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ISSN: 0959-3330 (Print) 1479-487X (Online) Journal homepage: http://www.tandfonline.com/loi/tent20

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To cite this article: T.K. Chaithanya & Sudhakar Yedla (2010) Adsorption of hexa#valent chromium using treated wood charcoal – elucidation of rate#limiting process, Environmental Technology, 31:14, 1495-1505, DOI: 10.1080/09593331003777144

To link to this article: http://dx.doi.org/10.1080/09593331003777144

Environmental Technology
Vol. 31, No. 14, 14 December 2010, 1495–1505

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Adsorption of hexa-valent chromium using treated wood charcoal – elucidation of rate-limiting process

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(*Received 21 October 2009; Accepted 11 March 2010*)

In the present study, locally available wood charcoal was used as an adsorbent to remove Cr (VI) from water. It was found to be giving poor removal efficiency whereby only 19% of Cr (VI) was removed. Considering the fact that wood charcoal possesses a honeycomb structure, an acid treatment was tried with HCl, H_2SO_4 and HNO_3. Treatment with concentrated hydrochloric acid has improved the removal efficiency of wood charcoal to 94%.

Kinetic studies were carried out with various systemic parameters, namely initial Cr (VI) concentration (0.5, 1, 2 mg/L), adsorbent size (0.11, 0.18, 0.25, 0.36, 0.51 mm) and agitation speed (130 to 180 rpm) to understand and determine the equilibrium time, order of reaction, rate constants, diffusion coefficients, and to determine the maximum adsorption capacity and also the rate limiting process. It was found that the uptake of Cr (VI) onto wood charcoal reached equilibrium within the first 6 h of contact time. Isothermal studies explained by using the Freundlich model revealed that the maximum adsorptive capacity (Q_{max}) of the treated wood charcoal is 677 μg/g, which is well within the standard/feasible value for a wood-based charcoal.

The process limiting the rate of adsorption (rate limiting step) was analyzed using the kinetic data as well as using various systemic parameters such as initial Cr (VI) concentration, adsorbent size, and agitation speed was finally confirmed by the multiple interruption test. It was concluded that the adsorption process was controlled by film diffusion.

Keywords: adsorption; Cr (VI); maximum adsorption capacity; rate limiting step; wood charcoal

1. Introduction

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, have also contributed to degradation of the environment all over the globe due to very little attention being paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting waters. The discharge of non-biodegradable heavy metals into the water stream is hazardous because the consumption of polluted water causes various health problems. Waste streams containing heavy metals such as Cu, Zn, Ni, Pb, Cd, Cr are often encountered in various chemical industries.

Chromium has both beneficial and detrimental properties. Two stable oxidation states of chromium persist in the environment, Cr (III) and Cr (VI), which have contrasting toxicities, mobilities and bioavailability. Whereas Cr (III) is essential in human nutrition (especially for glucose metabolism), hexa-valent compounds are toxic and several can even cause lung cancer. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [1].

Chromium is a priority metal pollutant introduced into water bodies from many industrial processes. Chromium occurs in aquatic environment both in trivalent and hexa-valent forms. Hexa-valent chromium – Cr (VI) – is primarily present in the form of chromate (Cr_2O_4–) and dichromate (Cr_2O_7–). The toxicity of Cr (VI) is well documented and it is considered a hazard to human health and also to animals [2].

Cr (III) and Cr (VI) are released into the environment primarily from stationary point sources resulting from anthropogenic activities. Of the total atmospheric chromium emissions in the United States, approximately 64% as Cr (III) comes from fuel combustion (residential, commercial, and industrial) and from steel production; about 32% as Cr (VI) comes from chemical manufacture, chrome plating, and industrial cooling towers that used chromate chemicals as rust inhibitors in the past [3].

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ISSN 0959-3330 print/ISSN 1479-487X online

DOI: 10.1080/09593331003777144
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Electroplating, leather tanning, and textile industries release relatively large amounts of chromium into surface waters. Leaching from top soil and rocks is the most important natural source of chromium entry into water bodies [4,5]. Solid wastes from chromate-processing facilities, when disposed of improperly in landfills, can be a source of contamination for groundwater, where the chromium residence time might be several years. Maximum contaminant level for chromium in drinking water, as set by BIS, Indian Standards (IS 10500:1991), is 0.05 mg/L [6].

The fact that Cr (VI) pollution originates from SMEs (small scale enterprises) makes it very relevant for smaller cities/towns in the developing countries where a lot of SMEs are clustered and their emissions norms are either relaxed or not so strictly enforced. The present study attempts at the removal of Cr (VI) from water (aqueous) environment using a low cost adsorbent. It is quite an established fact that charcoals have potential to uptake metals [1,5,7,8,9]. Therefore, the present study attempts to use treated wood charcoal to remove Cr (VI) from water. As it is established that wood charcoal has the potential to remove metals, the present study attempts to estimate the design parameters, namely the maximum adsorption capacity and the process that controls the rate of removal of Cr (VI).

