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# Optimization of Parameters for Cr(VI) Adsorption on Used Black Tea Leaves

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**Abstract.** Dynamic characteristics of Cr(VI) sorption on used black tea leaves (UBTLs) as a low-cost adsorbent are studied. Batch experiments were conducted to evaluate the effects of Cr(VI) concentration, solution pH and temperature on the removal process. Both of adsorption and reduction, involved in the process, are affected by the processing parameters. The adsorption kinetics is described successfully using pseudo-second order rate equation and the rate constant decreases with increasing the initial concentration of Cr(VI) up to 150 mg/L (for 0.1 g/L UBTLs) then becomes slow. Experimental and calculated kinetic data for equilibrium are well expressed by Langmuir isotherm. The solution pH has a profound effect on the adsorption rate. The rate constant increases linearly with an increase in temperature, and the low value of activation energy of adsorption, 16.3 kJ/mol, indicates that Cr(VI) is easily adsorbed on UBTLs. The maximum Cr(VI) adsorptive conditions, with a minimum reduction, were achieved from the dynamics of operational parameters: the initial Cr(VI) concentration $<150$ mg/L (for 0.1 g/L UBTLs); the initial solution pH $= 1.54$–$2.00$ and the processing temperature $<50\,^\circ$C, for the possibility of its practical application.

**Keywords:** chromium(VI), used black tea leaves, adsorption and reduction, sorption dynamics

## Introduction

The potential sources of hexavalent chromium are various effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminum manufacturing industries. These industrial effluents can contain Cr(VI), in the concentration range of 10 to 100 mg/L (Nakano et al., 2000), which is much higher than the standard limit; 0.5 mg/L in industrial wastewater (EPA). In aqueous systems, chromium usually exists in both trivalent [Cr(III)] and hexavalent [Cr(VI)] forms. Although Cr(III) is considered an essential trace element, Cr(VI) is toxic, carcinogenic, mutagenic and teratogenic (Wittbrodt and Palmer, 1995). Therefore, the removal of hexavalent chromium from industrial wastewater is of particular concern.

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Currently, existing techniques for the removal of Cr(VI) from aqueous system, such as ion exchange and reverse osmosis may not be applicable to small industries especially in under-developed countries because of their high capital investment and running costs. Various conventional methods are available for the removal of Cr(VI) with a series of limitations. Actually, Cr(VI) is a well-known oxidizing agent, easily reduced to Cr(III) by organics or reducing agents. This reduction reaction is not suitable for low concentration of Cr(VI). At low concentration, adsorption is one of the promising techniques, and the use of activated carbon is still very popular for wastewater treatment processes, but also expensive. Moreover, Bowers and Huang (1980) stated that the removal of Cr(VI) from aqueous systems by activated carbon is a complicated process due to the involvement of reduction simultaneously with adsorption that required the secondary treatment for Cr(III) removal.

In recent years, several studies have been reported about the sorption of Cr(VI) using waste materials as low-cost sorbents, such as bagasse fly ash (Park et al., 1999), hazelnut shell (Cimino et al., 2000), aquatic plants (Srivastava et al., 1994), bark (Alves et al., 1993), fungi (Lewis and Kriff, 1988), algae (Yu et al., 1999), green algae *Spirogyra* species (Gupta et al., 2001), red-mud (Gupta et al., 2001) and others. Their sorption capacities (less than 40 mg/g-sorbent), however, are far smaller than that of activated carbon (241–459 mg/g; Martiner et al., 1995). Therefore, there is a need for the development of low cost, highly efficient and easily available materials, which can adsorb Cr(VI) from aqueous solution.

