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SEM Characterization of the mass transfer of Cr(VI) during the adsorption on used black tea leaves

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This study presents the mass transfer mechanism of Cr(VI) during the adsorption on used black tea leaves (UBTLs) as a low cost biosorbent. Batch adsorption experiments were conducted in acidic media with different particle sizes of UBTLs and Cr(VI) concentrations, and the results were verified with different transport models to elucidate the mass transfer mechanism. Scanning electron microscope (SEM) and X-ray microanalysis (EDX) of adsorbed UBTLs were also carried out to search the mechanism. From the view point of transport modeling and SEM analysis, the effect of particle size and the concentration of Cr(VI) on the adsorption of Cr(VI) on the UBTLs suggest that the initial rapid step of adsorption is reaction-controlled dominated by the attraction of negative Cr(VI) species with the protonated UBTLs surface in acidic media, and the following slow step is intraparticle-diffusion-controlled which consisted of the high deposition of adsorbed species at the cavities on the surface. The overall mass transfer gradually shifts from the reaction controlled to the diffusion controlled with increasing of the initial concentration Cr(VI) in solution.

Key words: Hexavalent chromium, used black tea leaves, adsorption, SEM and EDX, mass transfer mechanism.

INTRODUCTION

The extensive use of chromate and dichromate in various industries has introduced large quantity of hexavalent chromium, Cr(VI), into the environment. Principal sources of Cr(VI) contamination of wastewater and solid waste are from electroplating, paints, dyes, chrome tanning and paper industries. The removal of Cr(VI) from wastewater has received considerable attention because of their toxic nature to the living systems (EPA, 1998). Adsorption is one of the important processes, and has greatly contributed to the removal of pollutants at very low level of concentration from industrial effluents. Activated carbon has been the standard adsorbent for the purification of municipal and industrial wastewater for potable use for almost three decades (Budinova et al., 1994). But due to the high cost of activated carbon, recent research efforts have been directed towards the use of biomass as an adsorbent material, alternative of activated carbon, in an attempt to minimize the processing cost.

Several authors have reported the use of biomass for Cr(VI) removal from polluted water. Bailey et al. (1999) made a review on the removal of Cr(VI) by bio-sorption processes using walnut shell, nut shell, leaf mould, exhausted coffee, others. Most of these biosorbents are less effective ($q_e < 43$ mg g^{-1}) and their adsorption kinetics as well as mechanism is not well understood. Very recently, we found that used black tea leaves (UBTLs) as a low-cost biosorbent has an excellent adsorptive capacity ($q_e > 454$ mg g^{-1}) for Cr(VI) from aqueous solutions (Hossain, 2003; Hossain et al., 2004), which is especially interesting for the removal of Cr(VI) from industrial wastewater. Adsorption mechanism is very important for its effective utilization.

Adsorption process is generally considered as the transport of solute from the bulk of solution phase through the laminar liquid film to the surface, transport onto the interior of the pores or onto active sites on the adsorbent surface where chemical transformation (chemisorption) takes place (Tse and Shang-Lien, 2002).

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Consequently, rate of adsorption depends on the mass transfer of solute into and within the adsorbent particles. Kinetically adsorption mechanism can be described by reaction-controlled or transport-controlled model (Tse and Shang-Lien, 2002; Jansson-Charrier et al., 1996; Onyango et al., 2003). In numerous studies available in literature reports, first order, pseudo-first order or pseudo-second order kinetics has been applied to describe the reaction-controlled mechanism. Our previous study (Hossain et al., 2004) showed that the pseudo-second order kinetic equation is successfully applicable to the adsorption of Cr(VI) on the UBTLs, in comparison with simple first order or pseudo-first order one, but is not sufficient for the complete description of the adsorption mechanism especially in the transport process.

