Efficient Adsorption of Chromium(VI) Ions from Aqueous Solution onto a Low-cost Adsorbent Developed from *Limonia acidissima* (Wood Apple) Shell

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**ABSTRACT:** The removal of chromium(VI) ions from aqueous solution was studied using *Limonia acidissima* (wood apple) shell activated carbon. The removal extent was found to be a maximum at a pH value of 2, with the low-cost adsorbent having an adsorption capacity of 13.74 mg/g. The material employed was characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and elemental analysis. The linear Freundlich and Langmuir adsorption isotherm models were applied to describe the experimental equilibrium isotherms. The results showed that the Langmuir equation gave a better fit to the experimental data than the Freundlich equation. The pseudo-first-order and pseudo-second-order models were applied to the adsorption kinetics of Cr(VI) ions onto wood apple shell activated carbon. Thermodynamic parameters such as the standard enthalpy (ΔH°), the Gibbs' free energy (ΔG°) and the standard entropy (ΔS°) were evaluated and indicated that the sorption process was spontaneous and endothermic in nature. The results demonstrated that wood apple shell activated carbon may be effectively used for the inexpensive removal of Cr(VI) ions from aqueous solution.

**INTRODUCTION**

The presence of heavy metal ions in drinking water sources and in agricultural crops is harmful to humans. It is well known that heavy metal ions can be toxic, e.g. they damage nerves, liver and bones as well as blocking the functional groups of vital enzymes (Gholami *et al.* 2006). The major sources of heavy metal ions in water and soil are wastewater streams from many industrial processes (Olayinka *et al.* 2007), the most usual and important of which are electroplating, leather tanning and textile industries, refineries, paper and pulp, dyes and pigments, and wood preservation, with concentrations varying between 5 mg/l and 220 mg/l (Saravanan *et al.* 2009; Tazrouti and Amrani 2009; Ghosh 2009). Chromium(VI) is considered by the International Agency for Research on Cancer (IARC) as a powerful carcinogenic agent that modifies the DNA transcription process, causing important chromosomic aberrations (Candela *et al.* 1995; IARC 1982).

Various technologies are employed for removing toxic ions from water, including chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption (Bhatti *et al.* 2007; Sarin and Pant 2006). However, many of these methods suffer from drawbacks such as incomplete metal ion removal, high capital and operational costs, requirements for expensive
equipment and monitoring systems, high reagent and energy requirements, membrane scaling, fouling and blocking, or the generation of toxic sludge and other waste products that require disposal (Demirbas et al. 2004; Demiral et al. 2008).

Adsorption by activated carbon is one of the effective techniques for Cr(VI) ion removal from wastewater because of the high surface area, highly porous character and relatively low cost of the adsorbent. The use of activated carbons for removing Cr(VI) ions from wastewater has received great attention over a number of decades (Hu et al. 2003; Gupta et al. 2010). Activated carbon is especially known for the effective removal of organic chemicals, inorganic and heavy metal ion pollutants from wastewater in the laboratory as well as in various industries (Monser and Adhoum 2002; Jiang et al. 2008). The formation of metallic complexes with chelating agents, e.g. thiourea and bromide ion for bismuth (Madrakian et al. 2003), followed by their adsorption onto activated carbon has been reported.

Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have a potential as inexpensive sorbents. Some low-cost activated carbons for removing Cr(VI) ions such as groundnut husk (Dubey and Gopal 2007), agro waste (Qaiser et al. 2007), neem leaves (Babu and Gupta 2008), sawdust (Baral et al. 2006), wheat bran (Nameni et al. 2008), rice bran (Oliveira et al. 2005), sago waste (Vennilamani et al. 2005), green coconut shell (Pino et al. 2006), hazelnut shell (Koby et al. 2004; Koby et al. 2004) and peanut shell (Romero et al. 2004) have all been reported as useful for preparing adsorbents for Cr(VI) ions. In addition, the algal biomass of Scenedesmus obliquus and Arthospira maxima have been employed as adsorbents for the removal of Cr(VI) ions from the aqueous phase (Fatma et al. 2009). Similarly, chitosan shows good adsorption properties towards Cr(VI) ions from aqueous solution, although the adsorption is highly pH-dependent (Yan and Quan 2009).

Limonia acidissima (wood apple) fruit is important medicinally, as well as being used for making sweets. The shell of this fruit, which is normally a waste product, is particularly tough. This study reports the economic preparation of microporous activated carbon with a good adsorption capacity from Limonia acidissima fruit shell. This material exhibited rapid adsorption of Cr(VI) ions from aqueous media. The adsorption isotherms obtained are reported as well as the application of kinetic and thermodynamic models to the experimental data.