2. Experimental methodology

2.1 Preparation of wood charcoal

Wood charcoal was purchased from a local market at a price of Rs.8/ kg.[1] Wood charcoal was pulverized to the required mean size of 256 μm using a set of Indian standard sieves. The sieved material was washed thoroughly with water and dried at 110°C for 10 h followed by cooling down to room temperature. This was done to get rid of foreign matter, impurities and unwanted moisture. Then the wood charcoal was treated with concentrated HCl and dried at 110°C for 10 h followed by cooling down to room temperature [9]. This was done to increase the surface area of wood charcoal. After acid treatment the treated wood charcoal (WC_T) was washed with distilled water and dried at 110°C for 10 h followed by cooling down to room temperature. After cooling down to room temperature it was stored in airtight bottles for use in adsorption experiments.

2.2 Reagents

All the reagents used in this study were of analytical grade. All glassware used was of borosil make. Distilled water was used for making synthetic water samples and is prepared once every day. Working samples for calibration of chromium were made using distilled water and technical grade potassium dichromate of 98.7% purity. Working samples were prepared everyday in order to avoid any deviations in experimental data.

2.3 Analytical methods

Hexa-valent chromium was determined by molecular absorption spectroscopy, at 540 nm, after reaction with 1,2-diphenylcarbazide. A calibration curve was made between known concentrations of chromium and percentage absorbance. This calibration curve, fitted by the method of least squares, was used to quantify chromium in the samples of unknown chromium concentrations. To avoid any deviation in measurement of chromium due to instrumental errors, a standard sample of known concentration was tested for every run of chromium analysis.

2.4 Sample preparation

Stock solution of chromium was made according to the Standard Methods [10]. Working samples were made by adding required stock solution to the predetermined quantity of distilled water. Stock solution was made every second day in order to avoid any experimental errors.

2.5 Kinetic studies

Polyethylene bottles (Tarson Co., India) of 125 mL capacity were used for kinetics experiment. Cr (VI) spiked synthetic water samples (100 mL) of a particular Cr (VI) concentration were taken in the bottles and 50 g/L adsorbent was added to them. The sample bottles were stirred on a mechanical shaker at 150 rpm. The experiments were carried out at 37°C. After required contact time the samples were withdrawn and the adsorbent from the sample bottles was separated by gravity. A representative sample was taken from the supernatant of each bottle and analyzed for chromium. Control sample (without adsorbent) was also carried out in all the experimental runs and analyzed with each set of experiments. This was to avoid any deviations in the results due to experimental errors. Hence, the standard error bars are not plotted in the graphical presentation of the results. This also ensures that the metal is not taken up by the Tarson bottles themselves, while conducting the experiments.

Except for the parameter under study, all other systemic parameters were kept constant in each of the experiments. The pH was monitored before and after for all the experiments. All the experiments were carried out in three sets and the reading that remained similar in two samples was considered for the analysis.

2.6 *Equilibrium studies*

Isothermal studies were carried out taking different initial concentration of chromium ranges from 0.25 to 5.00 mg/L and a reaction (equilibrium) time of 6 h was maintained. The samples with 50 g/L adsorbent added to each of them were agitated at speed of 150 rpm using a rotary shaker. After 6 h of contact time, the samples were removed from the shaker and the adsorbent is allowed to settle down by gravity. The supernatant was analyzed for residual Cr (VI) concentration.

3. Results and discussions

Locally available wood charcoal, when used in its fine granular form as an adsorbent, could remove only 19% of the Hexa-valent chromium present in a water sample with initial concentration of 1 mg Cr (VI)/L. As it is evident from the literature, wood-based charcoal particles possess a honeycomb structure and hence possess a potential for surface area enhancement when treated with acids of different strength [9,11,12,13,14]. Increase in surface area, as in most cases the adsorption is a surface phenomena, would increase the adsorption performance of wood charcoal [9,11]. When treated with different acids, namely H_2SO_4, HCl, and HNO_3 in order to enhance the surface area, removal efficiency of wood charcoal has been improved to 92.4%, 93.5%, and 92.8%, respectively from its original efficiency of 19%. With the treatment of HCl at a percentage removal efficiency of 93.5%, uptake of chromium onto wood charcoal was observed at 20 micro grams per gram of wood charcoal.

As explained in the literature [11,15], the reason for the enhancement of removal efficiency could be the burning off the free and un-cleaned carbon matter in the pores of wood charcoal. Normally, this would influence the degree of surface area enhancement. In the present study, concentrated acids are used in order to achieve the maximum improvement in efficiency. Based on its performance, HCl was selected for the treatment of wood charcoal and HCl-treated wood charcoal (WC_T) was used in all the rest of experiments in the present study.

3.1 *Removal efficiency of wood charcoal under equilibrium conditions*

The process of adsorption is a two-way process where adsorbate particles move onto the available sites on the adsorbent and the part of it gets back to the solution. This phenomenon, driven by various forces and the concentration gradient and the availability of adsorption sites, enters a state of equilibrium where the solute particles moving onto the adsorbent sites become equal to particles re-entering solution phase [16]. Hence, at equilibrium state, theoretically, no further removal of pollutant is expected. Determination of such time, termed as ‘equilibrium time’, is important in designing a treatment system where contact (resident) time is an important parameter.