The aim of the present paper is to clarify the transport mechanism of Cr(VI) adsorption from aqueous solution onto the UBTLs. Several studies (Onyango et al., 2003; McKay et al., 1983) have showed that the rate and the extent of adsorption are significantly affected by the particle size for the transport-controlled processes. On the other hand, Ho and McKay (1999) showed that when the interaction between the adsorbate and the binding sites of adsorbent is kinetically rate controlling, the adsorption rate is independent on the particle size of adsorbent. In this study, we investigated the effect of particle size on the adsorption rate and the equilibrium amount adsorbed and used different transport models for various concentrations of Cr(VI), to elucidate the mass transfer of Cr(VI) onto the UBTLs. SEM and EDX analysis of Cr(VI) adsorbed UBTLs surface were also performed to serve the above purpose.

MATERIALS AND METHODS

Potassium dichromate (Wako Pure Chem. Ind.) solution in pure water was used as a source of Cr(VI). All working solutions of various concentrations of Cr(VI) were freshly prepared from a stock solution of 1000 mg L^{-1}. Nitric acid was used to adjust the initial solution pH to minimize reduction of Cr(VI) to Cr(III). All reagents used were of AR grade chemicals.

Fresh black tea leaves were provided by Bangladesh Tea Research Institute, BTRI, where CTC (cut, tear and curl) is the main manufacturing process. Used black tea leaves (UBTLs) were prepared elsewhere (Hossain et al., 2003). The prepared UBTLs were grinded and sieved to give four categories in particle sizes. Elemental analysis using an energy-dispersed X-ray micro-analyzer (EDX, EMAX- 5770W, HORIBA) showed that the UBTLs contain 65.3% of C, 34.2% of 0, 0.1% of Ca and less than 0.1% of S and P.

The kinetic experiments were carried out in batch process by suspending 5 mg of the UBTLs in 50 mL of 100 mg L^{-1}-Cr(VI) solution in each of capped Taplon conical flasks (100 mL) at a specified temperature. Following our previous studies (Hossain et al., 2003), the solution pH was adjusted in the range of 1.5 to 2.0 to minimize the reduction (to be < 5%) of Cr(VI) to Cr(III). The suspensions were mixed on a thermo-stated shaker with a constant speed of 125 rpm. The flasks were withdrawn one by one at specified times and the solutions were analyzed with a reversed-phase HPLC-UV system for simultaneous determination of Cr(VI) and Cr(III) concentrations (Hossain et al., 2005). The amounts of Cr(VI) adsorbed at time t is q_t, was calculated by using the

Equation 1, based on the analysis of the initial and final solutions,

$$q_t = \frac{(C_O - C_t - C_{t\,III})}{W_S} \qquad (1)$$

Where C_o and C_t are the Cr(VI) concentrations of the solution at time $t = 0$ and $t = t$, respectively.

The concentration of Cr(III) in the solution at time t, generated by reduction of Cr(VI), is represented by $C_{t\,III}$. The symbol W_s represents the dose of the UBTLs. Similarly, batch adsorption experiments were performed with different particle sizes of the UBTLs and various initial concentrations of Cr(VI). After adsorption of Cr(VI) on UBTLs at equilibrium time of 15 days, dried UBTLs was analyzed by using scanning electron microscope (SEM; Hitachi, S-4500), and X-ray micro-analyzer (EDX, EMAX- 5770W, HORIBA).

RESULTS AND DISCUSSION

The results obtained from adsorption experiments for different particle sizes of the UBTLs and initial Cr(VI) concentrations, were used to evaluate the mass transfer mechanism of adsorption processes such as diffusion and chemical reaction, by linear regression with different transport models and SEM observation.

Effect of particle size

Various studies have been reported (Yiacoumi et al., 1995) about the transport-controlled model, in which adsorption is based on (a) the transfer of the solute from the bulk solution through the boundary film to the adsorbent surface, which describes film mass transfer resistance, that is, film diffusion; (b) the transfer of the solute from the adsorbent surface to the intra-particle active sites, which are related to the intraparticle diffusion model and (c) the uptake of the solute on the active sites on the adsorbent surface, via complexation, sorption and surface precipitation, which are related to the pore diffusion or surface diffusion model. A number of models, including single step of diffusion (external or intraparticle) or combined phenomena (Jansson-Charrier et al., 1996), have been extensively applied in batch reactors to successfully describe the molecule transport in the adsorbent particles (Wu et al., 2001).

