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# Kinetics of Cr(VI) Adsorption on Used Black Tea Leaves

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Kinetic investigations were carried out to evaluate the applicability of used black tea leaves (UBTLs) as a low-cost adsorbent to the removal of chromium(VI) from aqueous solutions. The effects of various kinetic parameters were investigated using a batch process. The adsorption of Cr(VI) on UBTLs occurs rapidly in the first day, followed by a slow process that requires more than 10 days to reach its equilibrium. The initial adsorption rate increases with increasing initial concentration of Cr(VI) in the solution and processing temperature. The adsorption kinetics follows Richie's pseudo-second order rate equation better than the Lagergren's pseudo-first order one. The rate constant of the pseudo-second order adsorption is affected by the processing conditions such as the initial Cr(VI) concentration, solution pH, temperature and foreign ions. The results of the kinetic experiments showed that the adsorption of Cr(VI) on UBTLs is an endothermic process and the activation energy of adsorption is 16.3 kJ mol<sup>-1</sup>.

## Introduction

Chromium is one of the contaminants, which exists in trivalent, Cr(III), and hexavalent, Cr(VI), oxidation states in natural aquatic systems. The hexavalent form is much more toxic and carcinogenic than the trivalent one and required more concern (International Agency for Research on Cancer, 1990). However, chromium(VI) rarely appears naturally, but it is produced from anthropogenic sources. High concentration of Cr(VI) is usually found in various industrial sewage including metallurgy, refractory, and chemical industries (Environmental Protection Agency, 1998). Chromium(VI) is not biodegradable like organic compounds and tends to accumulate in living organisms causing various diseases and disorders (Bailey *et al.*, 1999). The increase in Cr(VI) concentration above the consent or standard limits ( $5.0 \times 10^{-5}$  kg·m<sup>-3</sup> for drinking water) is becoming an important subject of public health (Environmental Protection Agency, 1998). It is needed therefore to develop suitable treatment processes to remove Cr(VI) from wastewater before being discharged into aquatic systems. The best treatment of Cr(VI) depends on the Cr(VI) concentration, existing species of chromium:  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  in

source water, other constituents in the water, existing treatment process, treatment cost and handling of residuals (Eligwe *et al.*, 1999).

The present treatment technologies such as a reverse osmosis, adsorption with activated carbons and ion exchange may not be applicable to small industries, especially in developing countries, because of their high capital investment and running costs. Thus, there is a need to develop low-cost and easily available materials that can effectively remove and recover hexavalent chromium.

Adsorption plays an important role in the removal of metal ions with low concentration from the wastewater. In recent years, we have been interested in the use of used black tea leaves (UBTLs) as a low-cost adsorbent because of their high removal capacity for Cr(VI) (Hossain, 2003). Earlier investigations were mainly focused on the conformational aspects of their removal or sorption capacities. The kinetics is an important physicochemical factor to evaluate the basic qualities of an adsorbent as well as the application of the adsorption process, whereas there is no report about the kinetic study on the removal of Cr(VI) by UBTLs. The prediction of the adsorption rate for a given system is the most important parameter for adsorber design with adsorbate residence time, ultimately controlled by the kinetics of the adsorption system (Eligwe *et al.*, 1999).

Various researchers have described the order of adsorptive reaction of metal ions in aqueous system using different kinetic models. The adsorptions of

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Hg(II), Cd(II) and Pb(II) on lignite, and Fe(II) on low-rank brown coal were explained by simple first order kinetics with respect to the solution concentration (Eligwe and Okolue, 1994; Eligwe *et al.*, 1999). Traditionally, adsorptive reactions are described by Lagergren's pseudo-first order rate equation, based on the concentration of adsorbate in the adsorbent phase (Lagergren, 1898). Numerous studies reported Lagergren kinetics for metal sorption; for example, the sorption of Ni(II) onto Wollastonite and China clay (Sharma *et al.*, 1990, 1991) and Cr(VI) onto bismuth trioxide in aqueous solutions (Bhutani and Kumari, 1994). On the other hand, a pseudo-second order rate equation known as Ritchie's model was also used to describe the adsorption of metal ions from aqueous solution onto peat (Ho *et al.*, 1995) and sludge solids (Tien and Huang, 1991).