EXPERIMENTAL

Preparation of the adsorbent

A standard stock solution of Cr(VI) ions was prepared from potassium dichromate (Vogel 1975). Samples of Limonia acidissima (wood apple) shell were collected, washed with de-ionized water, air-dried, crushed into small pieces and then washed once more. The crushed pieces were maintained in an oven at 383 K for 24 h, following which they were soaked in conc. H₂SO₄ (as the impregnating agent) in a 1:2 ratio (weight of raw material/volume of acid) for 24 h. The material thus obtained was activated at 573 K for 1 h in a muffle furnace. Any excess acid present after this process was removed by washing with distilled water until the washing liquid exhibited a neutral pH. The dried activated carbon powder was then sieved through a BSS-25 sieve and stored for further studies. The wood apple shell activated carbon adsorbent thus prepared is referred to below as WASAC.
Characterization of the adsorbent

Proximate analysis of WASAC was undertaken by FT-IR spectroscopy (Perkin Elmer Spectrum 100 instrument), scanning electron microscopy (SEM) (Quanta 3D FEI instrument) and a C,H,N,S elemental analyzer (EA 1108, Carlo Erba). The IR spectrum of the activated carbon samples exhibited peaks at 3359.52, 2918.72, 1614.94, 1396.66 and 1208.72 cm\(^{-1}\) corresponding to the functional groups O–H, C–H, C=C, S=O and C–C, respectively (Figure 1). SEM analysis (Figure 2) confirmed the microporous nature of WASAC. The properties of WASAC are summarized in Table 1.

Batch adsorption experiments

Batch adsorption isotherm experiments were conducted employing initial Cr(VI) ion concentrations within the range 90–200 mg/l together with an adsorbent dosage varying from 0.05 g/l to 1.0 g/l. The influence of time, agitation speed and pH were studied employing an initial Cr(VI) ion concentration of 90 mg/l and an adsorbent dosage of 0.5 g/l. The concentration of free Cr(VI) ions in the effluent was determined spectrophotometrically (Elico SL 171 instrument) employing 1,5-diphenylcarbazide (DPC) in acidic solution (Marczenko 1976).

Adsorption isotherm studies were conducted in Erlenmeyer flasks at 299 ± 2 K employing an initial Cr(VI) ion concentration of 90 mg/l, adjusting the pH value of the solution to 2, maintaining a contact time of 180 min and agitating the flasks at 140 rpm on an orbital shaker. For the thermodynamic studies, the temperature was varied from 303 K to 323 K. The equilibrium adsorption capacity of WASAC was evaluated using the equation:

\[
q_e = \frac{(C_0 - C_e)V}{M}
\]  

(1)

Figure 1. FT-IR spectrum of WASAC.
Table 1. Characteristics of Wood Apple Shell Activated Carbon (WASAC)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content (%)</td>
<td>8.12</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.734</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>8.85</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>65.10</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.60</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>0.04</td>
</tr>
<tr>
<td>Sulphur (%)</td>
<td>2.35</td>
</tr>
</tbody>
</table>
where $q_e$ (mg/g) is the equilibrium adsorption capacity, $C_0$ and $C_e$ are the initial and equilibrium concentrations (mg/l) of Cr(VI) ions in the solution, $V$ (m$^3$) is the solution volume and $M$ (g) is the weight of adsorbent employed.

RESULTS AND DISCUSSION

Effect of pH

The Cr(VI) ion removal efficiency of WASAC at different pH values with an initial Cr(VI) ion concentration of 90 mg/l is shown in Figure 3. Thus, to each flask in a series of Erlenmeyer flasks containing 50 ml of Cr(VI) ion solution was added 0.5 g of adsorbent. The pH values of the resulting mixtures were adjusted to values within the range 1–11, with each flask being subsequently agitated for 3 h. After such agitation, the resulting solution was separated from the solid adsorbent by filtration through a Whatman No. 1 filter paper and its Cr(VI) ion content determined spectrophotometrically employing DPC as the reagent. Over the pH range 1–3, the Cr(VI) ion removal efficiency was found to be 98.05%. Consequently, a pH value of 2 was chosen for subsequent studies.

