

Removal of Hexavalent Chromium Using Novel Adsorbent Prepared from *Wrightia tinctoria* Fruits under Microwave Heating

S. SAMINATHAN^{1,*}, M. ASAITHAMBI², V. SIVAKUMAR³ and P. SIVAKUMAR⁴

¹Department of Chemistry, Sakthi Polytechnic College, Sakthinagar, Erode-638 315, India

²Department of Chemistry, Erode Arts and Science College, Erode-638 009, India

³Department of Chemistry, Sri Vasavi College, Erode-638 316, India

⁴Department of Chemistry, A.A. Government Arts College, Namakkal-637 002, India

*Corresponding author: E-mail: ssaminathan91@gmail.com

Received: 11 April 2016;

Accepted: 30 June 2016;

Published online: 10 August 2016;

AJC-18019

An activated carbon prepared from unripe fruits of *Wrightia tinctoria* by two-step microwave irradiation with optimum duration produces activated carbon with a surface area of 911 m²/g. The prepared activated carbon (WAC) utilized for the removal of hexavalent chromium from wastewater. Effect of pH indicates that maximum quantity of Cr(VI) can be removed at a pH of 2. The correlation coefficient calculated using pseudo-second order model varies between 0.9819 < r² < 0.9968 at different initial concentrations and it varies between 0.9888 < r² < 0.9938 at various temperatures depicts that pseudo-second order kinetic model is more appropriate to describe the adsorption than pseudo-first order model. The Freundlich model is more appropriate to explain the adsorption of Cr(VI) onto WAC when compared with Langmuir isotherm model with good correlation coefficient. The positive enthalpy of adsorption indicates the endothermic nature of adsorption with good spontaneity.

Keywords: Microwave, Adsorption, Kinetics, Isotherm, Effluent, Surface area.

INTRODUCTION

The aquatic environment has been polluted greatly due to the discharge of effluent from various industries containing non-degradable and hazardous compounds. The heavy metals such as chromium, copper, lead, cadmium, nickel and mercury are the most important constituents among toxic compounds in the effluents [1]. Unlike other organic pollutants, the heavy metal contamination poses a serious threat due to its non-biodegradable nature. Among the various heavy metals, Cr(VI) has been classified as a top priority toxic pollutant by USEPA, as well as Chinese EPB due to its high solubility and acute toxicity to living organisms [2]. Industries like mining, electroplating, leather tanning, textile dyeing and metal finishing using large amount of chromium compounds.

Many technologies like chemical precipitation, oxidation/reduction, ion exchange, reverse osmosis and adsorption using activated materials have been used for the removal Cr(VI) from wastewater [3]. Among them, adsorption using activated materials seems to be an attractive choice for the removal of chromium, because of its removal efficiency and for the rapid adaptation to pollutant loading alteration [4]. Adsorbents with

excellent adsorption characteristics were prepared from the wastes such as olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used, hazelnut shell, coconut shell charcoal, banana peel and green alga [5-9].

Microwave heating is one of the most versatile methodologies for the preparation of activated carbon. Unlike conventional heating, the energy conversion in microwave heating occurs by two mechanisms: ion conduction and dipole rotation inside particles [10]. In the microwave carbonization process, the efficiency is very close to 100, *i.e.* almost all the carbon from biomass is converted into carbonized material, without generating CO and CO₂.

In the present work, unripe fruits of *Wrightia tinctoria* used as a precursor for the preparation of highly porous activated carbon. About the precursor, *Wrightia tinctoria* (Sweet Indrajao) is a small, deciduous tree with a light gray, scaly smooth bark. Native to India and Burma, *Wrightia* is named after a Scottish physician and botanist William Wright (1740-1827). The availability of fruits in large quantity without any cost makes *Wrightia tinctoria* fruits as good candidature for the preparation of a novel non-conventional activated carbon.

EXPERIMENTAL

Preparation of activated carbons: The fresh unripe fruits were collected from the various regions of Erode District, India. The unripe fruits were cut into pieces of 2 to 3 cm and dried in sunlight for about 1 week. The dried material was used for the preparation of activated carbon as per the following procedure.

The dried precursor was carbonized in microwave oven for 10 min at 600 w. The carbon was washed with plenty of water to remove all the washable contents. The washed carbon was dried, activated in microwave oven in an N₂ atmosphere at 600 w for 10 min, washed again, dried in hot air oven at 110 °C for 24 h and stored in tight lid container for further studies.

Characterization of the carbons: Physico-chemical characteristics of the activated carbon samples were studied as per the standard testing methods [11,12]. The N₂-adsorption-desorption isotherms of activated carbon were measured at 77 K using N₂ gas sorption analyzer (Nova 1000, Quanta Chrome Corporation) in order to determine the surface area using the BET equation. The morphological characteristics of the samples were studied using JSM-5610LV (Make: JEOL-JAPAN) scanning electron microscope (SEM).