In the present study, the kinetics of Cr(VI) adsorption on UBTLs is discussed through batch experiments under the various conditions: initial concentration of Cr(VI), solution pH, processing temperature and the presence of foreign ions. The factors affecting the rate constant and the adsorption capacity of this adsorption process were investigated with different kinetic models.

## 1. Experimental

### 1.1 Materials

Used black tea leaves were obtained after extracting tea liquor from fresh ones (CTC Manufacturing Process, Bangladesh Tea Research Institute) by boiling with distilled water for 8 hours. The tea leaves were dried at 378 K for 24 hours and then were sieved out in a diameter of  $0.25 \times 10^{-3}$  to  $0.50 \times 10^{-3}$  m. The prepared UBTLs were characterized by determining the apparent bulk density ( $0.31 \text{ kg}\cdot\text{m}^{-3}$ ) and the BET surface area ( $1340 \text{ m}^2\cdot\text{kg}^{-1}$ ) by a Krypton adsorption method. An elemental analysis using an energy-dispersive X-ray microanalyzer (EDX, EMAX-5770W, HORIBA, Ltd.) showed that the UBTLs contain 65.3% of C, 34.2% of O, 0.1% of Ca and less than 0.1% of S and P. The main ingredient of UBTLs is cellulose.

Analytical grade reagents were used in all experiments. A stock solution of synthetic wastewater containing  $1.0 \text{ kg}\cdot\text{m}^{-3}$  of Cr(VI) was prepared by dissolving potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) (Wako Pure Chemical Industries, Ltd.) into pure water. All working solutions of various concentrations of Cr(VI) were obtained by diluting the stock solution with distilled water. Nitric acid was used to adjust the initial solution pH to minimize reduction of Cr(VI) to Cr(III).

### 1.2 Methods

Kinetic studies were carried out with a simple batch technique. Experiments were conducted in capped Taplon conical flasks of 100 mL at a specified temperature, by suspending  $5.0 \times 10^{-6}$  kg of the UBTLs

in  $50 \times 10^{-6} \text{ m}^3$  of the Cr(VI) solution. The solution pH was adjusted in the range of 1.00–2.00 where the maximum change of pH during the experiments is less than 0.10. The suspensions were mixed on a shaker with a constant speed of 125 rpm. The flasks were withdrawn at regular time intervals, and the solutions were analyzed with a reversed-phase HPLC-UV system for simultaneous determination of Cr(VI) and Cr(III) (Andrle and Broekaert, 1993; Hossain *et al.*, 2005). A mixture of acetonitrile and water (67:33) was used as a mobile phase, and a silica-based analytical column ( $15 \times 4.6 \text{ cm}$ ;  $5 \mu\text{m}$ , TSK GEL ODS-120A, Tosoh Corp.) was used for separation. Absorbance was measured at 254 nm using UV-VIS recording spectrophotometer (UV-160A, Shimadzu Corp.). The amounts adsorbed and reduced were calculated, based on the analysis of the remaining solutions. Similarly, batch sorption experiments were performed with various initial concentrations of Cr(VI), initial solution pH values and processing temperatures. Experiments were also carried out separately under coexistence of As(III) and Cd(II) with a constant concentration of Cr(VI), pH and temperature.