The maximum adsorption of Cr(VI) ions occurred at acidic pH values because there was an increase in the number of H$^+$ ions on the carbon surface under these circumstances, and these exerted a strong electrostatic attraction on the HCrO$_4^-$ ions present in solution. However, with increasing pH value, an exponential decrease occurred in the extent of Cr(VI) ion adsorption and at pH > 6.0 no significant adsorption occurred. This was due to dual competition between CrO$_2$ and OH$^-$ ions present in solution for the available surface sorption sites, with OH$^-$ ions predominating:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$$

(2)
At pH 1.0, Cr(VI) ions exist in the H₂CrO₄ form; however, over the pH range 1–6 different forms of Cr(VI) ions such as Cr₂O₂⁷⁻, HCrO₄⁻, Cr₃O₂¹⁰⁻ and Cr₄O₂¹³⁻ co-exist, of which HCrO₄⁻ predominates. As the pH increases, this form shifts to CrO₂⁴⁻ and Cr₂O₂⁷⁻. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system (Babu and Gupta 2008; Vogel 1975).

Effect of time

Maintaining all other variables constant, the time necessary for adsorption was varied from 15 min to 300 min. Adsorption started at 15 min with 39.28% uptake and reached an uptake value of 98.05% at 170 min, when the quantity of Cr(VI) ions adsorbed was 8.83 mg/g. There was no significant change in adsorption of Cr(VI) ions after 170 min (Figure 4). For this reason, further sorption studies were conducted after 180 min had elapsed.

\[
HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \quad (3)
\]

\[
2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad (4)
\]

At pH 1.0, Cr(VI) ions exist in the H₂CrO₄ form; however, over the pH range 1–6 different forms of Cr(VI) ions such as Cr₂O₂⁷⁻, HCrO₄⁻, Cr₃O₂¹⁰⁻ and Cr₄O₂¹³⁻ co-exist, of which HCrO₄⁻ predominates. As the pH increases, this form shifts to CrO₂⁴⁻ and Cr₂O₂⁷⁻. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system (Babu and Gupta 2008; Vogel 1975).

Figure 4. Effect of agitation time on the percentage removal of Cr(VI) ions by WASAC together with the amount adsorbed (mg/g). Experimental conditions employed: initial conc. of Cr(VI) ions = 90 mg/l; pH = 2; temp. = 299 ± 2 K; dosage of WASAC (M) = 0.5 g, agitation speed = 140 rpm.

Effect of initial Cr(VI) ion concentration

As shown in Figure 5, the percentage removal of Cr(VI) ions was 98.05% at an initial Cr(VI) ion concentration of 90 mg/l. At constant temperature, increasing the initial concentration of Cr(VI) ions from 90 mg/l to 200 mg/l led to an increase in the amount adsorbed from 8.83 mg/g to 13.94 mg/g. In such experiments, the pH of the system was adjusted to 2, while agitation was conducted at 140 rpm for 180 min. However, the percentage removal of Cr(VI) ions decreased as the initial concentration of Cr(VI) ions increased. This may have been due to an increase in the number of Cr(VI) ions competing for a fixed number of adsorption sites on WASAC.
Effects of adsorbent dosage and agitation speed

The corresponding experiments were carried out under the conditions described earlier, varying the adsorbent dosage from 0.05 g/\(\ell\) to 1.0 g/\(\ell\). The effect of adsorbent dosage on the adsorption of Cr(VI) ions by WASAC is presented in Figure 6. It will be seen from the figure that the removal efficiency towards Cr(VI) ions increased as the adsorbent dosage increased. This may be attributed to the increase in the contact surface of the adsorbent particles, making it more probable for \(\text{HCrO}_4^-\) and \(\text{Cr}_2\text{O}_7^{2-}\) ions to be adsorbed onto the available adsorption sites (Nameni et al. 2008). The maximum adsorption occurred at 0.5 g/\(\ell\) and remained constant at higher adsorbate dosages.

Figure 5. Effect of initial Cr(VI) ion concentration (mg/\(\ell\)) on the amount adsorbed (mg/g) onto WASAC. Experimental conditions employed: time = 180 min; pH = 2; temp. = 299 ± 2 K; dosage of WASAC (M) = 0.5 g; agitation speed = 140 rpm.

Figure 6. Effect of adsorbent dosage on the percentage removal of Cr(VI) ions by WASAC together with the amount adsorbed (mg/g). Experimental conditions: initial conc. of Cr(VI) ions = 90 mg/\(\ell\); time = 180 min; pH = 2; temp. = 299 ± 2 K; agitation speed = 140 rpm.
To study the effect of the agitation speed on the removal of Cr(VI) ions, this speed was varied from 50 rpm to 200 rpm at constant temperature (Figure 7). It will be seen that the percentage removal of Cr(VI) ions attained a constant value at agitation speeds above 140 rpm.