In order to identify the adsorption process as reaction-controlled or transport-controlled one, the effect of adsorbent size on the uptake of Cr(VI) was studied. Figure 1 shows the uptake vs. time plots for four different sizes of the UBTLs. This figure shows that the uptake is initially independent of the particle size but after 1 - 2 days strongly depends on the particle size, suggesting that the Cr(VI) uptake by the UBTLs is the combination of reaction- (independent part) and transport-controlled (dependent part) process. The rate parameters of the process were calculated from the linear fits of the plots of t/q_t against t (Figure 2), based on Ho and McKay (2000)
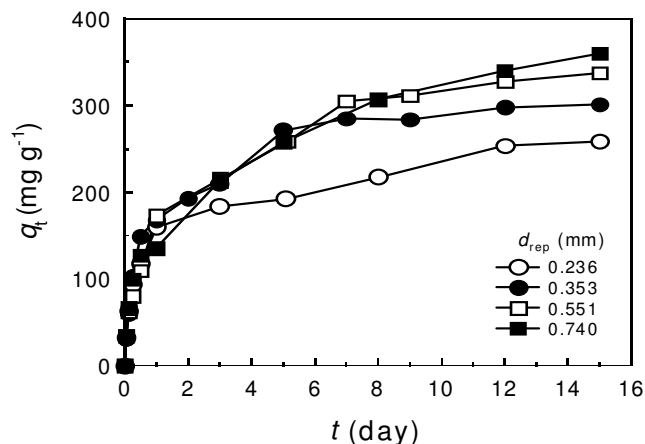
Figure 1. Effect of particle size on Cr(VI) uptake by UBTLs at a temperature of 25°C, pH = 2.00, W_s = 0.1 g L^{-1} and $C_o \approx 100$ mg L^{-1}.
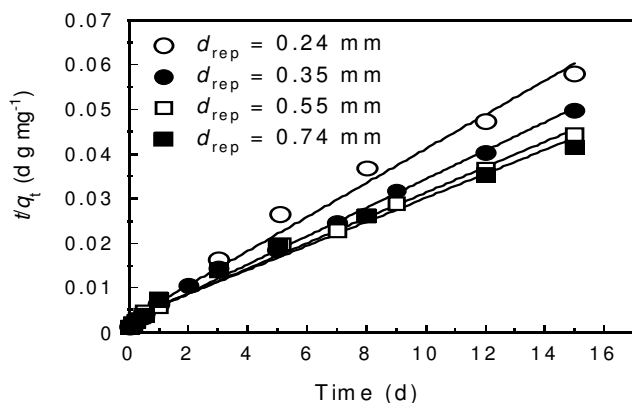

Figure 2. Pseudo-second order kinetics for the adsorption of Cr(VI) on different sizes of UBTLs at 25°C (C_o = 98.4 mg L^{-1}, W_s = 0.1 g L^{-1} and pH = 2.00).

pseudo-second order rate Equation 2 and presented in Table 1. Here the pseudo-second order rate constant decreases and the equilibrium amount adsorbed increases, with increasing the adsorbent size.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (2)$$

Where, q_e and q_t are the amount adsorbed at equilibrium and time t, respectively, and k is the rate constant of pseudo-second order adsorption.

Generally, the rate and the extent of adsorption per unit mass of adsorbent are proportional to the specific surface area, which is higher for smaller particles. This is due to the fact that small particles provide more windows through which adsorbate species diffuse to reach the active sites (Faust and Aly, 1987). The pore diffusion

distances to the sites are also shortened. But in our experimental results, increasing of the equilibrium amount adsorbed with an increase in particle size is anomalous. This observation supports that other phenomena, instead of pure diffusion, are involved which are independent on surface area. But it depends on active sites on the surface that might be present on the large size UBTLs. Mohan et al. (2001) also reported similar observation in case of Hg adsorption on activated carbon prepared from fertilizer waste but could not explain.