Equilibrium time in the present study was determined by developing time-decay curve as shown in Figure 1. When the adsorption kinetic profiles became

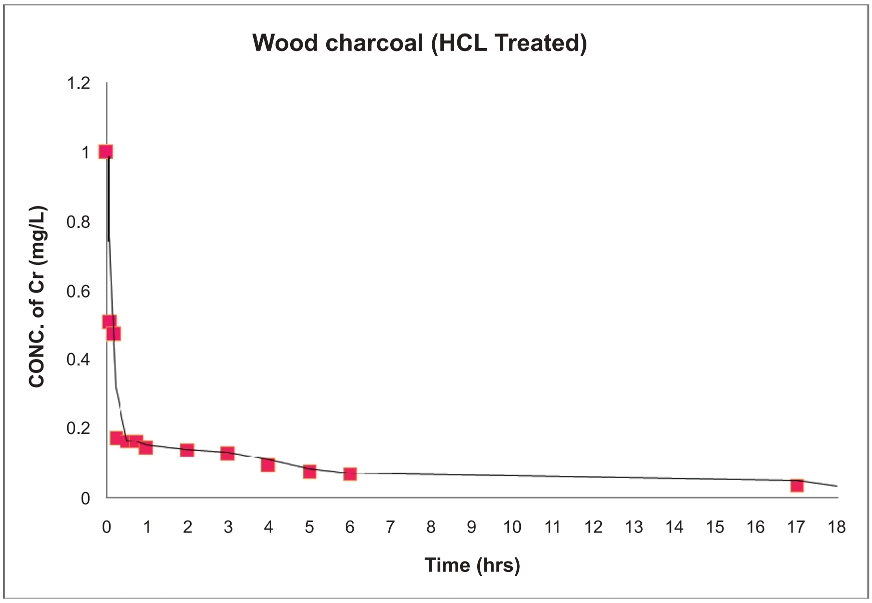

Figure 1. Time-decay curve for wood charcoal used for the removal of Cr (VI) from water.

asymptotic to time-axis (change of slope get less than 2%), it shows the state of equilibrium where no further removal is achieved and the corresponding time was treated as equilibrium time.

As explained by many researchers earlier in the literature [9,17,18], the major part of the adsorption took place within the first 3 h, after which the removal rate decreased. Treated wood charcoal was found to be at equilibrium in 6 h. Hence, 6 hours of contact time was maintained in all other kinetic studies conducted.

Two important aspects of adsorption and its design for practical applications are maximum capacity to adsorb the pollutant per unit quanitity of adsorbent (Q_{max}) and the process that limits the rate of adsorption (slowest one determines the rate) [17]. The following sections address these two important aspects of adsorption process.

3.2 *Determination of maximum adsorption capacity (Q_{max})*

Rate of adsorption and quantity of Cr (VI) adsorbed onto the treated wood charcoal also varies with the changing initial concentration of Cr (VI) and the dose of wood charcoal. Therefore, in order to assess the maximum capacity of the adsorbent (WC_T) in taking up adsorbate (Cr (VI)) it is essential to conduct 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’ [19]. Commonly, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion. In the literature there exist various models such as Langmuir, BET, and Freundlich which explains the phenomena of adsorption at varying concentration of adsorbate [16,19]. While the shape of isotherm developed (a plot between concentration of adsorbate in solution and on adsorbent) indicates which model explains it better, the linearized plot of the chosen model gives the value of maximum adsorption capacity (slope of the linearized plot).

In the present study, an isotherm was developed for treated wood charcoal by plotting equilibrium concentration of adsorbate on adsorbent (q_e) against the equilibrium concentration of adsorbate in water (C_e), as shown in Figure 2. As the shape shows, it could be the case that the Freundlich model explains it better. As a further confirmation, a linearized plot was used with all three models namely Langmuir, BET, and Freundlich and their correlation coefficients were determined.

Among the three models tried, r^2 value is in the acceptable range only for the Freundlich model at 0.987 (r^2 values for BET model and Langmuir model are 0.392 and 0.222, respectively). Hence, in order to determine the maximum adsorption capacity (Q_{max}) a linearized plot of the Freundlich model was used, as presented in Figure 3. The maximum adsorption capacity (Q_{max}) was found to be 676.6 μg of Cr (VI)/gram of treated wood charcoal. The maximum adsorption capacity reported in the literature for various wood based charcoals was in the similar range [11,20,21,22,23] which is testimony to the correctness in calculating Q_{max} for Cr (VI) removal using treated wood charcoal.