Used black tea leaves (UBTLs) are one of the attractive adsorbents for low-cost removal process of Cr(VI) because of their high adsorption capacity for this ion (Hossain, 2003). Both adsorption and reduction are involved in this removal or sorption process, but adsorption is predominant over reduction at low solution pH (Hossain, 2003). Whereas, in case of activated carbon, both adsorption and reduction are increasing with a decrease in solution pH (Bowers and Huang, 1980). This draws our attention to further study the use of UBTLs in order to find out the suitable conditions for minimum reduction, and to achieve maximum adsorption capacity, for application of UBTLs. Moreover, the previous investigations were mainly focused on the study of the conformational aspects of the adsorption capacity and no significant attempts were made to investigate the kinetic path of the adsorption process. The dynamics is an essential aspect of the adsorption process especially for practical applications. Therefore, the present investigation has been undertaken for studying the dynamic behavior of adsorption and reduction through batch experiments performed under different conditions of initial concentration of Cr(VI), solution pH and processing temperature. A well-fitted kinetic equation was used to evaluate the suitable operational conditions for the removal process, and a Langmuir-type isotherm was modeled using kinetic data and experimental results.

*Table 1.* Physical properties of UBTLs.

| Parameters | Units | Values |
|---|---|---|
| Mean particle diameter | mm | 0.38 |
| Bulk density | g/cm$^3$ | 0.34 |
| BET surface area/Kr | m$^2$/g | 1.34 |

## Experimental

### *Materials*

Used black tea leaves were obtained after extracting tea liquor from fresh black tea leaves (CTC Manufacturing Process, Bangladesh Tea Research Institute) by boiling with distilled water for 8 h. After extraction, the leaves were dried at 105 °C for 24 h and then sieved. Characteristic features of the UBTLs are given in Table 1. Elemental analysis using an Energy-dispersive X-ray Microanalyzer (EDX) (EMAX- 5770W, Horiba) shows that UBTLs contain 65.3% of C, 34.2% of O, 0.1% of Ca and less than 0.1% S and P.

Analytical grade reagents were used in all cases. A stock solution of synthetic wastewater containing 1000 mg/L of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Wako Pure Chem. Ind., Japan) in distilled 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 the reduction of Cr(VI).

### *Methods*

Batch sorption experiments were carried out in capped conical flasks (100 mL, Taplon) at a specified temperature, by suspending 5 mg of the UBTLs in 50 mL of Cr(VI) solution at specified solution pH. The suspensions were mixed on a shaker with a constant speed of 125 rpm. The solutions were withdrawn at certain time intervals and separated solutions were analyzed with a reversed-phase HPLC-UV system for simultaneous determination of Cr(VI) and Cr(III) in the solution (Hossain et al., 2005). The amounts adsorbed and reduced were calculated, based on the analysis of the remaining solutions. Similarly, the batch sorption experiments were conducted with various initial concentrations of Cr(VI), initial solution pH values and processing temperatures.

## Results and Discussion

### *Effect of Concentration*

Kinetic studies were conducted for different initial concentrations of Cr(VI) with the specified amount of UBTLs, 0.1 g/L, at 25°C. According to the previous study (Hossain and Tajmeri, 1998), the solution pH was adjusted to 1.54, where the maximum change of pH during the removal process is $<0.1$. Experimental results show that both adsorption and reduction depend on the initial concentration of Cr(VI). Figure 1 shows the concentration decays of Cr(VI) by both adsorption and reduction with time for different initial concentrations. At low concentration of Cr(VI), the removal is purely governed by adsorption. As the initial concentration of Cr(VI) increases above about 150 mg/L, the reduction increases gradually with time. This effect of concentration might be due to the unavailability of the free adsorption sites on the UBTLs surface after a specific amount has been adsorbed, as discussed later. The concentration decay curves show that within the first day, the amount of Cr(VI) adsorbed on the UBTLs rapidly reached 50–70% of the equilibrium value and then showed a slow increase for 10–15 days. It was attempted to analyze the kinetic behavior of this adsorption process using the pseudo-first order rate equation, Eqs. (1) given by Lagergren (Ho and McKay, 1999),

$$\log(q_\mathrm{e} - q_t) = \log(q_\mathrm{e}) - \frac{k_\mathrm{ad}}{2.303}t \qquad (1)$$

For the first several days, the change in the amount adsorbed with time was found to fit Eq. (1) and in case of low initial concentration of Cr(VI) exhibited a deviation from this equation. Therefore, the overall adsorption could not be expressed by this equation.