## 2. Results and Discussion

### 2.1 Adsorption rate

Batch experiments were carried out with respect to the reaction kinetics of Cr(VI) with the UBTLs. Our experimental results showed that both adsorption and reduction were involved in the removal of Cr(VI) by the UBTLs. The adsorption is more important than the reduction for the treatment process, because removal of Cr(III) from the solution is required in the latter treatments. Our previous studies showed that the adsorption of Cr(VI) on the UBTLs is predominant over the reduction in the range of solution pH  $< 2$  (Hossain *et al.*, 2000; Hossain, 2003). In the present study, therefore, the adsorption kinetics was performed in the range of solution pH 1.00–2.00, and the amount of Cr(VI) adsorbed,  $q_t$ , was calculated from Eq. (1):

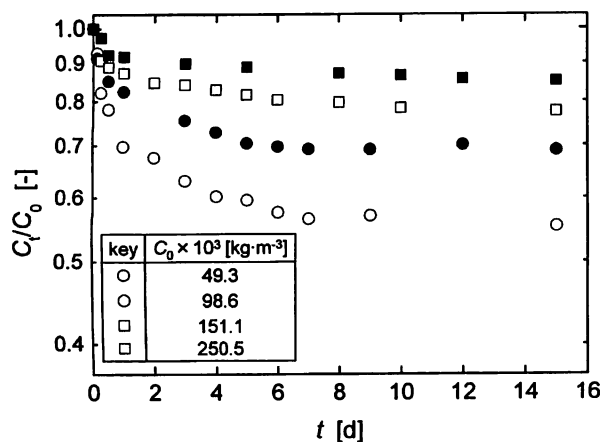
$$q_t = \frac{C_0 - C_t - C_{\text{III}}}{W_s} \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of Cr(VI) in the solution at time  $t = 0$  and  $t = t$ , respectively. The concentration of Cr(III), given by reduction of Cr(VI), in the solution at time  $t$  is represented by  $C_{\text{III}}$ . The symbol,  $W_s$  is the dose of the UBTLs.

The concentration of Cr(VI) for different initial concentrations rapidly decreases during the first one day and then gradually approaches to equilibrium in 10–15 days as shown in **Figure 1**. The figure also shows that the equilibrium amount adsorbed depends on the initial concentration of Cr(VI). The initial

**Table 1** The effect of initial concentration of Cr(VI) on the initial rate of adsorption on UBTLs

Initial concentration of Cr(VI) × 10 <sup>3</sup> [kg·m <sup>-3</sup> ]	Initial adsorption rate × 10 <sup>4</sup> [kg·kg <sup>-1</sup> ·d <sup>-1</sup> ]
49.3	23.0
98.6	32.0
151.0	38.0
250.5	42.0



**Fig. 1** Concentration change of Cr(VI) in the solution with time for different initial concentrations (pH = 1.54,  $W_s = 0.1 \text{ kg}\cdot\text{m}^{-3}$  and  $T = 298 \text{ K}$ )

adsorption rates were calculated from  $q_t$  vs.  $t$  plots according to Eq. (2). The values increase with an increase in initial concentration of Cr(VI) as shown in **Table 1**.

$$\left. \frac{dq_t}{dt} \right|_{t=0} = - \frac{1}{W_s} \left. \frac{dC_t}{dt} \right|_{t=0} \quad (2)$$

It is apparent that two different diffusion mechanisms played respective roles during this adsorption process. The first is a simple film diffusion driven by a large concentration difference between the bulk solution and the surface of the UBTLs, and the second is the surface diffusion of Cr(VI) to the active sites. Thus, this behavior was tried to describe from the kinetic aspects based on the concentration of the bulk solution and also on the concentration in the adsorbent phase. Various kinetic evaluations have been developed for adsorption study. Here we attempted to apply a simple first order kinetic model (Eligwe *et al.*, 1999) for changing the bulk concentration, and Lagergren's pseudo-first order rate equation (Lagergren, 1898) and Ritchie's pseudo-second order rate equation (Ho and McKay, 2000) for the adsorbent phase concentration, to describe the kinetic behavior of the system as follows.