3.3 *Determination of rate limiting step*

There are essentially three consecutive steps in the adsorption of materials from solution by porous adsorbents such as granular activated carbon. The first of these is the bulk diffusion which usually happens at a faster rate. The other two are film diffusion and pore diffusion. Slowest of these two essentially limits the rate of adsorption [16,24]. This phenomenon in a way

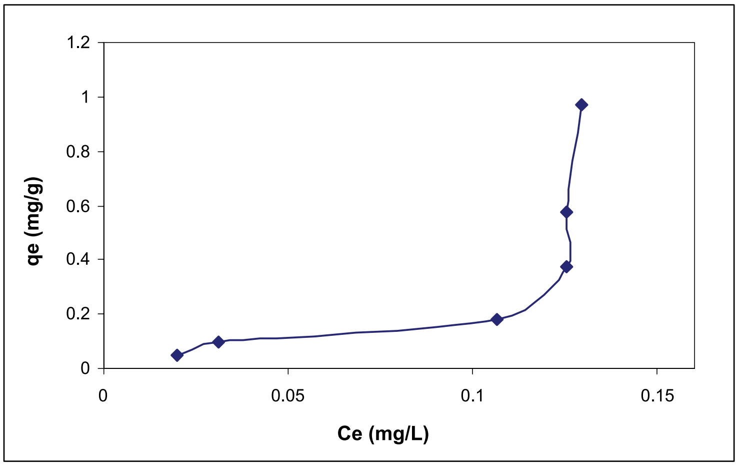

Figure 2. Isotherm developed for wood charcoal.

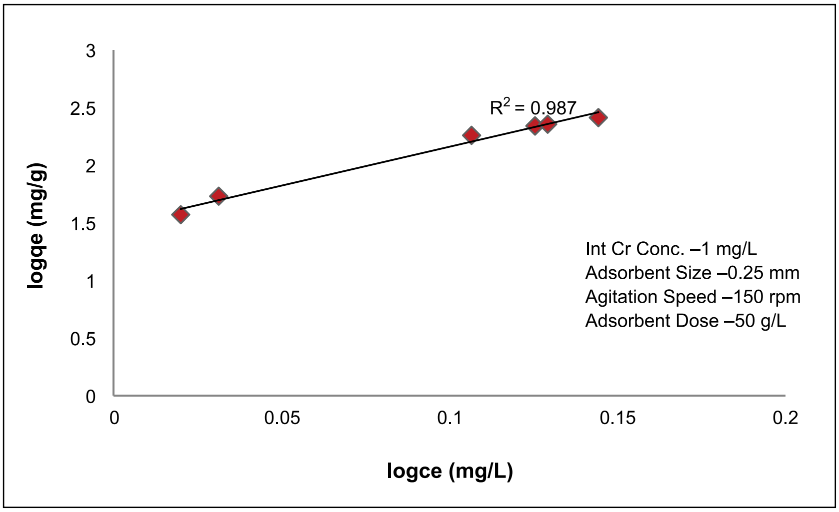

Figure 3. Linearized form of Freundlich isotherm for wood charcoal.

presents the 'rate of change of adsorption capacity'. The factors that affect the 'rate of change of adsorption capacity' include, apart from the diffusion coefficients themselves which can explain the process that is faster, rate of agitation of the solution, initial sorbate concentration, adsorbent dose, and adsorbent size.

In the present study, the rate limiting step was confirmed by various approaches, namely using kinetics data/diffusion coefficients; effect of rate of agitation; effect of sorbate concentration; effect of sorbent size; and effect of initial concentration of sorbate. This was further tested and confirmed by conducting a multiple interruption test suggested by Zogorski [25].

3.4 Using kinetic data/diffusion coefficients

The sorption of Cr (VI) from liquid phase (L) to the solid phase (S) can be considered as a reversible reaction with equilibrium established between two phases. A simple first-order reaction kinetics model was used to establish the rates of reaction, which can be expressed as:

$$\mathrm{L} \leftrightarrow \mathrm{S} \tag{1}$$

The rate equation for the reaction is expressed as:

$$\begin{aligned}\frac{dC_s}{dt} &= -\frac{dC_L}{dt} = CL_{\mathrm{o}}\frac{dX_A}{dt} = K_f C_L - K_r C_s \\ &= K_f(C_{Lo} - C_{Lo}X_A) - K_r(C_{so} + C_{Lo}X_A)\end{aligned} \tag{2}$$

where C_s is concentration of Cr (VI) on the sorbent in mg/g; C_L is concentration of Cr (VI) in the solution in mg/L; C_{so} is initial concentration of Cr (VI) on the sorbent in mg/g; C_{Lo} is initial concentration of Cr (VI) in the solution in mg/L; X_A is fractional conversion of Cr (VI); k_f is rate constant for forward reaction and k_r is rate constant for reverse reaction.

A graph was plotted between ln[1-u(t)] and t, where u(t) is the fractional attainment of equilibrium [26].

$$U(t) = \frac{C_{Lo} - C_L}{C_{so} - C_s} = \frac{X_A}{X_{As}} \tag{3}$$

According to Snoeyink and Jenkins [27], a linear plot between ln[1-u(t)] and t indicates that the reaction is first order reversible. Kinetic rate curves for different initial concentrations of Cr (VI) are presented in Figure 4.

A near straight line fit was observed for all concentrations of Cr (VI) indicating that sorption reaction can be approximated to first order reversible kinetics. The initial part of the curve, due to the initial drop, was not linear and to avoid error in rate calculation, the initial part was neglected. Only the linear portion was taken into consideration to calculate overall rate constant K'. All the rate constants namely overall, forward and reverse are presented in Table 1.