SEM and EDX studies on adsorbed surface

To find out the above reason and evaluate the active sites on UBTLs, we observed the surface morphologies of different sizes of UBTLs using Scanning Electron Microscope (SEM). It was observed that there are some cavities on the UBTLS surface, which become larger in size for large size of UBTLs. Again, whether these cavities are the active sites or not, we made a point analysis in six different places on the Cr(VI) adsorbed UBTLs surface using X-ray micro-analyzer (EDX) as shown in Figure 3a. Figure 3b shows the percent amount of chromium against the positions in Figure 3a. The maximum amount (>75%) of Cr observed at position C_1 and C_2, which are the cavity of the UBTLs surface. Again, the less amounts (<10%) of Cr observed at positions T_1 and T_2, which are the upper (top positions) sides of the surface. Figure 3(c) shows the SEM microgram with high magnification at position C_2 in Figure 3a. This microgram looks like a granular arrangement of Cr compound, which was confirmed by EDX analysis. Figure 3d shows the EDX spectrum of Figure 3c at position X which indicates the existence of chromium at specified point. The above observations suggest that the cavities on the UBTLs surface are the active places where Cr(VI) is attracted to adsorb. Thus the equilibrium amount adsorbed increases with increase in particle size of UBTLs.

Parabolic-diffusion model

An empirical parabolic-diffusion model (Jansson-Charrier et al., 1996), given in Equation 3, is used to describe Cr(VI) adsorption on UBTLs.

$$X = \frac{q_t}{q_e} = Dt^{1/2} + \text{constant} \qquad (3)$$

Where X is the ratio of the amount adsorbed at time t and that at equilibrium, D the overall coefficient of diffusion rate and t the contact time.

The model is particularly concerned with diffusion mechanisms: intraparticle (surface and/or pore) and film diffusion. The change of amount adsorbed with time for different initial concentrations of Cr(VI) were determined

Table 1. Effect of particle size on the pseudo-second order rate parameters for the adsorption of Cr(VI) on UBTLs at pH = 2.00.

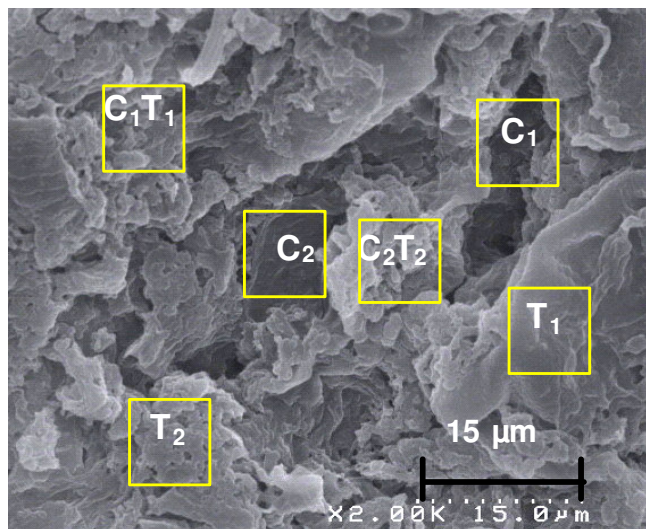| Representative size, d_{rep} (mm)	$k \times 10^6$ (g mg^{-1}min^{-1})	q_e(mg g^{-1})	R^2 (-)
0.236	3.34	263.2	0.989
0.353	2.85	312.5	0.996
0.551	1.81	357.2	0.992
0.740	1.54	370.4	0.983

Figure 3a. SEM and EDX analysis of Cr (VI) adsorbed UBTLs surface (d_{rep}= 0.353 mm, $C_o \approx$ 100 mg L^{-1}, W_s = 0.1 g L^{-1}, t = 15 days, and pH = 2.00, T = 25°C).
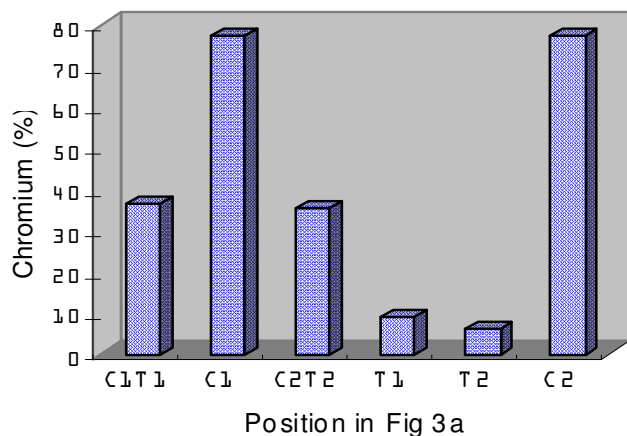

Figure 3c. SEM microgram of position C_2 in figure 3a with high magnification (× 70,000).