The change in the amount of the adsorbed Cr(VI) with time was found to fit the pseudo-second order rate equation, Eq. (2) (Ho and McKay, 2000), as shown in Fig. 2.

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

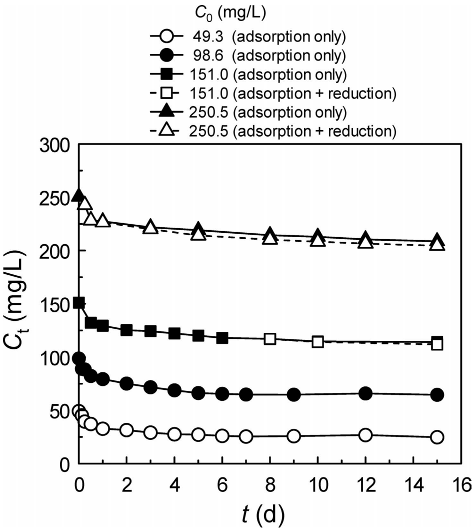


*Figure 1.* Change of the concentration of Cr(VI) with time for different initial concentrations ($W_s = 0.1$ g/L, pH = 1.54 and $T = 25°\mathrm{C}$).

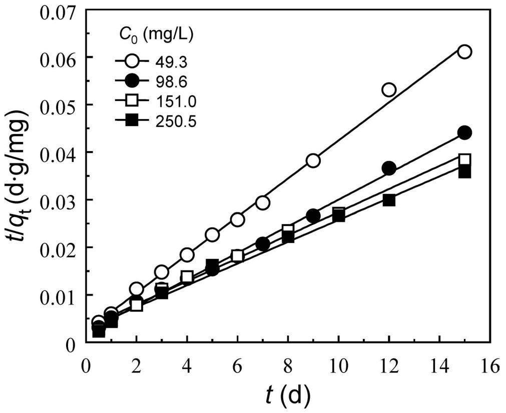


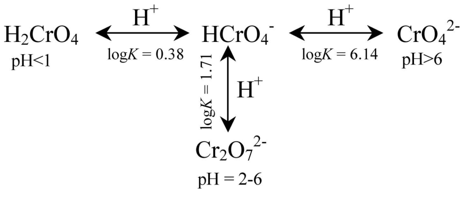
*Figure 2.* Plot of the pseudo-second order kinetics for the adsorption of Cr(VI) on UBTLs at different initial concentrations ($W_s = 0.1$ g/L, pH = 1.54, and $T = 25°\mathrm{C}$).

*Table 2.* Effect of concentration of Cr(VI) on the pseudo-second order rate parameters ($pH = 1.54$, $W_s = 0.1$ g/L and $T = 25°C$).

| $C_o$ (mg/L) | $C_e$ (mg/L) | $q_e$ expt. (mg/g) | $q_e$ cal. (mg/g) | $k \times 10^3$ (g/(mg·d)) | $R^2$ (−) |
|---|---|---|---|---|---|
| 49.3 | 24.8 | 245 | 250 | 6.67 | 0.997 |
| 98.7 | 64.7 | 340 | 357 | 3.73 | 0.997 |
| 151.0 | 114.2 | 368 | 417 | 2.16 | 0.992 |
| 250.5 | 208.6 | 419 | 435 | 1.89 | 0.989 |

where, $q_t$ is the amount adsorbed at time $t$ and $q_e$ the equilibrium amount adsorbed. The pseudo-second order rate constant, $k$, was calculated from $t/q_t$ *vs.* $t$ plot as shown in Fig. 2. The rate constant rapidly decreases with an increase in initial concentration of Cr (VI) up to ≈150 mg/L, then, decrease is slow with further increased initial concentration as given in Table 2.