Assuming spherical sorbent particle, Helfferich [26] has developed the following expression to correlate the slope of the first order reversible kinetics profiles to the pore diffusion and film diffusion coefficients:

$$D_p = 0.030\frac{r^2}{t_{\frac{1}{2}}} \tag{4}$$

$$D_F = 0.23\frac{r\delta C'}{t_{\frac{1}{2}}C} \tag{5}$$

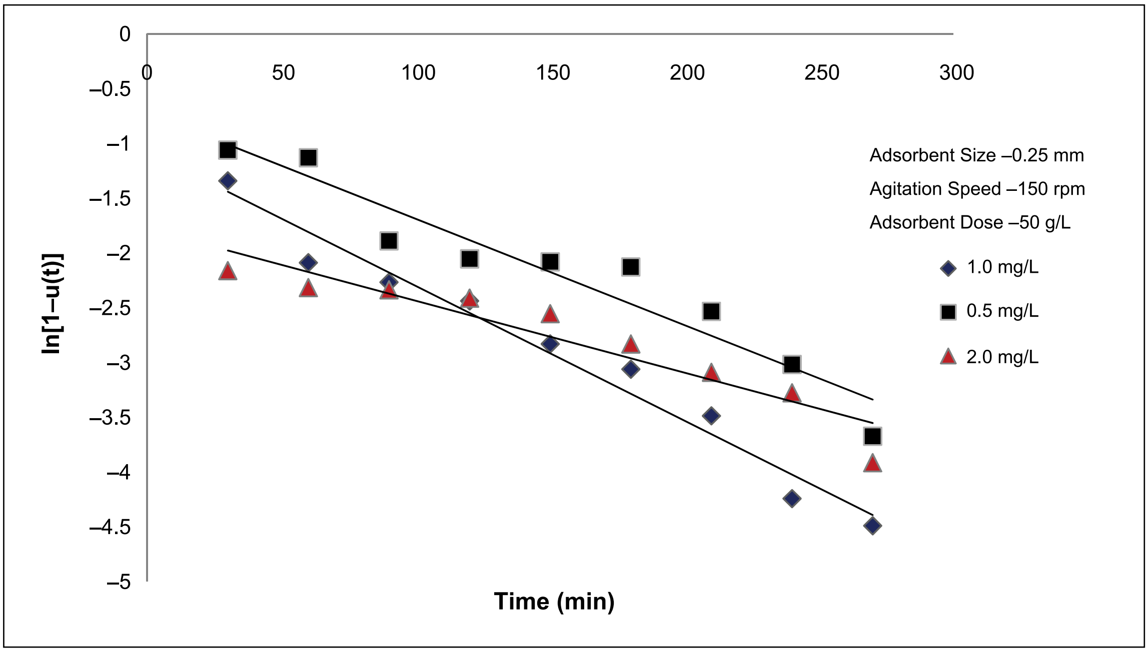

Figure 4. First order reversible kinetics for the removal of Cr (VI) using wood charcoal.

Table 1. Rate constants for different initial concentrations of Cr (VI).

Initial concentration of Cr (VI)(mg/L)	K' (per hour)	k_f (per hour)	k_r (per hour)
0.5	0.921	0.854	0.057
1	0.970	0.901	0.068
2	0.891	0.835	0.055

Table 2. Film and pore diffusion coefficients calculated based on kinetic data for different initial concentrations of Cr (VI).

Initial concentration of Cr (VI) in mg/l	K' (hr^{-1})	$t_{1/2}$ (h)	D_F (cm^2/s)	D_p (cm^2/s)
0.5	0.921	0.752	8.91×10^{-7}	9.92×10^{-8}
1	0.970	0.714	7.81×10^{-7}	10.13×10^{-8}
2	0.891	0.772	8.88×10^{-7}	10.81×10^{-7}

where $t_{1/2}$ is the time necessary to obtain half the initial concentration in sec; r is the radius of the adsorbent particle in cm; D_f and D_p are the film and pore diffusion coefficients, respectively, in cm^2/s; C' and C are the concentrations of sorbate on the sorbent and in solution at equilibrium, respectively, in mg/L; and δ is the film thickness in cm. $t_{1/2}$ can be calculated using the relationship suggested by Asher *et al.* [28].

$$t_{\frac{1}{2}} = -\frac{\ln(0.5)}{k'} \tag{6}$$

The values of k' were calculated from the slopes of the linear portion of the first order reversible kinetic profiles shown in Figure 4. A film thickness of 0.001 cm was taken as suggested by Helfferich [26]. Film and pore diffusion coefficients (D_F and D_p) were calculated for different initial concentrations of Cr (VI) and presented in Table 2.

According to Michaels [29], for film diffusion to be rate limiting, the value of film diffusion coefficient (D_F) should be in range of 10^{-6} to 10^{-8} cm^2/s whereas for pore diffusion to be rate limiting, the pore diffusion coefficient (D_P) should be in the range of 10^{-11} to 10^{-13} cm^2/s for heavy metals. From this explanation, in the present study, film diffusion appears to be the rate limiting process.