Adsorption experiments: Adsorption of Cr(VI) on to the adsorbent was studied by batch mode experiments. The stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 2.828 g of AR grade K₂Cr₂O₇ in 1000 mL of double distilled and de-ionized water. Required concentration of Cr(VI) solution was prepared by diluting the stock solution using double distilled water as and when required. The adsorption experiments were carried out in 250 mL tight lid glass (borosil-R) bottles by agitating 100 mg of adsorbent with 200 mL of Cr(VI) solution of specified concentration. For the study of pH effect, the pH of solutions was adjusted by micro-additions of 0.1 M HCl and 0.1 M NaOH.

The contents of the flask were agitated in a temperature controlled orbital shaker (REMI make). After the specified time, the bottle is taken out from the shaker then centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 min and un-adsorbed supernatant liquid was analyzed for the residual Cr(VI) concentration using Elico make Bio UV-visible spectrometer (BL-198). The concentration of Cr(VI) was determined through the development of a purple-violet colour with 1,5 diphenyl carbazide in an acidic solution at 540 nm. 1 mL of a 0.2 % (w/v) of 1,5 diphenyl carbazide solution prepared in 95 % ethyl alcohol and 1 mL of 0.2 M H₂SO₄ solution was added to the filtered sample (1 mL) containing less than 100 mg/L of Cr(VI) ions and diluted to 100 mL with double distilled water. All the experiments were conducted in duplicate and mean of the two values were taken for calculation. Maximum deviation is 4 %.

Amount of Cr(VI) adsorbed per gram of adsorbent was calculated with the following equations:

$$q_e = (C_o - C_e) \frac{V}{W} \quad (1)$$

$$\text{Cr(VI) removal(\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

where, C_o and C_e (mg/L) are the liquid-phase concentrations of Cr(VI) initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g). Adsorption isotherms were performed at 30, 40 and 50 °C, respectively. The flasks were shaken to ensure that the sorption process reached equilibrium.

Desorption experiments: The re-usage ability of the adsorbent was investigated by desorption experiments. Desorption studies as a function of pH were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. For the desorption studies, 500 mg of Cr(VI) loaded adsorbent was agitated with distilled water of varying pH above the equilibration time. The desorbed Cr(VI) concentration was analyzed similar to adsorption experiments.

RESULTS AND DISCUSSION

Adsorbent characteristics: The characteristics of the activated carbon (WAC) prepared from unripe fruits of *Wrightia tinctoria* using microwave hydrothermal process is given in Table-1. The activated carbon WAC has very small conductivity values due to the presence of least number of surface functionalities. Moisture content of WAC is slightly high, this may due to the adsorption of atmospheric water molecules by highly porous carbon. Rapid and uniform heating results the less amount of ash in carbon synthesized by microwave heating. The carbon WAC is highly porous with a BET surface area of 911 m²/g.

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF WAC

S. No.	Properties	WAC
1	pH	7.34
2	Conductivity (mS/cm)	0.08
3	pH _(ZPC)	6.81
4	Moisture content (%)	8.91
5	Ash (%)	12.7
6	Volatile matter (%)	11.4
7	Matter soluble in water (%)	0.28
8	Matter soluble in 0.25 N HCl (%)	1.22
9	Bulk density (g/mL)	0.45
10	Surface area (BET) (m ² /g)	911
11	Methylene blue value (mg/g)	1080
12	Iodine number (mg/g)	1124
13	Fixed carbon (%)	65.5
14	Yield (%)	53.7

The electron microscope study reveals highly porous and branched particles. Small cavities, pores and more rough surfaces on the carbon sample indicate the presence interconnected porous network. The Activated carbon WAC with 1000x magnification (Fig. 1) clearly shows the morphology of highly porous activated carbon sample. Most of the particles are having very fine pores of < 1 μm size.

Effect of agitation time and initial Cr(VI) concentration: In order to examine the effect of initial Cr(VI) concentration on the adsorption of Cr(VI) onto WAC, the experiment was conducted at room temperature with different initial Cr(VI) concentrations (Fig. 2a) under various time intervals. The adsorption was rapid during the first 100 min of contact time