Equation (2) was derived for adsorption of divalent ions, by assuming that two surface sites could be occupied by one adsorbate ion. Depending on the chromium concentration and solution pH, Cr(VI) can exist mainly as $Cr_2O_7^{2-}$, $HCrO_4^-$, $CrO_4^{2-}$ and $H_2CrO_4$ according to Eq. (3) (Cotton and Wilkinson, 1972). Thus Eq. (2) would be expected to be applicable for the adsorption of $Cr_2O_7^{2-}$ and $CrO_4^{2-}$ ions only. But the present experimental results do not support this assumption. In case of the test solution ($pH = 1.54$), with $K_2Cr_2O_7$ concentrations below 152 mg/L, $HCrO_4^-$ ions predominantly exist in the solution over $Cr_2O_7^{2-}$ ions (Cimino et al., 2000; Ramsey and McGreery, 1999). In addition, the ionic size of $HCrO_4^-$ is smaller than that of $Cr_2O_7^{2-}$ (Brito et al., 1997). At the lower concentration of $K_2Cr_2O_7$, thus, these mono-valent $HCrO_4^-$ ions should be more easily transferred and adsorbed onto the surface of the UBTLs, compared to $Cr_2O_7^{2-}$ ions. These values of pseudo-second order rate constant, which we obtained, decrease with an increase in initial concentration of $K_2Cr_2O_7$ (i.e., decreasing of $HCrO_4^-$ ions) up to 151.0 mg/L, and also support the predominant adsorption of $HCrO_4^-$ ions over that of $Cr_2O_7^{2-}$ at low concentration (<151 mg/L). Despite this fact, our experimental results show that the adsorption dynamics follows Eq. (2), better than that of pseudo-first order kinetics. On the other hand, Davis and Leckie (1980) also found that each divalent ion ($CrO_4^{2-}$) covers 3 to 4 hydroxyl (protonated) surface sites ($C_xOH$) in the adsorption process. Similarly, our experimental results and the electro-affinity of the surface functional-group concept, according to which surface-attached groups are weaker than equivalent groups in solution, suggest that one $HCrO_4^-$ ion is adsorbed by two surface functional groups.



(3)

Furthermore, at high concentration of $K_2Cr_2O_7$, the predominant species $Cr_2O_7^{2-}$ ions might produce Cr(III) and $HCrO_4^-$ ions according to Eq.(4), which suggests the reduction of Cr(VI) at high concentration (Cimino et al., 2000).

$$3C_xOH + Cr_2O_7^{2-} + 4H^+ \rightleftharpoons 3C_xOH + HCrO_4^- + Cr^{3+} + 3H_2O \quad (4)$$

The equilibrium amounts adsorbed for different initial concentrations of Cr(VI) were also calculated from $t/q_t$ *vs.* $t$ plot and compared with experimental ones as shown in Table 2. Figure 3 shows the fitness of the Langmuir Eq.(5) for equilibrium data calculated from kinetic Eq. (2).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

where $C_e$ is the equilibrium concentration of Cr(VI). Langmuir monolayer amount adsorbed is represented by $q_m$ and $b$ is the Langmuir constant. The Langmuir parameters for experimental values are lower than those

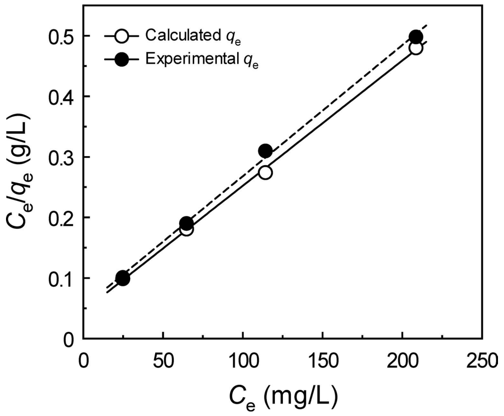


*Figure 3.* Modeling of Langmuir isotherm using experimental ($C_e$ and $q_e$) and calculated ($q_e$ from pseudo-second order rate equation) equilibrium parameters ($pH = 1.54$ and $T = 25°C$).