![Figure 7](image)

**Figure 7.** Effect of agitation speed on the percentage removal of Cr(VI) ions by WASAC together with the amount adsorbed (mg/g). Experimental conditions: initial conc. of Cr(VI) ions = 90 mg/L; time = 180 min; temp. = 299 ± 2 K; dosage of WASAC (M) = 0.5 g.

**Adsorption isotherms**

Of the various isotherm models available, the application of those of Langmuir and Freundlich to the experimental data was tested in the present study.

**Langmuir isotherm**

This isotherm model assumes that chemisorption occurs between the adsorbent and adsorbate via the formation of an ionic or covalent bond. The Langmuir equation may be written as:

\[
\frac{C_e}{q_e} = \frac{1}{K_Lq_m} + \frac{C_e}{q_m}
\]

(5)

where \(K_L\) is the Langmuir adsorption equilibrium constant (1/mg), \(q_m\) is the quantity of adsorbate required to form a single monolayer and \(q_e\) is the amount adsorbed onto unit mass of the solid at an equilibrium concentration of \(C_e\). A plot of \(C_e/q_e\) versus \(C_e\) should yield a straight line if the Langmuir equation is obeyed by the equilibrium adsorption data (Sharma and Bhattacharyya 2004; Shekinah et al. 2002).

Further analysis of the application of the Langmuir equation may be made on the basis of a dimensionless equilibrium parameter, \(R_L\), also known as the separation factor (Hall *et al.* 1966), given by:

\[
R_L = \frac{1}{1 + K_LC_e}
\]

(6)
The value of $R_L$ lies between 0 and 1 for favourable adsorption, $R_L > 1$ represents unfavourable adsorption, $R_L = 1$ corresponds to linear adsorption while the adsorption process is irreversible if $R_L = 0$.

It was found that the adsorption of Cr(VI) ions onto WASAC followed the Langmuir isotherm model (plot not shown), allowing the values of $q_m$ and $K_L$ to be evaluated (Table 2). The magnitude of the dimensionless parameter $R_L$ of 0.016–0.364 is consistent with the requirement for favourable adsorption. The high value of the correlation coefficient, $R^2$, indicates good agreement between the parameters and confirms the monolayer adsorption of Cr(VI) ions onto the adsorbent surface.

| TABLE 2. Langmuir and Freundlich Constants for the Adsorption of Cr(VI) Ions onto WASAC |
|---------------------------------|---------------------------------|
| Constants                       | Values                          |
| **Langmuir**                   |                                 |
| $q_m$ (mg/g)                   | 13.74                           |
| $b$ (1/mg)                     | 0.999                           |
| $R^2$                          | 0.998                           |
| **Freundlich**                 |                                 |
| $K_F$                          | 8.72                            |
| $n$                            | 8.42                            |
| $R^2$                          | 0.969                           |

*Freundlich isotherm*

The logarithmic form of the Freundlich isotherm equation (Arivoli et al. 2008) may be written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(7)

where $q_e$ is the amount adsorbed (mg/g), $C_e$ is the equilibrium concentration of adsorbate (mg/l), and $K_F$ and $n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The values for $K_F$ and $n$ obtained in the present work are presented in Table 2. The value of the correlation coefficient, $R^2$, obtained in this case indicates that the Freundlich model gave a poorer fit to the experimental data than the Langmuir equation.

*Adsorption kinetics*

Samples of WASAC were agitated at 140 rpm with a fixed concentration of adsorbate solution (50 mg/l) in a series of Erlenmeyer flasks maintained at the desired temperature in a thermostatted bath. The time at which the adsorbent was introduced to the reaction flasks was taken as zero and samples were then removed from these flasks at various time intervals from 0 min to 180 min and their Cr(VI) ion content determined.
Several kinetic models (most notably the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion models) are employed to explain the mechanism of adsorption processes. For simplicity and ease of graphical presentation, the pseudo-first-order kinetic equation may be written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (8)

where \(q_e\) and \(q_t\) are the amount of solute adsorbed (mg/g) at equilibrium and at time \(t\) (min), respectively, and \(k_1\) is the rate constant for the pseudo-first-order adsorption process (Babu and Gupta 2008; Ozturk and Kavak 2005). If pseudo-first-order kinetics are obeyed, a plot of \(\log(q_e - q_t)\) versus time should be linear, thereby allowing the computation of the adsorption rate constant, \(k_1\) (Arivoli et al. 2008).