### 2.1.1 First order kinetics

In our experimental conditions, bichromate ( $\text{HCrO}_4^-$ ) ions are the main species in the test solution (Cimino *et al.*, 2000). Therefore, we described the change in the bulk concentration of the system using the following simple first order rate Eq. (3):

$$C_t = C_0 e^{-k't} \quad (3)$$

where  $k'$  is the first order rate constant. The experimental results showed that the  $C_0/C_t$  vs.  $t$  plots (Figure 1) for different initial concentrations of Cr(VI) did not follow each of the straight line, which indicates the failure in expressing this adsorption process by the simple first order kinetics. On the other hand, the literature review has shown that most Cr(VI) adsorption follows first order kinetics (Bhutani and Kumari, 1994; Gupta *et al.*, 2001). However, Sparks (1989) has proposed that the simple kinetic models such as first- or second-order rate equations are not applicable to the adsorption system with solid surfaces, which are rarely homogeneous like our UBTLs, because the effect of transport phenomena and chemical reactions are often experimentally inseparable.

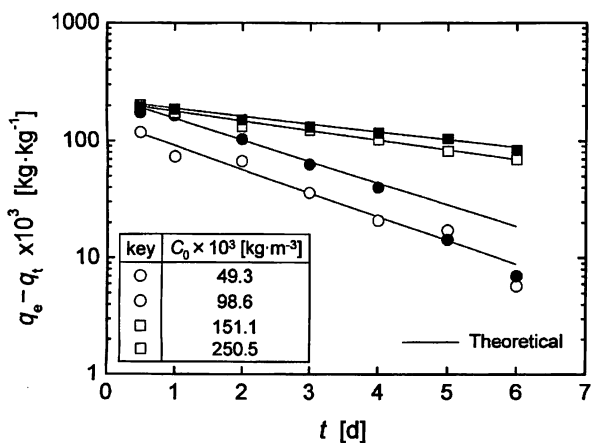
### 2.1.2 Lagergren pseudo-first order kinetics

A Lagergren pseudo-first order rate equation has been applied to the adsorption of the liquid/solid system based on adsorption capacity. According to this model, one adsorbate species reacts with one active site on surface. Lagergren's pseudo-first order rate, Eq. (4), cited by Ho and McKay (1999) was applied to the kinetic behavior of Cr(VI) adsorption on the UBTLs.

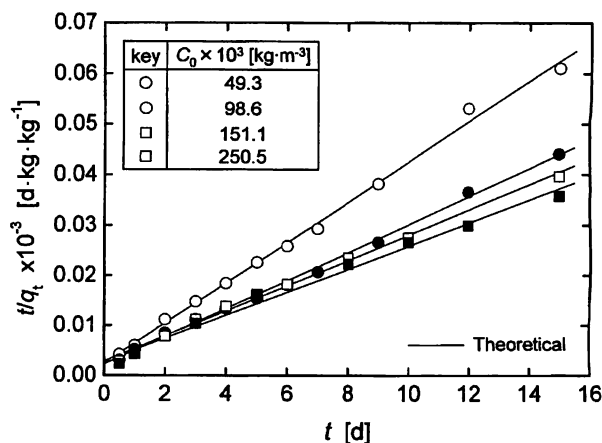
$$q_t = q_e (1 - e^{-k_{ad}t}) \quad (4)$$

where  $q_e$  is the amount adsorbed at equilibrium,  $q_t$  is the amount adsorbed at time  $t$ , and  $k_{ad}$  is the rate constant of pseudo-first order adsorption. In our experimental data, for the first four days,  $q_e - q_t$  have an almost linear relationship with time, but thereafter deviate from the straight lines for the low initial concentration of Cr(VI) as shown in **Figure 2**. For the high initial concentration of Cr(VI), the deviation is also observed for the longer contact time more than 10 days. This deviation indicates that the adsorption of Cr(VI) on the UBTLs did not completely follow the pseudo-first order kinetics. The equilibrium amount adsorbed,  $q_e$ , calculated from the intercepts of the straight lines are different from the experimental values.