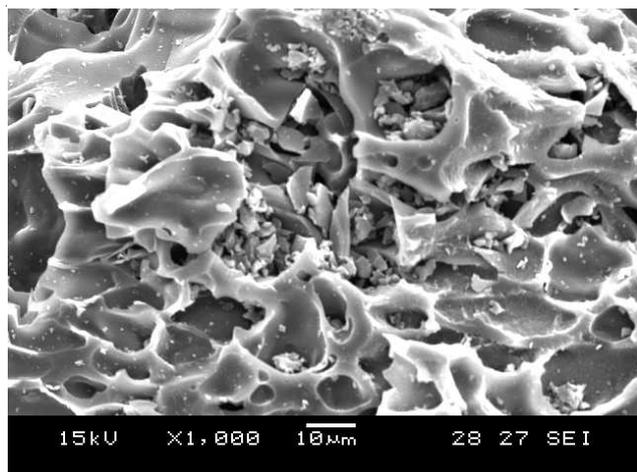


Fig. 1. SEM image of WAC

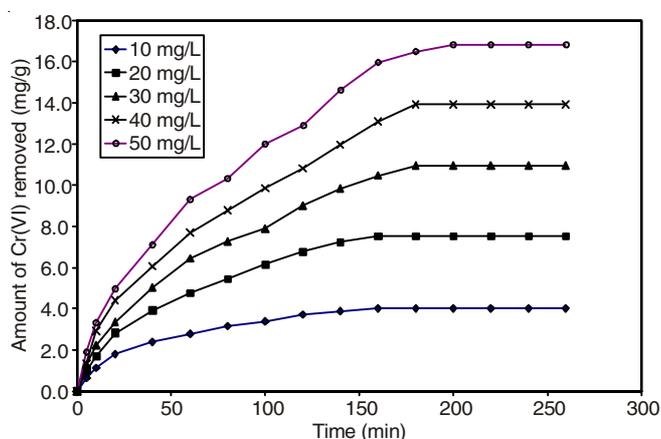


Fig. 2a. Effect of initial Cr concentration on adsorption

and it slowly reaches equilibrium at 175 min. More than 70 % of uptake was achieved during the first 100 min and then the rest is adsorbed from 100 to 175 min and the adsorption reaches equilibrium at 175 min. During the initial stages, the concentration gradient across the boundary is very high (*i.e.* the concentration of solute between the solid phase and liquid phase is very large), which leads to the rapid uptake during the initial stages of adsorption. On increasing the initial Cr(VI) from 10 to 50 mg/L the amount of Cr(VI) adsorbed by WAC increased from 4.0 to 16.84 mg/g though the percentage of adsorption decreases from 80.0 to 67.35. When the adsorption progresses, the concentration difference of Cr(VI) between the solution and solid phase decreases which will minimize the driving force and ultimately the rate of adsorption decreases. Based on the results of this study the optimum contact time is fixed as 180 min for all the equilibrium adsorption studies.

Effect of temperature: The effect of temperature on the adsorption of Cr(VI) is shown in Fig. 2b. As the solution temperature increased from 30 to 45 °C, the percentage of Cr(VI) adsorption increases from 73.12 to 78.49 % and the amount of Cr(VI) adsorbed by WAC increases from 10.97 to 11.77 mg/g. The temperature studies indicated that the adsorption of Cr(VI) by WAC is highly depends on the temperature, increase of solution temperature favors the adsorption. High adsorption at elevated temperature indicates that the adsorption of Cr(VI) by WAC is endothermic in nature.

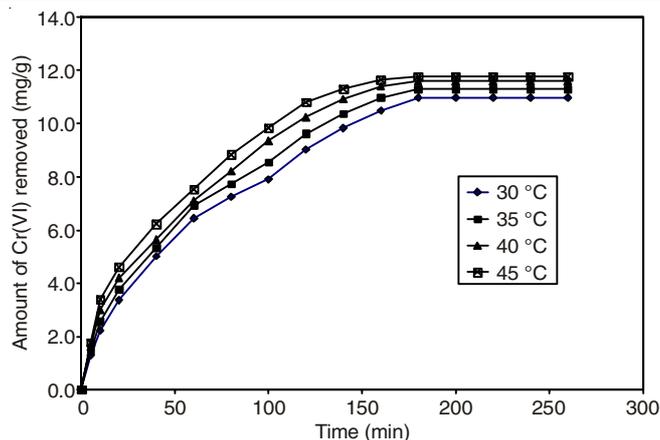


Fig. 2b. Effect of temperature on adsorption of chromium(VI)

Effect of pH: Fig. 3 showed the percentage of Cr(VI) adsorption by WAC is highly dependent on the pH of the solution. The percentage of adsorption of Cr(VI) decreases from 90.2 to 48.4 on increasing the solution pH from 2 to 10. The best pH for the effective adsorption of Cr(VI) is 2. The high electrostatic force of attraction between the adsorbent and adsorbate is responsible for the high adsorption at lower pH and this force of attraction decreases while increasing the pH and ultimately the adsorption decreases. The existence of Cr(VI) in the solution is highly pH dependent. At lower pH (2 to 6), the species like $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and CrO_4^{2-} are predominant and at higher pH (above 6), $\text{Cr}_2\text{O}_7^{2-}$ ion predominates [13].