Figure 3b. Variation of amount adsorbed chromium with positions in figure 3a.
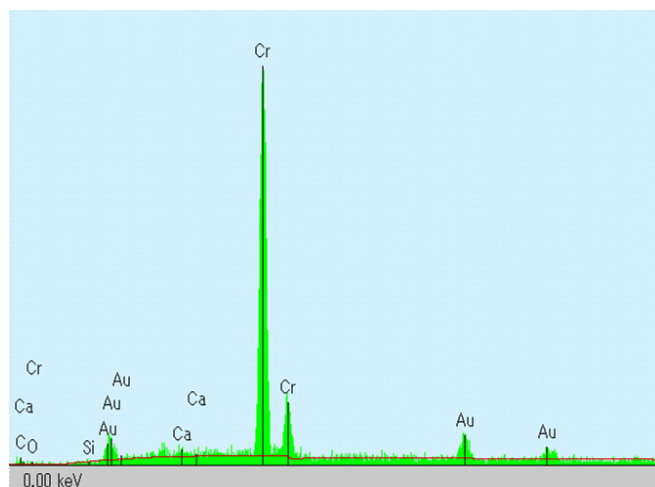
Figure 3d. EDX spectrum of figure 3c at position X.

with 0.1 g L^{-1} of UBTLs at pH = 2.00. A plot of X against $t^{1/2}$ gives the diffusion-controlled reaction rate (Tse and Shang-Lien, 2002; Sparks and Jardine, 1984). Figure 4 shows our experimental data as a plot of fractional
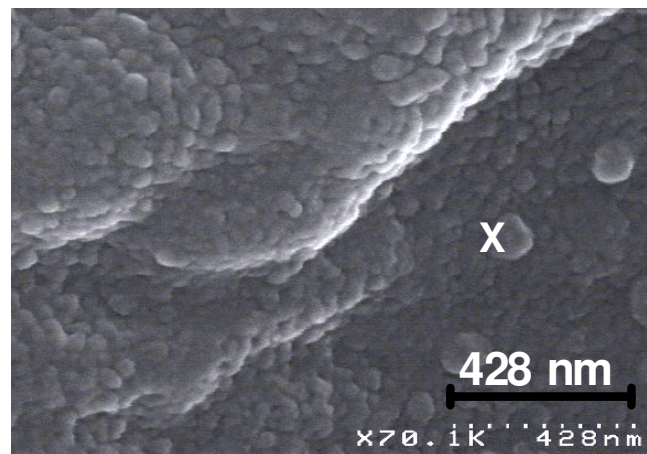
adsorbed against square root of time. In this figure, the linear regression values, R^2, are ranging from 0.809 to 0.997. The value drops from 0.997 to 0.809 with a decrease in the initial concentration of Cr(VI). This result suggests that the adsorption of Cr(VI) on the UBTLs is diffusion-controlled when the concentration of Cr(VI) is
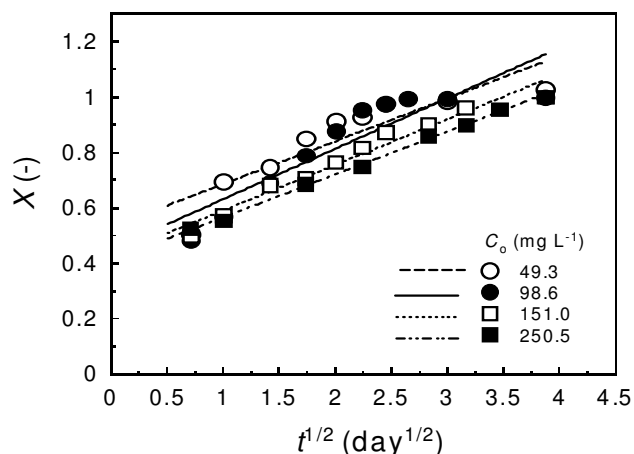
Figure 4. Fitting of parabolic diffusion model to Cr (VI) adsorption by UBTLs at a temperature of 25°C, $W_s = 0.1$ g L^{-1} and pH = 2.00.
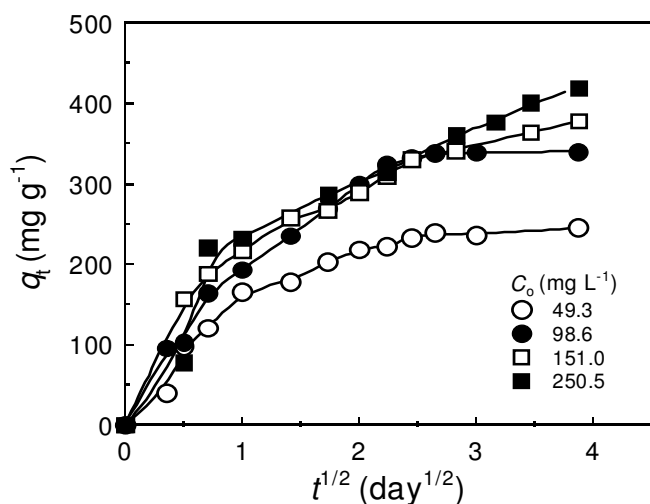