Ho and McKay (1999, 2000) reported that the Lagergren's pseudo-first order equation does not fit well for the whole range of contact time. In order to fit this equation to the experimental data, the equilibrium adsorption capacity,  $q_e$ , must be known. Actually, the



**Fig. 2** Applicability of the pseudo-first order kinetics for the adsorption of Cr(VI) on the UBTLs at different initial concentrations of Cr(VI) (pH = 1.54,  $W_s = 0.1 \text{ kg}\cdot\text{m}^{-3}$  and  $T = 298 \text{ K}$ )



**Fig. 3** Applicability of the pseudo-second order kinetics for the adsorption of Cr(VI) on the UBTLs at different initial concentrations of Cr(VI) (pH = 1.54,  $W_s = 0.1 \text{ kg}\cdot\text{m}^{-3}$  and  $T = 298 \text{ K}$ )

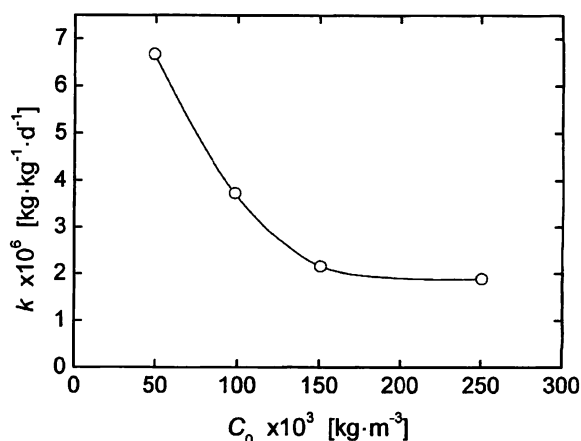
Lagergren rate equation, applicable to experimental results, generally differs from a simple first order equation in two ways: (a) the parameter  $k_{ad}(q_e - q_t)$  does not represent the number of available active sites, (b) the parameter  $\log q_e$  is adjustable and is not equal to the intercept of the plot of  $\log(q_e - q_t)$  vs.  $t$ , whereas in a simple first order process  $\log q_e$  should be equal to the intercept of the plot of  $\log(q_e - q_t)$  against  $t$  (Aharoni and Sparks, 1991). The value of  $q_e$  can be determined by trial and error where time is constant;  $t_0$  is an adjustable parameter, i.e. the plot of  $\log(q_e - q_t)$  vs.  $(t - t_0)$  that makes the equilibrium adsorption capacity,  $q_e$ , suitable for use in the kinetic expression. Lagergren's equation is suitable for homogeneous surface, but the surfaces of UBTLs are not so homogeneous.

### 2.1.3 Ritchie's pseudo-second order kinetics

Ritchie's pseudo-second order rate equation was also applied to the adsorption kinetics of the present system. The model also derived on the basis of the concentration of the adsorbate in the adsorbent phase (Ho and McKay, 2000; Cheung *et al.*, 2001). The linearized form of Ritchie's equation is given as:

$$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (5)$$

The linear plots of  $t/q_t$  against  $t$ , as shown in **Figure 3**, represent a good fit over the whole range of the initial concentration of Cr(VI) and contact time. Ritchie's pseudo-second order rate equation was derived by assuming that two surface sites could be occupied by one divalent adsorbate ion. Thus Eq. (5) would be expected to be applicable for the adsorption of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ions only. However, the present experimental results are against this expectation because accord-



**Fig. 4** The effect of initial concentration of Cr(VI) on the pseudo-second order rate constant (pH = 1.54,  $W_s = 0.1 \text{ kg}\cdot\text{m}^{-3}$  and  $T = 298 \text{ K}$ )