3.5 Using the effect of initial concentrations of Cr (VI)

Adsorption rate, expressed as milligrams of Cr (VI) absorbed per gram of treated wood charcoal, keeps changing over time and also for different initial concentrations of Cr (VI). The slope of plot between square root of time and the adsorption capacity expressed in terms of mg of adsorbate per gram of adsorbent gives the rate of adsorption R_A [25]. Figure 5 presents such plots for different initial concentrations of Cr (VI). The linear portions of the q versus $t^{1/2}$ curves were consid-

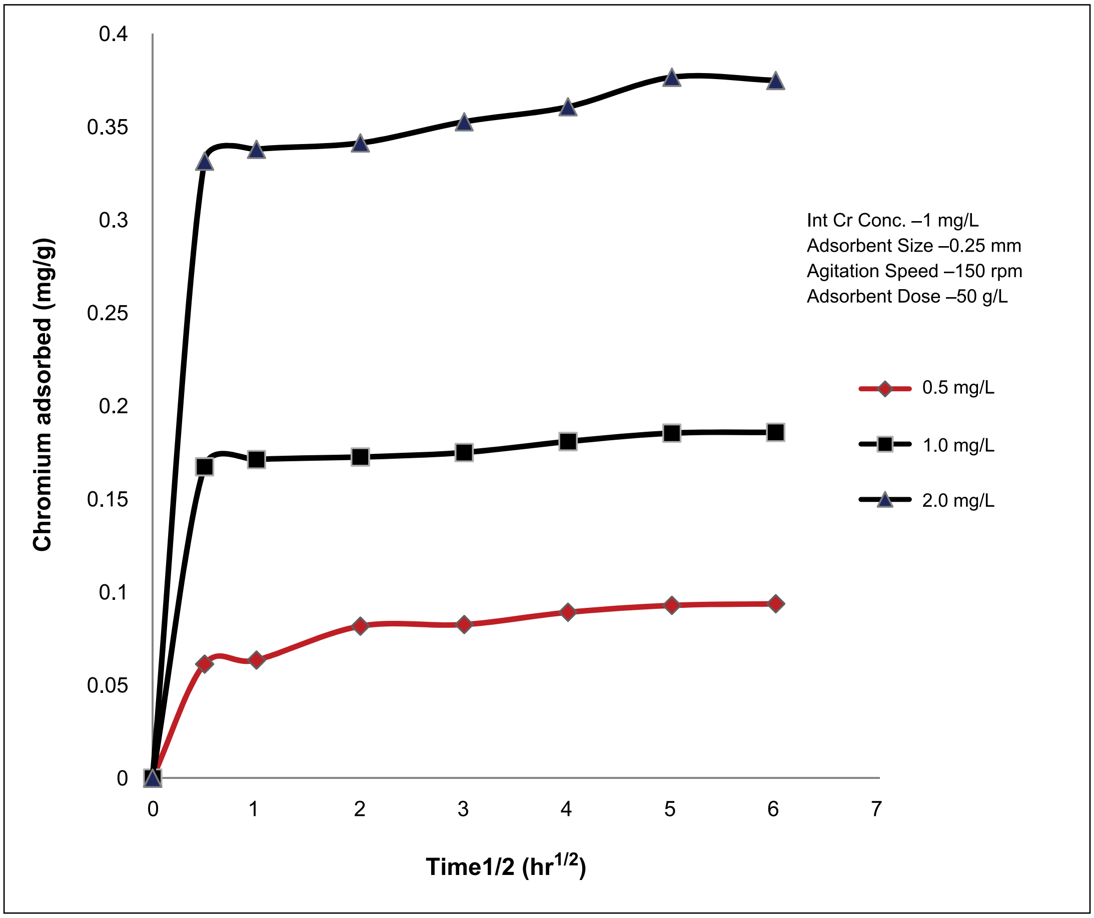

Figure 5. Amount of Cr (VI) adsorbed vs. square root of reaction time ($t^{1/2}$).

ered for calculating the values of adsorption rate R_A (mg/g-hr$^{1/2}$).

According to the earlier work done by Helfferich [26] and Zogorski *et al.* [25] a linear fit between the adsorption rates (R_A) for different initial concentrations of Cr (VI) demonstrates that film diffusion as rate limiting. For the present study, the values of R_A (mg/g-hr$^{1/2}$) were plotted against respective Cr (VI) concentrations. With an r^2 value over 0.98, it certainly follows a linear fit which shows that film diffusion is indeed the controlling process. Had it been pore diffusion, the curve would have become non-linear in nature [24,26,30].

3.6 Using the effect of different adsorbent sizes

The diameter of the adsorbent particles has a definite function with the mechanism of adsorption [31,32, 33,34]. Based on diffusion theory, the rate of adsorption (R_A – mg/g-hr$^{1/2}$) should increase with some inverse function of the diameter of the adsorbent particle [26]. When the removal rate is inversely proportional to particle size, the external transport or film diffusion controls the rate of reaction; whereas, if removal rate is inversely proportional to the square of particle diameter, the internal transport or pore diffusion controls the rate of adsorption [26]. Figure 6 is a plot between adsorption rates (mg/g) over time for different sizes of treated wood charcoal particles (112 µm to 512 µm). With the increase in the diameter of treated wood charcoal from 112 µm to 512 µm, the rate of adsorption (R_A) varied from 18 mg/g-hr$^{1/2}$ to 14 mg/g-hr$^{1/2}$. This could be due to increasing surface area with decreasing diameter of the adsorbent particles.