Figure 5. Fitting of intraparticle diffusion model to Cr(VI) adsorption by UBTLs at a temperature of 25°C, $W_s = 0.1$ g L^{-1} and pH = 2.00.

high, and when the concentration becomes lower; other mechanisms would begin to control the adsorption process. The overall coefficient of diffusion rate for different concentrations was calculated from the slope of plots in Figure 4 and given in Table 2. It shows that the overall coefficient of diffusion rate is generally decreases with increasing the initial concentration of Cr(VI), which is a general phenomenon for the movement of ions in solution.

Intraparticle diffusion model

Our experimental results were also verified with Weber

and Morris's intraparticle diffusion model, shown in Equation (4), to clarify the possibility that intraparticle diffusion of Cr(VI) ions in the UBTLs is rate-controlling (Namasivayam and Ranganathan, 1995).

$$q_t = k_{id} t^{1/2} \qquad (4)$$

Where k_{id} is the intraparticle diffusion constant, which can be obtained from the slope of the linear plot of q_t vs. $t^{1/2}$. Figure 5 shows the changes in the amount adsorbed for different initial concentrations against square root of time for different initial concentrations of Cr(VI). Three plots for C_o = 49.3 to 151.0 mg L^{-1}, have the same general features: an initial rapid increase portion followed by linear increase portion and a plateau. According to McKay et al. (1983), a multi-linearity portion might be appearing in the q_t vs. $t^{1/2}$ plot of metal ion sorption on biosorbents, which indicates that two or more steps occur. That is, the first sharp increase portion is the external surface adsorption or instantaneous stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate-controlling step. The third is the final equilibrium stage where the intraparticle diffusion becomes slow due to extremely low solute concentrations in the solution. The correspondences of the data in Figure 5 to the above mechanisms are thought as follows: the initial increase portion would be due to boundary layer transfer, the linear increase portion to the intraparticle diffusion, and the plateau to the equilibrium, respectively. In addition, the linear portion of the curves are extended in time with concentration i. e. the linear portion increases with increase the initial concentration of Cr(VI) which revealed that the intraparticle diffusion becomes predominant at high concentration of Cr(VI). A good correlation of the kinetic data in the linear portion with the intraparticle diffusion model suggests that the adsorption rate is mainly controlled by intraparticle diffusion. Earlier discussions on point analysis (Figure 3a) of chromium on the adsorbed UBTLs surface also supports the intraparticle diffusion on the UBTLs surface by the deposition of high amount chromium in the surface cavities.