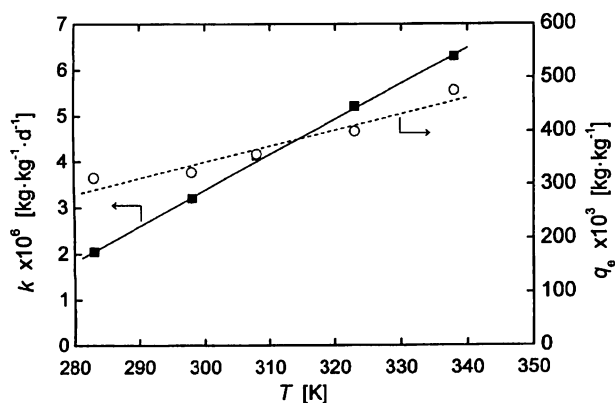
ing to our experimental conditions (pH = 1.54)  $\text{HCrO}_4^-$  is the main species in the solution (Cimino *et al.*, 2000). The result suggested that one adsorbed  $\text{HCrO}_4^-$  occupied the two active sites on the UBTLs surface. The sorption of Cu(II), Ni(II) and Pb(II) onto sphagnum moss peat followed the pseudo-second order mechanism (Ho and McKay, 2000). A similar trend was observed for the sorption of arsenic ions onto iron-conditioned zeolite (Onyango *et al.*, 2003).

The pseudo-second order rate constants,  $k$ , were calculated from the linear plots of  $t/q_t$  vs.  $t$  like **Figure 3**, and the effects of the initial concentration of Cr(VI), solution pH, processing temperature and the presence of foreign ions, on the rate constant were investigated.

### 2.2 Effect of concentration

The influence of the initial concentration of Cr(VI) on the pseudo-second order rate constants are presented in **Figure 4**. This figure shows that the rate constant





**Fig. 8** The effect of temperature on the pseudo-second order rate constant and the equilibrium amount adsorbed ( $C_0 = 98.9 \times 10^{-3} \text{ kg}\cdot\text{m}^{-3}$ ,  $W_s = 0.1 \text{ kg}\cdot\text{m}^{-3}$  and  $\text{pH} = 2.00$ )

observed that at  $\text{pH} \leq 1.30$ , the reduction of Cr(VI) to Cr(III) becomes predominant. Therefore, the value of  $k$  and  $q_e$  at  $\text{pH} = 1.0$  and  $1.3$  are apparent values based on the dose of the UBTLs. It is meaningless to discuss the changing tendency of these values in the same way to that of the values in the  $\text{pH}$  range of  $1.54$  to  $2.00$ . Thus, the UBTLs is applicable for the treatment of Cr(VI) at the initial  $\text{pH} > 1.54$ .

#### 2.4 Effect of temperature

The effect of the processing temperature on the rate constant is important to determine the thermodynamic parameters to predict the adsorption behavior. Batch experiments were carried out at different temperatures specified in the range of  $283$  to  $338 \text{ K}$  with a constant concentration of Cr(VI),  $0.1 \text{ kg}\cdot\text{m}^{-3}$ , the amount of the UBTLs,  $0.1 \text{ kg}\cdot\text{m}^{-3}$ , and  $\text{pH} = 2.00$ . **Figure 8** shown that the obtained rate constant increases almost linearly with an increase in temperature, and the equilibrium amount adsorbed also increases with the increase in temperature. These experimental facts suggest that the adsorption process is controlled by chemical reaction, which is general for most of the chemically controlled adsorption processes. The activation energy of adsorption calculated from the Arrhenius' plot of the data is  $16.3 \text{ kJ}\cdot\text{mol}^{-1}$  suggesting the endothermic nature of this adsorption. This small value of activation energy suggests that the adsorption easily occurs.

#### 2.5 Effect of the presence of foreign anions and cations

Either positive or negative ions, or both of them commonly exist in the real wastewater. Generally, Cd(II) is found in some industrial wastewaters and recently As(III) is found in the ground water of some developing countries. Therefore, we select these two ions to evaluate the effect of positive and negative ions on the potential of UBTLs to adsorb Cr(VI), and the sorption experiments were carried out in the presence

**Table 2** Rate constants of pseudo-second order kinetics for the adsorption of Cr(VI) on UBTLs with and without foreign ions

	Foreign ions		
	Absent	Cd(II)	As(III)
$k \times 10^6$ [kg.kg <sup>-1</sup> .d <sup>-1</sup> ]	20.5	4.7	11.1
$q_e \times 10^3$ [kg.kg <sup>-1</sup> ]	170	172	145
$R^2$ [—]	0.999	0.976	0.999