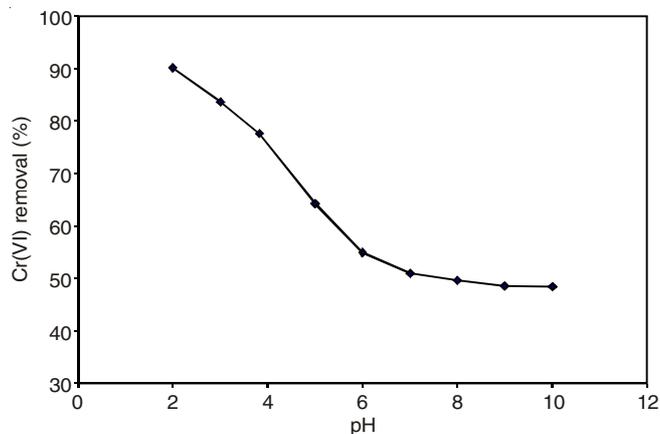


Fig. 3. Effect of pH on adsorption of Cr(VI)

At high pH range (above 6), there is a competition between the CrO_4^{2-} and OH^- ions for the adsorption sites, which ultimately reduces the amount of Cr(VI) adsorption when the pH goes higher than 6. Based on the above findings, the optimum pH for further adsorption studies was fixed as 2.

Kinetics of adsorption: In order to investigate the mechanism of adsorption and its potential rate controlling steps, it is essential to study the kinetics of adsorption. For this purpose, the kinetic models like pseudo-first order [14] and pseudo-second order [15] were selected and the adsorption kinetic data were analyzed.

Pseudo-first order kinetic model: The adsorption kinetic data were described by the Lagergren pseudo first order model

[12], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{3}$$

where, q_e and q_t are the amount of metal ion adsorbed at equilibrium at time 't' respectively (mg/g), k_1 is the rate constant of first order adsorption (L/min). Integrating eqn. 3 for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303} t \tag{4}$$

Eqn. 4 can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t by plot of $\log(q_e - q_t)$ versus t to give a linear relationship, from which k_1 and predicted q_e can be determined from the slope and intercept of the plot respectively.

The pseudo-first order plot for the adsorption of Cr(VI) onto WAC at various concentrations and temperatures are shown in Fig. 4 and the results are presented in Table-2. The pseudo-first order rate constant k_1 increases from 1.198×10^{-2} to $1.681 \times 10^{-2} \text{ min}^{-1}$ on increasing the initial Cr(VI) concentration from 10 to 50 mg/L. On increasing the Cr(VI) concentration by keeping all other operating parameters constant, the driving force from the solution side increases which then increases the rate of adsorption at higher concentrations. Similarly, on increasing the temperature from 30 to 45 °C, the rate constant increases from 1.451×10^{-2} to $2.050 \times 10^{-2} \text{ min}^{-1}$. This may due to fact that the high temperature, the kinetic energy of solute molecules increases which makes more contact between the different solute with the surface of the adsorbent. The q_e values derived from the pseudo-first order kinetic model shows good similarities with the experimentally calculated q_e values especially at a moderate initial Cr(VI) concentrations (30 and 40 mg/L).

Whereas the effect of temperature indicates that the calculated q_e values are extremely closer to the experimentally calculated q_e values. The correlation coefficient values ($0.5376 < r^2 < 0.9607$ at various concentrations and $0.9819 < r^2 < 0.9968$

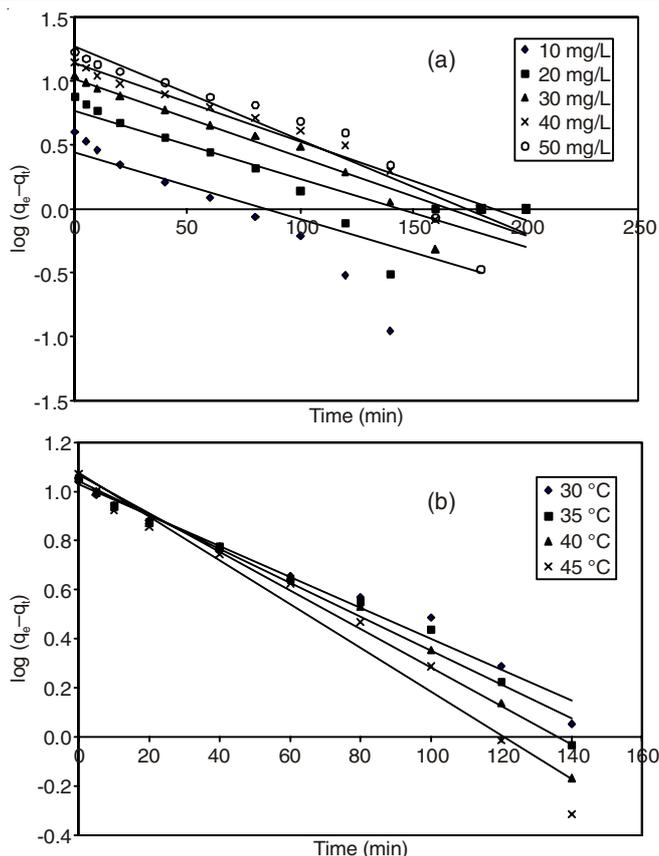


Fig. 4. Pseudo-first order plot (a) concentration variation, (b) temperature variation

at various temperatures) indicates that the pseudo-first order kinetic model could not describe the adsorption of Cr(VI) onto WAC properly and the adsorption needs to be analyzed with other suitable kinetic models like pseudo-second order kinetic models.