The value of rate constant for intraparticle diffusion, k_{id}, was obtained from the slope of the linear portion of the q_t vs. $t^{1/2}$ curve in Figure 5 for each initial concentration and shown in Table 3. The rate constant for the intraparticle diffusion increases with increasing initial Cr(VI) concen-tration up to about 100 mg L^{-1}, and then decreases. The initial increasing of k_{id} indicates that an increase in the bulk liquid concentration raises the driving force of Cr(VI) to transfer from the bulk solution onto and into the solid particle. Moreover, in the test solution of pH = 2.00, in the range of Cr(VI) concentrations below 152 mg L^{-1}, HCrO$_4^-$ ion predominantly exist in the solution over Cr$_2$O$_7^{2-}$ ion (Cimino et al., 2000). And the ionic size of HCrO$_4^-$ is (44.0 cm^3 mol^{-1}) smaller than that of Cr$_2$O$_7^{2-}$ (73.0 cm^3 mol^{-1}) (Brito et al., 1997). At the lower concentration of Cr(VI),

Table 2. Effect of initial concentration of Cr (VI) on the overall coefficient of diffusion rate for the adsorption on UBTLs at pH = 2.00.

Initial concentration of Cr(VI), C_o (mg L^{-1})	Range of linear portion (day)	Overall coefficient of diffusion rate, D (min$^{-1/2}$)	Regression coefficient R^2 (-)
49.3	1 - 7	0.154	0.809
98.6	0.5 - 6	0.182	0.814
151.0	0.5 - 8	0.164	0.959
250.5	0.5 - 15	0.155	0.997

Table 3. Effect of initial concentration of Cr (VI) on the intraparticle diffusion constant for the adsorption on UBTLs at pH = 2.00.

Initial concentration of Cr(VI), C_o (mg L^{-1})	Range of linear portion (day)	Intraparticle diffusion constant, k_{id} (mg g^{-1} min$^{-1/2}$)	Regression coefficient R^2 (-)
49.3	1 - 7	1.28	0.976
98.6	0.5 - 6	2.50	0.986
151.0	0.5 - 8	1.93	0.984
250.5	0.5 - 15	1.74	0.997

therefore, this mono-valent $HCrO_4^-$ ion is expected to be more easily transferred to the UBTLs and migrate to the active sites on the surface, compared to $Cr_2O_7^{2-}$ ion. Therefore, the value of intraparticle diffusion constant would decrease with increasing concentration over than 150 mg L^{-1}. There is no report to-date about the adsorption of Cr(VI) by UBTLs, to be compared with the present values of intraparticle rate constant.

Conclusions

Summarizing the experimental results for different particle sizes of adsorbent and solute concentrations, verification of different kinetic models, and SEM surface analysis of adsorbed UBTLs, we propose that the possible mechanism during the adsorption of Cr(VI) onto UBTLs is as follows: in the acidic media (our experimental condition) UBTLs surface become protonated and the negative species of Cr(VI) are attracted by electrostatic force as a fast reaction-controlled step, followed by the migration of attracted species to the surface cavities as like more active sites on the UBTLs surface as a slow intraparticle diffusion process. Increasing the initial Cr(VI) concentration shifts the overall mechanism from the reaction-controlled one to the diffusion-controlled. The intraparticle diffusion is the main step, determining the rate of late uptake of Cr(VI) from aqueous solution.

ACKNOWLEDGEMENTS

NOMENCLATURE

C_e	Equilibrium concentration of Cr(VI) (mg L^{-1}).
C_o	Initial concentration of Cr(VI) (mg L^{-1}).
C_t	Concentration of Cr(VI) at time t (mg L^{-1}).
$C_{t\,III}$	Concentration of Cr(III) at time t (mg L^{-1}).
D	Overall coefficient of diffusion rate (min$^{-1/2}$).
d_{rep}	Representative particle diameter of UBTLs (mm).
k	Pseudo second-order rate constant, (g mg^{-1}min^{-1}).
k_{id}	Intraparticle diffusion coefficient (mg g^{-1}min$^{-1/2}$).
q_e	Equilibrium amount adsorbed (mg g^{-1}).
q_t	Amount adsorbed at time t (mg g^{-1}).
R^2	Regression coefficient (-).
t	Time (min or day).
T	Experimental temperature (^{o}C).
W_s	Dose of UBTLs (g L^{-1}).
X	Ratio of adsorbed Cr(VI) at time t and equilibrium Time t_e, = q_t/q_e (-).

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