*Table 3.* Langmuir parameters for the adsorption of Cr(VI) on UBTLs (pH = 1.54 and $T$ = 25°C).

| Data | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ (−) |
|---|---|---|---|
| Experimental | 455 | 0.0425 | 0.996 |
| Calculated from pseudo -second order rate equation | 476 | 0.0463 | 0.999 |

*Table 4.* Effect of pH on the pseudo-second order rate parameters ($C_o$≅100 mg/L, $W_s$ = 0.1 g/L and $T$ = 25°C).

| pH (−) | $q_e$ expt. (mg/g) | $q_e$ cal. (mg/g) | $k \times 10^3$ (g/(mg · d)) | $R^2$ (−) |
|---|---|---|---|---|
| 1.00 | 364 | 400 | 2.40 | 0.998 |
| 1.30 | 317 | 333 | 6.00 | 0.995 |
| 1.54 | 340 | 357 | 3.73 | 0.997 |
| 2.00 | 302 | 323 | 3.20 | 0.997 |

for calculated values at higher equilibrium concentration of Cr(VI) as shown Table 3. This might be due to the reduction effects on the equilibrium condition at high concentration. The lower value of experimental Langmuir parameters might also be due to the existing species of Cr(VI) in high concentration as described previously. However, the monolayer adsorption capacity of UBTLs for Cr(VI) is comparatively higher than that of activated carbon (241–459 mg/g; Martiner et al., 1995).

### *Effect of Solution pH*

The effect of the initial solution pH on the sorption was studied in the range of 1.00 to 2.00 with 100 mg/L of Cr(VI) and 0.1 g/L of UBTLs at 25°C. Figure 4 shows that at the initial pH = 2.00, the sorption occurs purely by an adsorption mechanism and at the initial pH = 1.54, the reduction plays an increased role in the sorption process. As the initial pH decreases from 1.54, the amount of Cr(VI) reduced increases and also the reduction starts earlier as the initial pH decreases. At the different initial pH values, the pure adsorption of Cr(VI) on UBTLs was found to follow Eq. (2) and the maximum amount adsorbed was observed at initial pH 1.54. The pseudo-second order rate constant strongly depends on the initial solution pH and increases rapidly with increasing solution pH in the pH range of 1.00 to 1.30, and then decreases as shown in Table 4. This behavior can be interpreted as follows: the pH dependence of metal adsorption can largely be related to the type and the ionic state of surface functional-groups and also on the metal chemistry in the solution. According to a previous article, the zero point charge pH ($pH_{zpc}$) of UBTLs is 3.6, indicating that the surface of UBTLs is positive at solution pH less than this $pH_{zpc}$ value (Hossain and Tajmeri, 1998). On the other hand, the distribution of the Cr(VI) species in aqueous solution depends on pH and Cr(VI) concentration according to equilibrium equation, Eq. (3) (Cimino et al., 2000). Therefore, the neutral species $H_2CrO_4$, formed predominantly at pH $\leq$ 1.00 is not rapidly adsorbed on the positively charged UBTLs surface. It was also observed experimentally that at pH $<$ 1.30, the reduction of Cr(VI) to Cr(III) becomes predominant accompanying the decomposition of UBTLs, after the maximum amount of Cr(VI) adsorbed. That is, the maximum protonation of UBTLs surface occurs at pH = 1.30. Thus, the adsorption rate constant is high at this pH, and decreases with increasing pH due to the decrease of protonation of UBTLs. Furthermore, in the higher pH region, larger $Cr_2O_7^{2-}$ ions become predominant over $HCrO_4^-$, and this fact further supports the observed decrease of the rate constant. Therefore, from the viewpoint of the start of reduction of Cr(VI) and the decomposition (pH $<$ 1.30) of Cr(VI) adsorbed UBTLs, an initial pH range of 1.54–2.00 might be considered suitable in order to achieve the maximum adsorption with minimum reduction. The previous study (Hossain, 2003) showed that the reduction does occur and gradually increases, and the adsorption rapidly decreases, with increasing the initial solution pH beyond a value

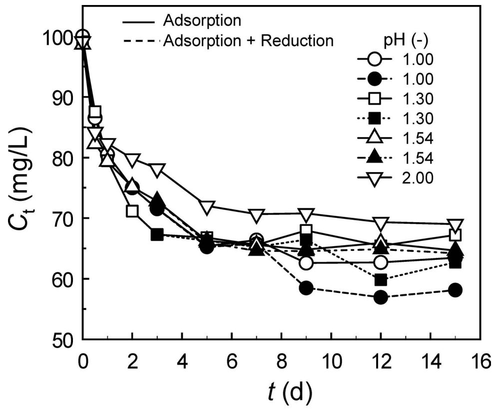


*Figure 4.* Change of the concentration of Cr(VI) with time for different initial pH values of solutions ($C_o$ ≅ 100 mg/L, $W_s$ = 0.1 g/L and $T$ = 25°C).

