removal of Cr(VI) from aqueous solution.

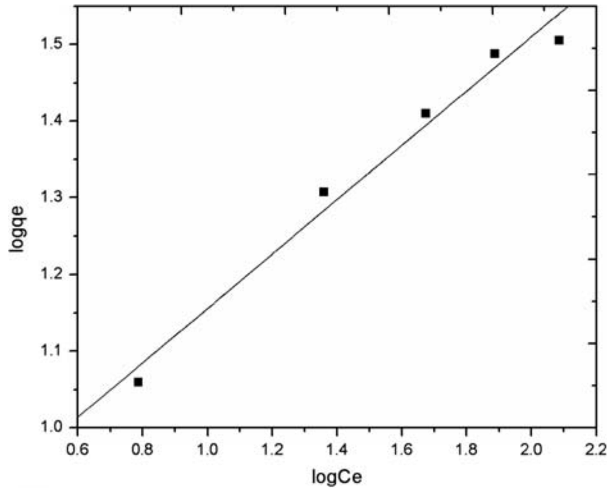

Fig. 7. Freundlich adsorption isotherm for Cr(VI) ions adsorption on ACCW.

3.6. Thermodynamic parameters

The values of ΔH° and ΔS° were calculated from the slope and intercept of the Van't Hoff plot (ln Kc vs. $1/T$) shown in Fig. 8. The calculated values are given in Table 2. The negative values of the Gibbs free energy change indicate that the adsorption process is spontaneous. In addition, more negative value with the increase of temperature shows that the amount adsorbed at equilibrium must increase with increasing temperature [33]. The positive value of ΔH° ($15.02\,\mathrm{kJ\,mol^{-1}}$) suggests an endothermic nature of

Table 1
Parameters of the Langmuir and Freundlich isotherm models

T (K)	Langmuir				Freundlich		
	Q_0 ($\mathrm{mg\,g^{-1}}$)	b ($\mathrm{L\,mg^{-1}}$)	R_L	R^2	K ($\mathrm{mg\,g^{-1}}$) ($\mathrm{L\,mg^{-1}})^{1/n}$	n	R^2
293	36.22	0.062	0.308	0.9956	6.33	2.82	0.9724

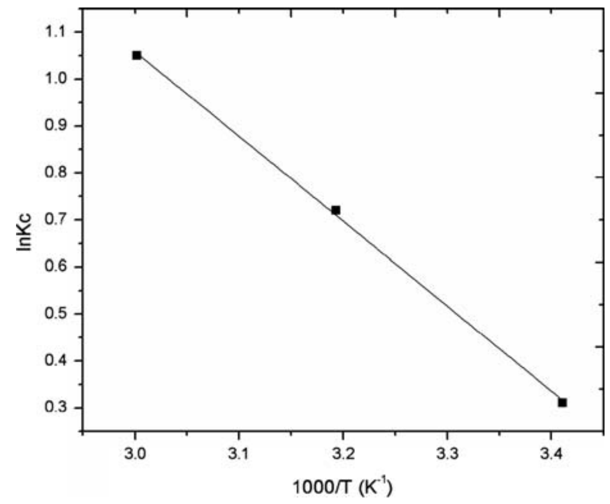

Fig. 8. Plot of log K_c vs. $1/T$ for Cr(VI) ions adsorption on ACCW.

Table 2
Thermodynamic parameters for adsorption of Cr (VI) on ACCW

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
293	−0.76		
303	−1.84	15.02	53.85
313	−2.91		

adsorption of Cr(VI) ions on the ACCW, and the extent of the endothermic reaction will increase at higher temperatures. The entropy change (ΔS°) was 53.85 J mol^{-1} K^{-1}, the positive values of ΔS° show the increasing randomness at the solid/solution interface during the adsorption process. As the free energy changes are negative and accompanied by positive entropy changes, the adsorption reactions are spontaneous with a high affinity.

3.7. Adsorption kinetics

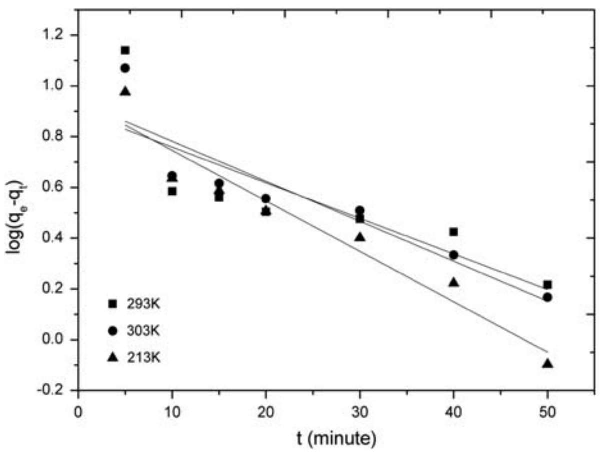

Fig. 9. Lagergren-first-order kinetic plot for the sorption of Cr(VI) ions on ACCW.