Pseudo-second order plot: The adsorption may also be described by pseudo second order kinetic model. The differential equation is generally given as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

where, k_2 (g/mg/min) is the second order constant for adsorption. Integrating eqn. 6 for the boundary conditions $q_t = 0$ to $q_t = q_e$ and $t = 0$ to $t = t$ is simplified as can be rearranged and linearized to obtain:

TABLE-2 KINETIC STUDIES FOR THE ADSORPTION OF Cr(VI) ONTO WAC									
Parameters	Initial Cr(VI) concentration (mg/L)					Temp. (°C)			
	10	20	30	40	50	30	35	40	45
q_e exp. (mg/g)	4.00	7.54	10.97	13.93	16.84	10.97	11.29	11.61	11.77
Pseudo-first order kinetics									
$k_1 \times 10^{-2}$ (min ⁻¹)	1.198	1.221	1.405	1.428	1.681	1.451	1.589	1.819	2.050
q_e cal (mg/g)	2.73	5.79	10.31	13.90	18.75	10.72	11.08	11.67	11.95
r^2	0.5376	0.767	0.9179	0.9607	0.9002	0.9787	0.9776	0.9717	0.9698
Pseudo-second order kinetics									
$k_2 \times 10^{-3}$ (g/mg/min)	6.69	2.38	1.15	0.79	0.65	1.15	1.33	1.52	1.84
h	0.1419	0.20	0.22	0.26	0.3111	0.225	0.261	0.300	0.355
q_e cal (mg/g)	4.60	9.15	13.95	18.08	21.88	13.95	13.99	14.06	13.89
r^2	0.9968	0.9937	0.9888	0.9839	0.9819	0.9888	0.9909	0.9913	0.9938

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The second order rate constants were used to calculate the initial sorption rate, h (mg/g/min) given by the following equation:

$$h = k_2 q_e^2 \quad (8)$$

A plot of " t/q_t " versus " t " should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e can be calculated from the intercept and slope of the plot.

The pseudo-second order plot (t versus t/q_t) for the adsorption of Cr(VI) onto WAC at various initial Cr(VI) concentrations and temperature is shown in Fig. 5 and the results calculated from the slope and intercept are given in Table-2. As seen from the table, the pseudo-second order rate constant decreases from 6.69×10^{-3} to 0.65×10^{-3} (g/mg/min) on increasing the initial Cr(VI) concentration from 10 to 50 mg/L and it increases from 1.15×10^{-3} to 1.84×10^{-3} (g/mg/min) while increasing the temperature from 30 to 45 °C. The q_e calculated using pseudo-second order plot show slight deviation from the experimental q_e values. The correlation coefficient calculated using pseudo-second order model varies from $0.9819 < r^2 < 0.9968$ at different initial concentrations and it varies from $0.9888 < r^2 < 0.9938$ at various temperatures depicts that pseudo-second order kinetic model is more appropriate to describe the adsorption than pseudo-first order model [1].

Adsorption isotherm: The equilibrium existence between adsorbed metal ions on the adsorbent (q_e) and metal ions

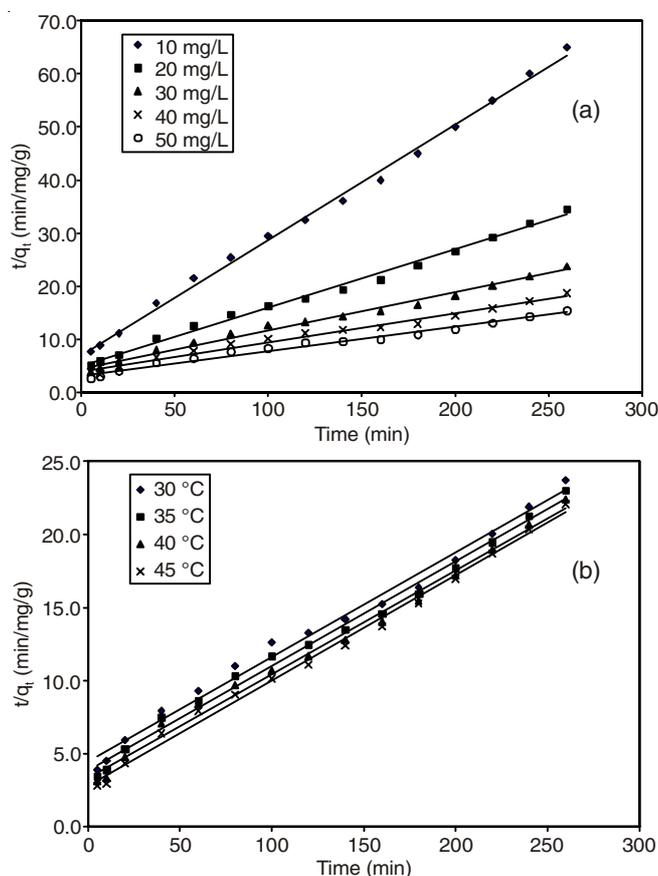


Fig. 5. Pseudo-second order plot (a) concentration variation, (b) temperature variation