of 2.00. In the range of initial pH of 1.54 to 2.00, the concentration of $H^+$ ion (0.03 to 0.01 M) has no influence to reduce Cr(VI) to Cr(III) in the presence of UBTLs. But in presence of activated carbon, reduction increases with decreasing initial pH in the range below a value of 4 ($1 \times 10^{-4}$ M of $H^+$), and the amount of Cr(VI) adsorbed showed a maximum at the initial pH = 2.5, with the production of a large amount of Cr(III) (Bowers and Huang, 1980). Thus, the UBTLs seems superior over activated carbon (Bowers and Huang, 1980). The amount adsorbed calculated from experimental data and that from kinetic Eqs. (2) are compared in Table 4. Experimental values are slightly smaller than the calculated values which might be due to the effect of pH on the existence of Cr(VI) species in solution.

### *Effect of Temperature*

The effect of temperature on the sorption of Cr(VI) on UBTLs was also investigated in the range of 10 to 65°C at pH = 2.00. The influence of temperature on the sorption kinetics is presented in Fig. 5. The reduction was observed in this sorption process when the processing temperature is 50°C or above. This observation might be due to the enhancement of the reaction given in Eq. (4) at high temperature. Pure adsorption kinetics in the range of 10 to 65°C also follows the pseudo-second order rate equation as shown in Fig. 6 and Table 5. The obtained rate constant increases linearly with an increase in temperature (Table 5). The equilibrium amount absorbed also increases with an increase in processing temperature (Table 5), indicating that this adsorption system might be controlled by chemisorption. The activation energy of adsorption was calculated from the Arrhenius plot, shown in Fig. 7, and found to be 16.3 kJ/mol. This low value indicates

*Table 5.* Effect of concentration of Cr(VI) on the pseudo-second order rate parameters ($C_o \cong 100$ mg/L, $W_s = 0.1$ g/L and pH = 2.00).

| $T$ (°C) | $q_e$ expt. (mg/g) | $q_e$ cal. (mg/g) | $k \times 10^3$ (g/(mg · d) | $R^2$ (–) |
|---|---|---|---|---|
| 10 | 284 | 313 | 2.05 | 0.995 |
| 25 | 302 | 323 | 3.20 | 0.997 |
| 35 | 355 | 357 | 3.73 | 0.995 |
| 50 | 391 | 400 | 5.21 | 0.999 |
| 65 | 480 | 476 | 6.30 | 0.999 |

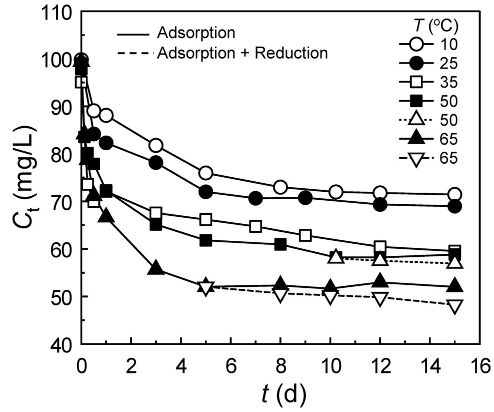


*Figure 5.* Change of the concentration of Cr(VI) with time for different temperatures ($C_o \cong 100$ mg/L, $W_s = 0.1$ g/L and pH = 2.00).