The corresponding pseudo-second-order rate equation (Ho and McKay 1998) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (9)

where \(k_2\) is the rate constant for the pseudo-second-order adsorption process (Igwe and Abia 2006). The values obtained graphically for both adsorption models are listed in Table 3. The results show that the pseudo-first-order model provided a better approximation to the experimental kinetic data than the pseudo-second-order model.

### TABLE 3. Kinetic Parameters for the Adsorption of Cr(VI) Ions onto WASAC

<table>
<thead>
<tr>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-first-order</strong></td>
<td></td>
</tr>
<tr>
<td>(q_e) (exp.) (mg/g)</td>
<td>8.99</td>
</tr>
<tr>
<td>(q_e) (calc.) (mg/g)</td>
<td>9.77</td>
</tr>
<tr>
<td>(k_1 \times 10^{-3}) (min(^{-1}))</td>
<td>1.04</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9671</td>
</tr>
<tr>
<td><strong>Pseudo-second-order</strong></td>
<td></td>
</tr>
<tr>
<td>(q_e) (calc.) (mg/g)</td>
<td>11.24</td>
</tr>
<tr>
<td>(k_2) [mg/(g min)]</td>
<td>0.031</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9881</td>
</tr>
<tr>
<td><strong>Intra-particle diffusion</strong></td>
<td></td>
</tr>
<tr>
<td>(k_{id}) [mg/(g min)]</td>
<td>0.698</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9812</td>
</tr>
</tbody>
</table>

The possibility that intra-particle diffusion played a significant role in the adsorption process was explored by using the intra-particle diffusion model. A diffusion step as predicted by this model is of major concern from the industrial viewpoint since it would constitute the rate-determining step in liquid adsorption systems. Intra-particle diffusion varies with the square root of time (Babu and Gupta 2008):
where \( c \) is a constant and \( k_{\text{id}} \) is the intra-particle diffusion rate constant \([\text{mg/(g min}^{1/2}]\). \( q_t \) is the amount adsorbed at a time \((\text{mg/g})\) while \( t \) is the time \((\text{min})\). The intra-particle diffusion rate constant may be determined from the slope of the linear plot of \( q_t \) versus \( t^{1/2} \). The rate constant for intra-particle diffusion at different temperatures is also listed in Table 3.

### Adsorption thermodynamics

The thermodynamics of an adsorption process may be obtained from a study of the influence of temperature on the process. This effect has been studied for the sorption of Cr(VI) ions by WASAC. It has been found that the adsorption capacity increased from 13.98 mg/g to 19.78 mg/g as the temperature was increased from 303 K to 323 K at an initial Cr(VI) ion concentration of 200 mg/L and a pH value of 2.0.

The standard Gibbs’ free energy, \( \Delta G^0 \), may be expressed by the equation:

\[
\Delta G^0 = -RT \ln K_c
\]

(11)

where \( K_c \) is the equilibrium constant for the process at a given temperature. Other thermodynamic parameters such as the change in the standard enthalpy (\( \Delta H^0 \)) and standard entropy (\( \Delta S^0 \)) may be determined via the following equation (Demiral et al. 2008):

\[
\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

(12)

with \( \Delta H^0 \) and \( \Delta S^0 \) being obtained from the slope and intercept of the van’t Hoff plot of \( \ln K_c \) versus \( 1/T \). A positive value of \( \Delta H^0 \) indicates that the adsorption process is endothermic, while the negative values of \( \Delta G^0 \) reflect the feasibility of the process with values becoming more negative with increasing temperature. The standard entropy change, \( \Delta S^0 \), determines the disorderliness of adsorption at the solid–liquid interface (Table 4).

### Table 4. Thermodynamic Parameters for the Adsorption of Cr(VI) Ions onto WASAC

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
<th>( \Delta H^0 ) (kJ/mol)</th>
<th>( \Delta S^0 ) [J/(mol K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-1.110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>-1.604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>-1.824</td>
<td>1.582</td>
<td>5.707</td>
</tr>
<tr>
<td>318</td>
<td>-1.971</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-2.115</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Relative magnitude of WASAC adsorption capacity towards Cr(VI) ions

A comparison was made, in terms of the adsorption capacity \( (q_m) \) towards Cr(VI) ions, of the behaviour of WASAC with that of other low-cost adsorbents (Table 5). The present study has
shown that WASAC is an effective low-cost adsorbent for the removal of Cr(VI) ions from aqueous solutions. It was observed that a pH value of 2.0 was the optimum for the adsorption of Cr(VI) ions in nearly all cases, irrespective of the method of activation employed.