The values of R_A (mg/g-hr$^{1/2}$) were plotted against the reciprocal of diameter as well as square root of the diameter. Good correlation (with r^2 value of 0.967) between (R_A – mg/g-hr$^{1/2}$) and the inverse of diameter indicate that the film diffusion may be limiting the rate of adsorption of Cr (VI) onto the treated wood charcoal.

3.7 Using the effect of different agitation speeds

The rate of agitation, which is one of the prominent factors influencing adsorption process in continuously mixed batch reactor, not only helps in the suspension of solids, but also gives adequate mixing for hydrophobic

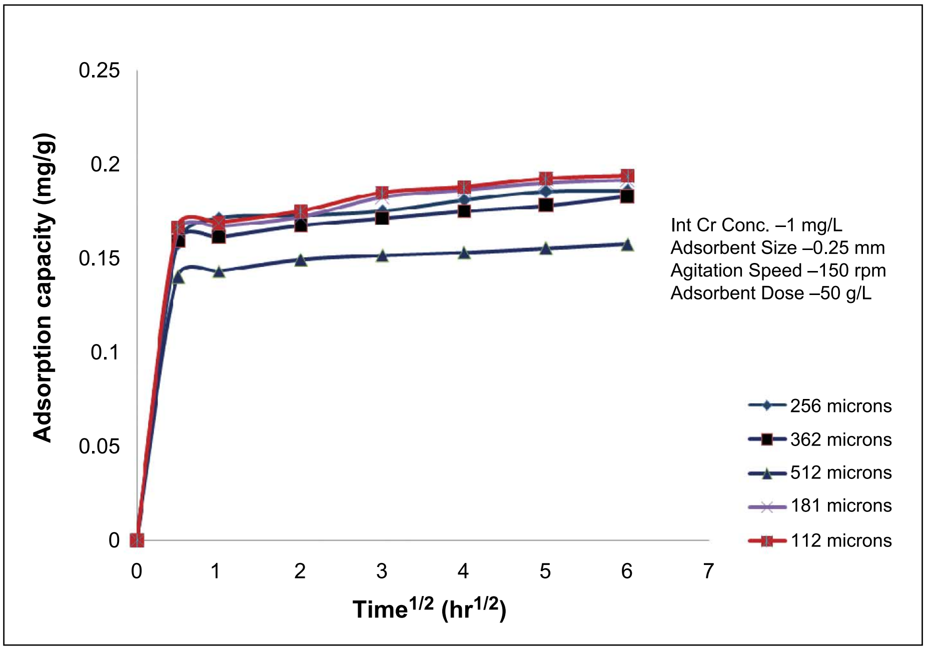

Figure 6. Amount of Cr (VI) adsorbed vs. square root of contact time.

solutes in the reactor. Figure 7 in the present study depicts the influence of changing the agitation speed from 130 to 180 rpm on the sorption of Cr (VI) onto the treated wood charcoal. The adsorption rates (R_A – mg/g-hr$^{1/2}$) calculated for the agitation speeds of 130 to 180 rpm indicated no change with the increasing agitation speed. R_A value should increase with the increasing agitation speed for the film diffusion to be controlling

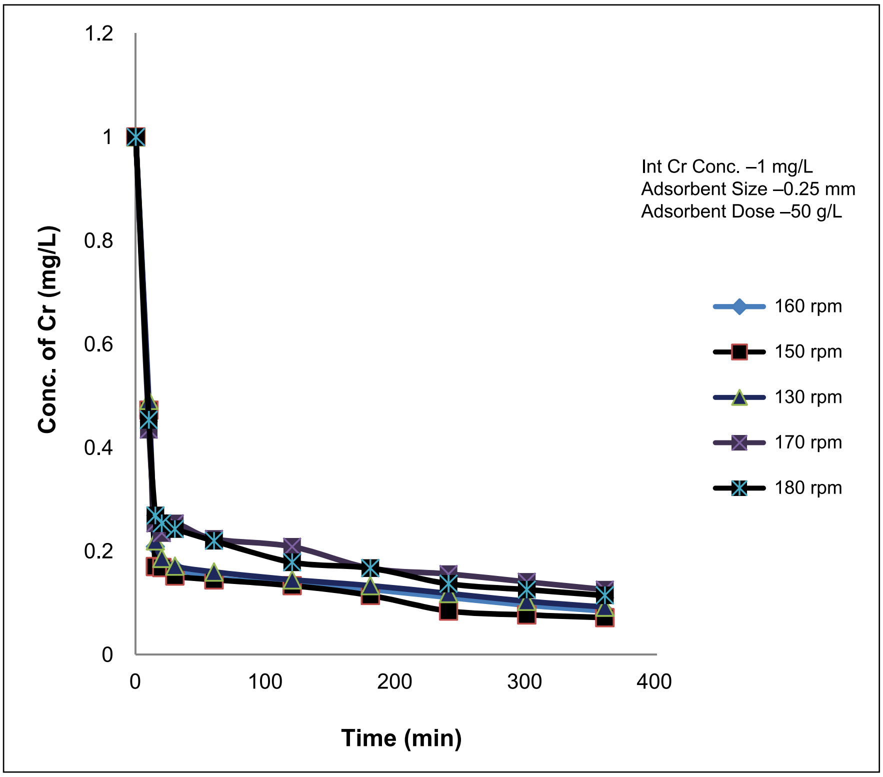

Figure 7. Effect of agitation speed on removal of Cr (VI).

the process. As the rate of adsorption (R_A) remained unchanged it gets inconclusive on which diffusion is controlling the process in the present study.