remaining in solution (C_e) at a constant temperature is called as adsorption isotherm [16]. In-order to understand the real adsorption phenomenon for the adsorption of Cr(VI) onto WAC, the isotherm data were analyzed using Langmuir [17] and Freundlich [18] isotherm models.

Langmuir isotherm: Langmuir isotherm [17] is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The Langmuir isotherm can be expressed as:

$$q_e = \frac{Q_0 b_L C_e}{(1 + b_L \cdot C_e)} \quad (9)$$

where, b_L is the Langmuir constant, C_e is the equilibrium metal ion concentration in solution, C_0 is the initial concentration (mg/L) and Q_0 is a constant related to monolayer adsorption capacity.

Linear form of the rearranged Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b_L} + \frac{C_e}{Q_0} \quad (10)$$

A plot of C_e/q_e vs. C_e should indicate a straight line of slope $1/Q_0$ and an intercept of $1/(b_L \cdot Q_0)$.

The essential characteristics of Langmuir isotherm can also be described by a dimensionless separation factor R_L which is defined by the following equation.

$$R_L = 1/(1 + b_L \cdot C_e) \quad (11)$$

The value of separation factor R_L indicates the nature of the adsorption process as given below:

$$\begin{aligned} R_L > 1 &\rightarrow \text{Unfavourable} \\ R_L = 1 &\rightarrow \text{Linear} \\ 0 < R_L < 1 &\rightarrow \text{Favourable} \\ R_L = 0 &\rightarrow \text{Irreversible} \end{aligned}$$

A plot of C_e versus C_e/q_e is shown in Fig. 6 and results calculated from the slope and intercept are given in Table-3. As observed from the results, the Langmuir monolayer adsorption capacity (Q_0) increases from 17.24 to 18.32 mg/g on increasing the temperature from 30 to 45 °C. As observed from the kinetic studies, the adsorption increases with temperature under similar set of operating conditions. When the adsorption increases with temperature, accordingly the monolayer adsorption capacity also increases. The Langmuir rate constant b_L initially increases from 1.59 to 1.61 when the temperature increased upto 40 °C and then it decreases to 1.59×10^{-2} at 45 °C. The dimensionless factor R_L varies from 0.012 to 0.926, indicating the favourability of Cr(VI) adsorption onto WAC. The regression coefficient varies from 0.9701 to 0.9935, indicating a minor deviation of data points from the straight line.

Freundlich isotherm: Freundlich [18] isotherm model is an exponential equation that applies to the adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a monolayer.

TABLE-3 ISOTHERM PLOTS FOR THE ADSORPTION OF Cr(VI) ONTO WAC				
Parameters	Temperature (°C)			
	30	35	40	45
Langmuir isotherm				
Q ₀ (mg/g)	17.24	17.48	17.70	18.32
b _L × 10 ⁻² (L/mg)	1.59	1.60	1.61	1.59
R _L	0.012 to 0.926			
r ²	0.9935	0.9856	0.9812	0.9701
Freundlich isotherm				
n	1.41	1.44	1.49	1.56
k _f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	1.59	1.75	1.96	2.27
r ²	0.9968	0.997	0.9972	0.9969

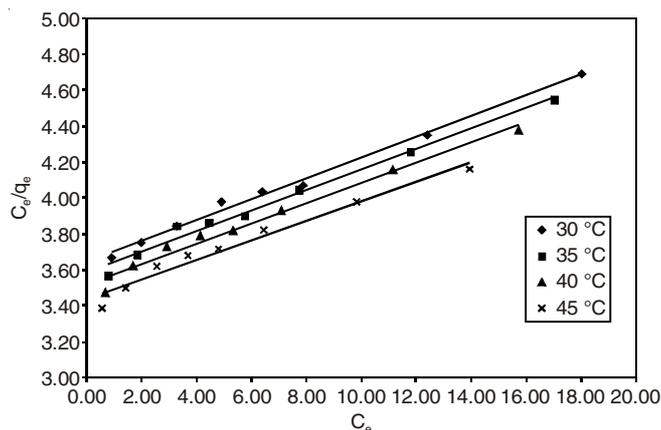


Fig. 6. Langmuir Isotherm plot

This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly that sorption energy exponentially decreases on completion of the sorption centres of an adsorbent. The well-known expression for the Freundlich model is given as:

$$q_e = k_f \cdot C_e^{1/n} \tag{12}$$

Linear form of Freundlich equation is:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{13}$$

where, k_f is the Freundlich constant, k_f [mg/g(L/g)^{1/n}] related to the binding energy and n is the heterogeneity factor (n is a measure of deviation from linearity of the adsorption). It indicates the degree of non-linearity between solution concentration and adsorption. The value of k_f and n were calculated from the linear plot of “log q_e” versus “log C_e”. When 1/n is > 1.0, the change in adsorbed Cr(VI) concentration is greater than the change in the solute concentration.