CONCLUSIONS

*Limonia acidissima* (wood apple) shell is a waste product which may be converted into a carbonaceous adsorbent and used for the removal Cr(VI) ions from aqueous solution. Characterization of the adsorbent showed that it was porous and very effective in the removal of Cr(VI) ions from wastewater. Thus, the removal of Cr(VI) ions with an initial concentration 90 mg/g was found to be 98.05% after shaking for 180 min at 140 rpm at constant temperature. The increase in the adsorption capacity observed with increasing temperature showed that the adsorption process was chemical in nature, being feasible, spontaneous and endothermic as confirmed by the evaluation of the relevant thermodynamic parameters, viz. $\Delta H^0$, $\Delta G^0$ and $\Delta S^0$. The experimental data for the adsorption process were well fitted by the Langmuir adsorption isotherm model relative to the fit of the Freundlich adsorption model. The adsorption of Cr(VI) ions obeyed the pseudo-first-order kinetic equation. The ready availability of wood apple shell and the ease with which the corresponding activated carbon may be produced favours its use as a means of effectively removing Cr(VI) ions from aqueous solution.

NOMENCLATURE

- $c$: constant
- $C_e$: equilibrium concentration of Cr(VI) ion in solution (mg/l)

### TABLE 5. Comparison of the Adsorption Capacity of WASC for Cr(VI) Ions with that of Other Adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_m$ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-modified waste activated carbon</td>
<td>10.929</td>
<td>Ghosh (2009)</td>
</tr>
<tr>
<td>Agro waste</td>
<td>5.66</td>
<td>Qaiser <em>et al.</em> (2007)</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>0.942</td>
<td>Nameni <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>Green coconut shell</td>
<td>4.182</td>
<td>Pino <em>et al.</em> (2006)</td>
</tr>
<tr>
<td>Sago waste</td>
<td>5.78</td>
<td>Vennilamani <em>et al.</em> (2005)</td>
</tr>
<tr>
<td>Modified oak sawdust</td>
<td>1.7</td>
<td>Argun <em>et al.</em> (2007)</td>
</tr>
<tr>
<td>Activated rice husk carbon</td>
<td>0.8</td>
<td>Bishnoi <em>et al.</em> (2004)</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>13.4</td>
<td>Sharma and Foster (1994)</td>
</tr>
<tr>
<td>Biogas residual slurry</td>
<td>5.87</td>
<td>Namasivayam and Yamuna (1995)</td>
</tr>
<tr>
<td>Coconut tree sawdust</td>
<td>3.60</td>
<td>Selvi <em>et al.</em> (2001)</td>
</tr>
<tr>
<td>Treated sawdust of Indian rosewood</td>
<td>10.00</td>
<td>Garg <em>et al.</em> (2004)</td>
</tr>
<tr>
<td>Bael fruit (<em>Aegle marmelos correa</em>) shell</td>
<td>17.27</td>
<td>Anandkumar and Mandal (2009)</td>
</tr>
<tr>
<td>Wood apple shell</td>
<td>13.74</td>
<td>Present work</td>
</tr>
</tbody>
</table>
**Adsorption of Cr(VI) Ions onto Limonia acidissima (Wood Apple) Shell**

C₀ initial concentration of Cr(VI) ions in solution (mg/ℓ)

ΔG⁰ standard Gibbs’ adsorption energy (kJ/mol)

ΔH⁰ standard adsorption enthalpy (kJ/mol)

Kₑ equilibrium constant

Kₐ Freundlich multilayer adsorption capacity (mg/g)

Kₐ Langmuir equilibrium adsorption constant (ℓ/mg)

k₁ pseudo-first-order adsorption rate constant (1/min)

k₂ pseudo-second-order adsorption rate constant [mg/(g min)]

M adsorbent dosage (g)

qₑ amount of Cr(VI) ions at equilibrium (mg/g)

qₐ Langmuir monolayer adsorption capacity (mg/g)

qₜ amount of Cr(VI) ions adsorbed at time t (mg/g)

Rₑ dimensionless equilibrium parameter

R² correlation coefficient

ΔS⁰ standard entropy of adsorption [J/(mol K)]

T temperature (K)

t time (min)

V solution volume (ℓ)

**REFERENCES**