Based on diffusion coefficients and the effects of initial concentration of Cr (VI), adsorbent size on the rate of adsorption it was found that film diffusion is controlling the rate of removal of Cr (VI) using treated wood charcoal. However, effect of agitation speed on the rate removal did not give any conclusive result. Therefore, it is felt necessary to conduct multiple interruption test developed by Zogorski *et al.* [25] in order to determine, conclusively, the rate limiting process.

3.8 Interruption test

The process that controls the rate of adsorption can be determined more precisely by performing an interruption test and the method developed by Zogorski *et al.* is very effectively used by many researchers [9,20]. Hence, a multiple point interruption test was adopted in the present study. The sample was interrupted after 1, 2, 3, 4, 6 h and the sorbent was re-immersed after 30 minutes. Removal of Cr (VI) was monitored at regular intervals. A similar adsorption test was carried out without any interruption under the similar conditions. Figure 8 depicts the effect of interruption on adsorption process. As shown in the figure, there is no change of slope that could be observed in interruption test curve and it is almost parallel to the continuous test curve. It indicates that the process is controlled by external diffusion [25]. During interruption test, the interruption disturbs the concentration gradient in the film; however, gradients are assumed to be established almost instantaneously [26]. The fall in overall removal efficiency is due to the reduced contact time in the case of an interrupted sample.

In summary of various parametric tests conducted to determine the rate limiting step in the removal of Cr (VI) using treated wood charcoal, diffusion coefficients calculated based on kinetic data; adsorbate concentration; adsorbent size; multiple interruption test confirmed that film diffusion controls the rate of removal. With the effect of agitation speed remained inconclusive on which diffusion controls the rate it can be inferred that film diffusion is the slowest of diffusions and hence controls the rate of Cr (VI) removal using treated wood charcoal.

4. Conclusions

These are the conclusions drawn based on the present study:

1. Locally available wood charcoal showed potential to be used as an adsorbent to remove Cr (VI) from water. Treatment with concentrated hydrochloric acid could improve the removal efficiency of wood charcoal up to 94%.
2. The sorption of Cr (VI) onto the treated wood charcoal was found to be rapid for the first three hours and reached the state of equilibrium within 6 h. The reaction followed a first order reversible kinetic model.
3. The equilibrium partitioning for Cr (VI) onto the treated wood charcoal was well described by the Freundlich isotherm. The adsorption capacity of the treated wood charcoal was found to be 677 µg/g.

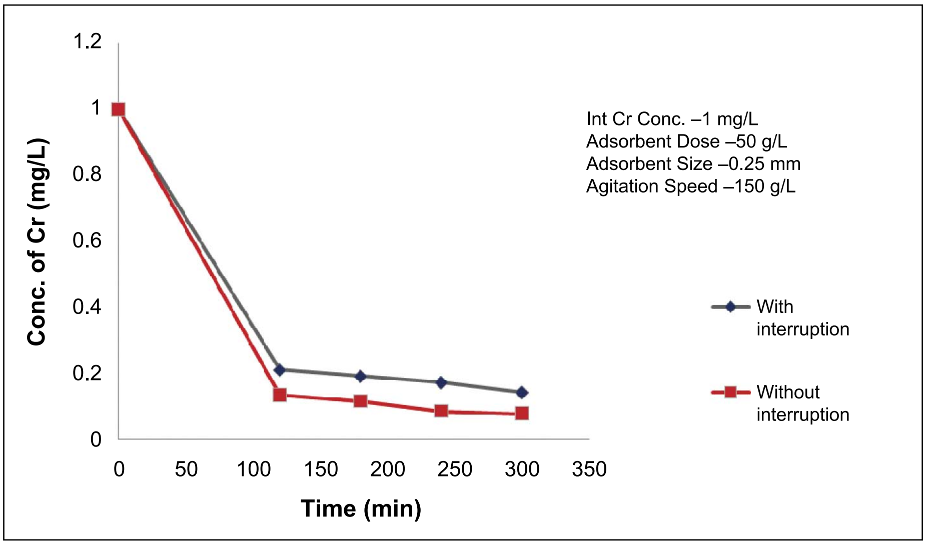

Figure 8. Multiple interruption test for treated wood charcoal.

(4) Based on kinetic data, diffusion coefficients, effect of initial sorbate concentration, adsorbent size, agitation speed film diffusion was found to be the rate limiting process in removing Cr (VI) using treated wood charcoal. This was further confirmed by the multiple interruption test.

Acknowledgement

The authors are thankful to anonymous reviewers for their valuable suggestions which have helped improve the manuscript.

Notes

1. US$ is equal to 49 Indian Rupees.

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