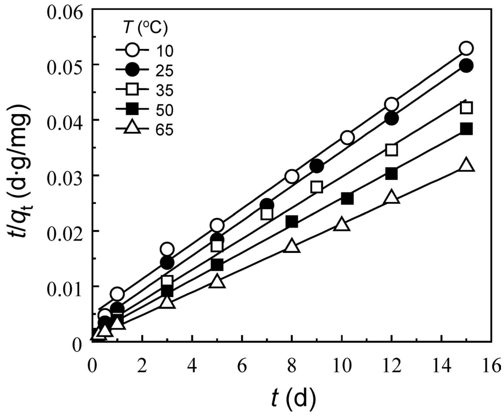


*Figure 6.* Plot of the pseudo-second order kinetics for the adsorption of Cr(VI) on UBTLs at different temperatures ($C_o \cong 100$ mg/L, $W_s = 0.1$ g/L and pH = 2.00).

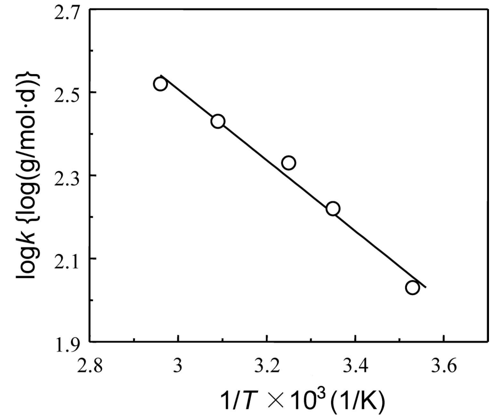


*Figure 7.* The Arrhenius plot of log$k$ against $1/T$ for the adsorption of Cr(VI) on UBTLs (pH = 2.00, $C_o \cong 100$ mg/L and $W_s = 0.1$ g/L).

that the adsorption occurs rapidly. The close agreement between calculated and experimental values of equilibrium amounts adsorbed for different temperatures indicates that there is no effect of different Cr(VI) species of varying temperature on equilibrium amount adsorbed due to the existence of same species of Cr(VI) at different temperature at equal concentration. In case of different concentrations and pH, existence of different species of Cr(VI) ($HCrO_4^-$ and $Cr_2O_7^{2-}$) might be the cause of deviation of calculated Langmuir parameters values from experimental one as described in the previous two sections.

## Conclusion

Both the adsorption and reduction involved in the sorption of Cr(VI) on used black tea leaves, are affected by the initial concentration of Cr(VI), the initial solution pH, and the processing temperature. The pure adsorption kinetics is well expressed by the pseudo-second order rate equation and the rate constant decreases with increasing initial concentration of Cr(VI) up to 150 mg/L. Beyond this concentration, reduction starts, and at higher concentrations adsorption rate becomes very low. The equilibrium amount adsorbed calculated from the kinetic study is well expressed by the Langmuir equation. The solution pH has a profound effect on the adsorption rate. The low value of the activation energy indicates that Cr(VI) is easily adsorbed on UBTLs. The UBTLs is superior to activated carbon for the removal of Cr(VI) from aqueous solution. The suitable operational conditions for maximum adsorption with minimum reduction are: initial Cr(VI) concentration $<150$ mg/L (for 0.1 g/L UBTLs); the initial solution pH $= 1.54$–$2.00$ and the processing temperature $<50°$C.

## Nomenclature

| | |
|---|---|
| $b$ | Langmuir constant (L/mg) |
| $C_e$ | equilibrium concentration of Cr(VI) (mg/L) |
| $C_o$ | initial concentration of Cr(VI) (mg/L) |
| $C_t$ | concentration of Cr(VI) at time $t$ (mg/L) |
| $k$ | pseudo second-order rate constant (g/mg·d) |
| $k_{ad}$ | pseudo first-order rate constant (1/d) |
| $K$ | equilibrium constant (−) |
| $pH_{ZPC}$ | pH of zero point charge (−) |
| $q_e$ | equilibrium amount adsorbed (mg/g) |
| $q_t$ | amount adsorbed at time $t$ (mg/g) |
| $q_m$ | monolayer amount adsorbed (mg/g) |
| $R^2$ | regression coefficient (−) |
| $t$ | contact time (d) |
| $T$ | experimental temperature (°C) |
| $W_s$ | amount of UBTLs (g/L) |
| UBTLs | used black tea leaves |
| CTC | cut, tear and curl |

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