The Freundlich constants k_f and n for the adsorption of Cr(VI) onto WAC are calculated from the slope and intercept of a plot log q_e versus log C_e (Fig. 7). The Freundlich constant related to adsorption intensity “n” varies from 1.41 to 1.56. For a better adsorption system the adsorption intensity (n) should be in the range between 1 to 10. The rate constant k_f increases from 1.59 to 2.27 on increasing the temperature from 30 to 45 °C. The Freundlich model is more appropriate to explain the adsorption of Cr(VI) onto WAC when compared with Langmuir isotherm model with good correlation coefficient of 0.9968 < r² < 0.9972.

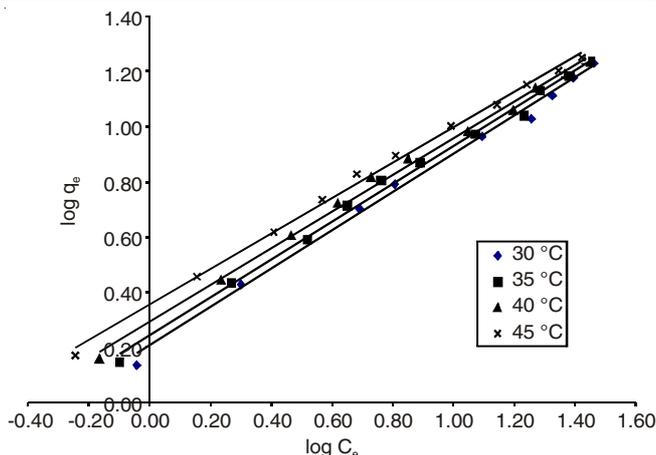


Fig. 7. Freundlich Isotherm plot

Thermodynamic parameters: Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption. Therefore, these parameters should be accurately evaluated. Changes in ΔG°, ΔH° and ΔS° were calculated to elucidate the process of adsorption. The Langmuir isotherm was applied to calculate the thermodynamic parameters via eqns. 14 and 15.

$$\ln b_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R T} \tag{14}$$

where, b_L is a Langmuir isotherm constant, R is the gas constant (8.314 × 10⁻³ kJ/K/mol) and T is temperature in Kelvin. Both ΔH° and ΔS° were determined from the slope and intercept of the Van’t Hoff plots of “ln (b_L)” versus “1/T” [19].

The free energy of specific adsorption ΔG° (kJ/mol) is calculated from the following expression:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

The van’t Hoff plot for the adsorption of Cr(VI) onto WAC is shown in Fig. 8 and the ΔH° and ΔS° values obtained from the slope and intercept are presented in Table-4. The values ΔH° (11.87 kJ/mol) is within the range of 1 to 40 kJ/mol indicates that the adsorption of Cr(VI) is physisorption. From the results we could make out that physisorption is much more favourable for the adsorption of chromium ion. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption.

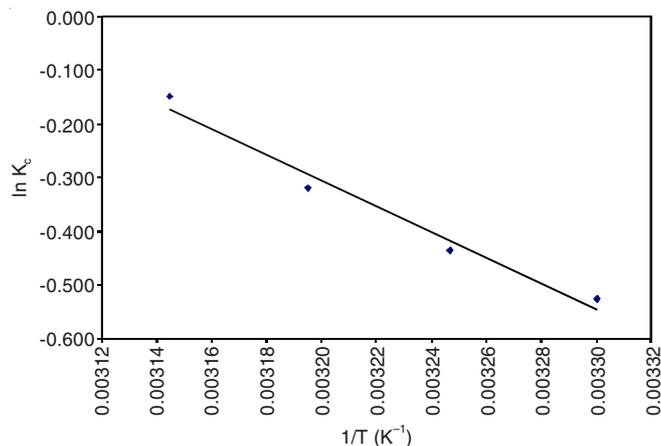


Fig. 8. van’t Hoff plot for the adsorption of Cr(VI) onto WAC

TABLE-4
THERMODYNAMIC STUDY FOR THE
ADSORPTION OF Cr(VI) ONTO WAC

Temp. (°C)	ΔG° (J/mol)	ΔH° (KJ/mol)	ΔS° (J/K/mol)
30	-1326.17		
35	-1115.93	11.87	35.98
40	-830.54		
45	-393.26		

The negative values of ΔG° shows the adsorption is highly favourable and more spontaneous in nature. The positive values of ΔS° shows the increased randomness at the solid solution interface of chromium ion with WAC. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

Desorption studies: Desorption studies are helpful to elucidate the nature of adsorption and recycling of the spent adsorbent. If the adsorbed chromium ions can be desorbed using neutral pH water, then the attachment of the chromium ions of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorbs the chromium ion then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the chromium ions, then the chromium ions has held by the adsorbent through chemisorption [20].