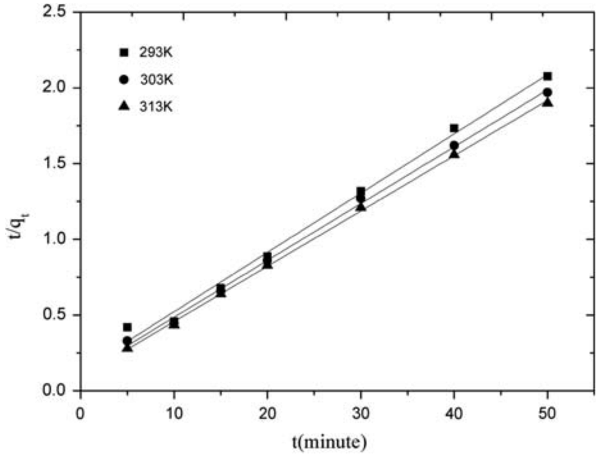

Fig. 10. Second-order kinetic plot for the sorption of Cr(VI) ions on ACCW.

Fig. 9 shows a plot of log ($q_e - q_t$) vs. t for sorption of Cr(VI) for the pseudo-first-order equation. Fig. 10 shows the application of pseudo-second-order equation by plotting t/q_t vs. t. The kinetic parameters together with correlation coefficients (R^2) have been postulated from the slopes and the intercepts of respective plots and are listed in Table 3. It is important to note that for a pseudo-first-order model, the correlation coefficient is always less than 0.9222 which is indicative of a bad correlation. In contrast, the

Table 3
Kinetic parameters for pseudo-first order and pseudo-second order

T (K)	Pseudo-first order				Pseudo-second order		
	$q_{e,\,exp}$ (mg g^{-1})	K_1 (min^{-1})	q_{e1} (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_{e2} (mg g^{-1})	R^2
293	25.73	0.0323	7.92	0.5918	0.0116	25.56	0.9918
303	26.85	0.0362	8.69	0.8065	0.0126	26.66	0.9977
313	27.31	0.0458	8.80	0.9222	0.0143	27.40	0.9991

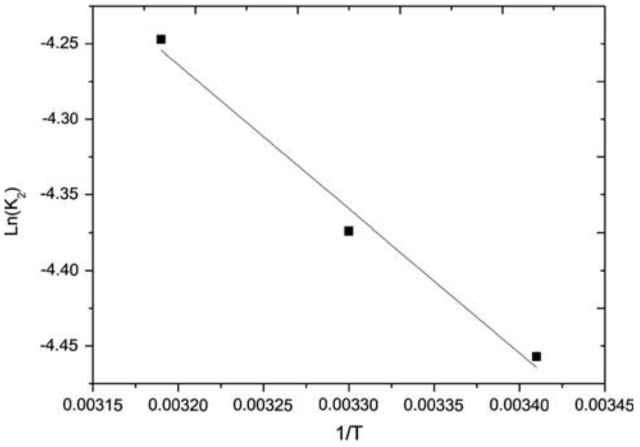

Fig. 11. Arrhenius equation plot for the pseudo-second-order adsorption of Cr(VI) ions on ACCW.

correlation coefficients for the pseudo-second-order equation were greater than 0.9918 for all concentrations. The results of the regression analysis proved that Cr(VI) adsorption on the ACCW was best described by the pseudo-second-order equation for all three of studied concentrations. Fig. 11 shows a plot of $\ln(k_2)$ vs. $1/T$ yields a straight line, with slope $-E_a/R$. The calculated value of E_a was found to be $7.94\,\mathrm{kJ\,mol^{-1}}$, suggesting that the adsorption of Cr(VI) on the ACCW involves a physical adsorption process.

4. Conclusions

The present investigation showed that crofton weed can be effectively used as a raw material for the preparation of activated carbon for the removal of Cr (VI) from aqueous solutions. The Cr(VI) adsorption behavior on the prepared activated carbon has been studied under various conditions of different solution pH values and adsorption contact times. Adsorption equilibrium is attained within a short contact time of 40 min. The Cr(VI) ions adsorption was favored at higher temperatures and at slightly initial acid pH values in the equilibrium under acidic conditions ($\mathrm{pH} \leq 3$). Experimental isotherms of Cr(VI) ions were successfully fit to Langmuir isotherms models. The values of ΔH°, ΔS°, and ΔG° prove that the adsorption of chromium hexavalent ions on ACCW is an endothermic and a spontaneous process. The results indicate that activated carbon from crofton weed is an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions. Easy availability and suitability for the production of activated carbon from crofton weed makes it one of the biomass wastes that can be effectively utilized for the removal of Cr(VI) from waste waters.

Acknowledgments

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