$R^2$ : regression coefficient

of them, separately. The effect of foreign ions on the rate constant was investigated by performing batch experiments at  $298 \text{ K}$ , in the presence of  $10 \times 10^{-3} \text{ kg}\cdot\text{m}^{-3}$  of As(III) as  $\text{H}_2\text{AsO}_4^-$  with  $25 \times 10^{-3} \text{ kg}\cdot\text{m}^{-3}$  of Cr(VI) and  $0.1 \text{ kg}\cdot\text{m}^{-3}$  of UBTLs at  $\text{pH} = 2.00$ . A similar experiment was carried out in the presence of  $10 \times 10^{-3} \text{ kg}\cdot\text{m}^{-3}$  Cd(II) instead of As(III). The values of the pseudo-second order rate constant and the equilibrium amount adsorbed of Cr(VI) are listed in **Table 2**. The adsorption rate constants for the presence of foreign ions are smaller than that for their absence. The rate constant is significantly affected by Cd(II) compared with As(III), because of the interaction of  $\text{Cd}^{2+}$  with the negative species of Cr(VI),  $\text{HCrO}_4^-$ . On the other hand, the equilibrium amount adsorbed in the absent case is almost the same value as that for the presence of Cd(II) and is larger than that for the presence of As(III). For the coexistence of As(III),  $\text{H}_2\text{AsO}_4^-$  might be easily adsorbed on the protonated UBTLs, and resultantly the active sites for Cr(VI) decreased. Thus the presence of anions causes the adsorption capacity of the UBTLs for Cr(VI) at the low  $\text{pH}$  to decrease.

#### Conclusions

The adsorption of Cr(VI) on the used black tea leaves following the pseudo-second order kinetics is better than the pseudo-first order one. The rate constant of the adsorption increases with decreasing the initial concentration of Cr(VI). The solution  $\text{pH}$  also has a significant effect on the adsorption rate, and the maximum rate constant is observed at the solution  $\text{pH}$  of  $1.30$ . The rate constant increases linearly with an increase in temperature, suggesting that the endothermic process. For the presence of As(II) anions and Cd(II) cations, the rate constant decreases compared with the case where they're absent, and the presence of anions brings about a decrease in the equilibrium amount of adsorbed Cr(VI). The equilibrium amount adsorbed increases with an increase in processing temperature. The Arrhenius' plot of the rate constants gives a small value of activation energy, indicating that Cr(VI) is easily adsorbed on the UBTLs.

The present study shows the feasibility of the practical use of waste black tea leaves as a low cost adsorbent for the removal of Cr(VI) from aqueous systems.

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#### Nomenclature

$C_0$	=	initial concentration of Cr(VI)	[kg·m <sup>-3</sup> ]
$C_t$	=	concentration of Cr(VI) at time $t$	[kg·m <sup>-3</sup> ]
$C_{III}$	=	concentration of Cr(III) at time $t$	[kg·m <sup>-3</sup> ]
$K$	=	equilibrium constant	[—]
$k$	=	pseudo-second order rate constant	[m <sup>3</sup> ·kg <sup>-1</sup> ·d <sup>-1</sup> ]
$k_{ad}$	=	pseudo-first order rate constant of adsorption	[d <sup>-1</sup> ]
$k'$	=	first order rate constant	[d <sup>-1</sup> ]
$pH_{zpc}$	=	zero point charge pH	[—]
$q_e$	=	amount of Cr(VI) adsorbed at equilibrium time per unit mass of UBTLs	[kg·kg <sup>-1</sup> ]
$q_t$	=	amount of Cr(VI) adsorbed at time $t$ per unit mass of UBTLs	[kg·kg <sup>-1</sup> ]
$T$	=	temperature	[K]
$t$	=	time	[d]
$W_s$	=	dose of adsorbent	[kg·m <sup>-3</sup> ]

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