The effect of various reagents used for desorption studies indicate that sodium hydroxide is a better reagent for desorption, when the pH goes beyond 8 more than 63 % of adsorbed chromium is desorbed (Fig. 9). The more percentage of chromium ions by alkaline water indicates that the chromium ions were adsorbed onto the activated carbon by weak forces of attraction.

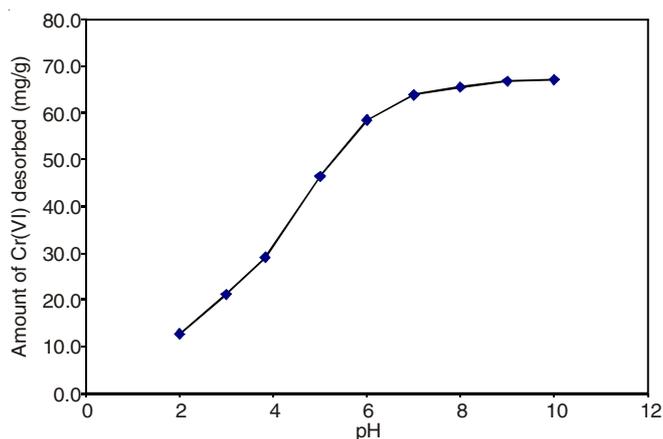


Fig. 9. Desorption of Cr(VI) – Effect of pH

Conclusion

The activated carbon prepared from *Wrightia tinctoria* by microwave heating with optimum duration gives a highly porous activated carbon with high surface area. The adsorption of Cr(VI) by WAC is pH dependent and the best results were obtained at system pH of 2. The adsorption Cr(VI) by WAC depends upon the concentration of Cr(VI), pH, dosage of adsorbent and temperature of the system. The adsorption reaches equilibrium at 175 min of contact time and beyond that there is no appreciable adsorption. The adsorption of chromium by WAC follows pseudo-second order kinetics with good correlation coefficient. Freundlich isotherm model is more appropriate to describe the adsorption behaviour than Langmuir model. The positive enthalpy of adsorption substantiates that the adsorption is favoured by high temperature. The activated carbon prepared from *Wrightia tinctoria* by microwave heating is a promising adsorbent for the removal of chromium from wastewater.

REFERENCES

- V.K. Gupta, D. Pathania, S. Sharma and P. Singh, *J. Colloid Interf. Sci.*, **401**, 125 (2013).
- M. Costa, *Toxicol. Appl. Pharmacol.*, **188**, 1 (2003).
- L.V.A. Gurgel, J.C. Perin de Melo, J.C. de Lena and L.F. Gil, *Bioresour. Technol.*, **100**, 3214 (2009).
- J. Fang, Z.M. Gu, D.C. Gang, C.X. Liu, E.S. Ilton and B.L. Deng, *Environ. Sci. Technol.*, **41**, 4748 (2007).
- D. Mohan and C.U. Pittman Jr., *J. Hazard. Mater.*, **137**, 762 (2006).
- M. Ahmedna, W.E. Marshall, A.A. Hussein, R.M. Rao and I. Goktepe, *Water Res.*, **38**, 1062 (2004).
- T. Yang and A.C. Lua, *J. Colloid Interf. Sci.*, **267**, 408 (2003).
- T. Zhang, W.P. Walawender, L.T. Fan, M. Fan, D. Daugaard and R.C. Brown, *Chem. Eng. J.*, **105**, 53 (2004).
- U. Zielke, K.J. Huttinger and W.P. Hoffman, *Carbon*, **34**, 983 (1996).
- M.J. Ahmed and S.K. Theydan, *Chem. Eng. J.*, **214**, 310 (2013).
- ISI, Indian Standards Institute. IS-877, (1977).
- APHA, American Public Health Association, Washington, D.C (1980).
- A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, *J. Hazard. Mater.*, **140**, 104 (2007).
- S. Lagergren, *Kung. Sven. Vetén. Hand.*, **24**, 1 (1898).
- Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999).
- U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud, *J. Hazard. Mater.*, **140**, 60 (2007).
- I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
- H. Freundlich, *Z. Phys. Chem.*, **57**, 387 (1906).
- A. Ozcan, E.M. Oncu and A.S. Ozcan, *Colloids Surf. A*, **277**, 90 (2006).
- S. Arivoli, Ph.D. Thesis, Gandhigram Rural University, Gandhigram, India (2007).