Study on process development for removal of Cr(6) from wastewater by sorption on used black tea leaves

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	（使用済み紅茶葉への収着を応用した排水からのCr(VI)除去プロセスの開発に関する研究）
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ABSTRACT

This study provides a new cost-effective recovery process for the removal of carcinogenic Cr(VI) from aqueous system by sorption on used black tea leaves (UBTLs). Although both adsorption and reduction are involved in this removal process, operational conditions have been optimized to precede the removal by adsorption. Equilibrium adsorption, adsorption kinetics and mechanism, desorption, etc. were studied in detail to evaluate the feasibility of the process. Equilibrium studies show that the UBTLs have extremely high adsorption capacity (455 mg g^{-1} at 25^0C) to Cr(VI) at low solution pH. Kinetically, the adsorption followed two steps mechanism: very rapid initial adsorption for few hours to one day, followed by a long period of much slower uptake to approach the equilibrium for 10–15 days. The initial rapid step is reaction-controlled and the slow step intraparticle-diffusion-controlled. A model mechanism of this adsorption is established from the elucidation of transport phenomena, orientation and speciation of adsorbed species and the electrochemical approach at interface; where the UBTLs become protonated in acidic media as a very fast process followed by adsorption of HCrO$_4^-$ ions on protonated positive surface due to an electrostatic force of attraction. The adsorbed HCrO$_4^-$ ions gradually migrated to the cavities on the UBTLs surface as active sites accompany with the transformation of Cr(VI) to Cr(III) by the acceptance of electrons from the surface functional groups and form surface complex. The surface complex of Cr(III) becomes protonated, adsorbs HCrO$_4^-$ ions, again transforms them to Cr(III) and in such way forms a multimolecular arrangement at the surface cavities. At the final stage all chromium existed on the adsorbed UBTLs are Cr(OH)$_3$ or Cr$_2$O$_3$. Desorption study shows that all chromium can be recollected from adsorbed UBTLs by addition of alkali. A comparative study shows that the removal efficiency of UBTLs is better than that of commercial activated carbon.

INTRODUCTION

Chromium is a unique element, functioning as both an essential micronutrient and a carcinogenic substance depending on the valence state. Hexavalent one, Cr(VI), is carcinogenic and mutagenic, and readily soluble in water, allowing it to move easily in aquatic environments. Many industrial processes such as iron and steel manufacturing, chromium plating, chrome tanning, refractory, chemical industries, etc. are known to generate large amount of Cr(VI)-laden wastewater which must be treated before release.

A number of techniques have been developed for the removal of Cr(VI) from water and wastewaters. Currently, existing treatment methods 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). For low concentration, adsorption is one of the most important process, and activated carbon is the standard adsorbent for wastewater treatment processes, but also expensive. Several studies have been reported about the removal of Cr(VI) by low-cost sorbents but their sorption capacities are not sufficient to practical uses.

My recent study showed that used black tea leaves (UBTLs) as a low cost waste material having high adsorption capacity to remove Cr(VI) from aqueous solution (Hossain, 2003). Therefore, UBTLs becomes an attractive biosorbent for developing a new recovery process for removal of Cr(VI) as the alternative of activated carbon. The basic objective of the present study is to evaluate the feasibility of UBTLs for its practical application and develop a recovery system, in laboratory scale, for the removal of Cr(VI) from aqueous solution by adsorption on UBTLs. Various investigations such as adsorption kinetics, optimization of operational parameters, equilibrium adsorption capacity, desorption, etc., were performed to estimate the efficiency of the process. Removal mechanism was studied based on (i) kinetic evaluation of transport process, (ii) analysis of adsorbed surface and (iii) electrochemical approach to adsorption process. A comparative study with activated carbon was also performed and finally proposed a possible flow chart for the recovery process.

EXPERIMENTAL

Fresh black tea leaves were collected from Bangladesh Tea Research Institute, BTRI, where CTC (cut, tear and curl) is the main manufacturing process. Used black tea leaves were obtained after extracting tea liquor from the fresh ones by boiling with distilled water for 8 hours. The remained tealeaves were dried at 105°C and then were grinded and sieved to give different sizes of UBTLs. The prepared UBTLs were characterized by determining particle size distribution from the SEM images, specific surface area by using N_2/BET and Methylene blue adsorption methods, pore volume and pore size distribution, chemical composition, etc.

All reagents used were of AR grade chemicals. Potassium dichromate ($K_2Cr_2O_7$) solution was used as a source of Cr(VI). Batch kinetic experiments were carried out with different concentrations of Cr(VI), solution pHs, doses and particle sizes of the UBTLs, processing temperature, etc. Equilibrium sorption studies were carried out with different

pH and processing temperatures in batch process. Concentrations of Cr(VI) and Cr(III) were simultaneously determined using a reversed-phase HPLC-UV system (Hossain *et al*, 2005). Chromium(VI) adsorbed UBTLs were analyzed using different spectroscopic methods such as EDX, FTIR, Raman scattering, and XPS. Acid-base titration method was used to determine the surface charge parameters of UBTLs before and after sorption. Desorption study was carried out with different solvents and desorption kinetics one was performed with sodium hydroxide solution.

RESULTS AND DISCUSSION

Characteristics of UBTLs

Used black tea leaves (UBTLs) are low cost bio-mass materials. Prepared UBTLs were characterized by determining particle size distribution with a SEM, specific surface area (N_2/BET and Methylene blue adsorption methods), pore size and volume distribution, chemical composition, etc. The particle shapes of UBTLs were not perfectly spheric, but ellipsoidal. The specific surface area of UBTLs is very small and the values for different particle sizes increase with increasing the size diameter. SEM micrograms of different sizes of UBTLs showed that the surface is not homogeneous; there are some cavities on the surface of which size increases with increasing the particle size. Chemical analysis showed that cellulose and lignin are the main components of the UBTLs.

Optimization of Remediation Phenomena

Preliminary study (Hossain, 2003) showed that both sorption and reduction are involved in the removal of Cr(VI) by UBTLs. Since the reduction is not suitable for removal process because further treatment is required for Cr(III), an optimum condition is needed for this removal process where reduction will be minimum. Generally, oxidation-reduction reaction of chromium mainly depends on the total chromium concentration, solution pH, temperature and the nature of other components present in solution. Therefore, the effects of concentration, pH and temperature on adsorption as well as reduction with time were investigated for a specified amount of UBTLs and the optimum conditions were reached at concentration of Cr(VI) $\geq$ 150 mg L^{-1}, pH > 1.54 and the temperature $\geq$ 50 $^\circ$C, where reduction is negligible. At these conditions, species of Cr(VI) existing in solution was calculated using procedure given by Ramsey (2001) and $HCrO_4^-$ is shown to be the main species in solution with trace amount of $Cr_2O_7^{2-}$, which is also supported by Ramsey's Raman spectroscopic data.

Equilibrium Studies

Using the optimized conditions and predetermined equilibrium time, equilibrium sorption studies were performed to determine the maximum sorption capacity of UBTLs. Figure 1 shows the sorption isotherms as a relation of amount sorbed and equilibrium concentration in solutions, at three different temperatures. The three equilibrium curves are well represented by Langmuir isotherm, compared with Freundlich one, which indicates a monolayer adsorption on the UBTLs surface. The Langmuir constants obtained for different temperatures are given in Table 1. The maximum adsorption capacity, q_m, at
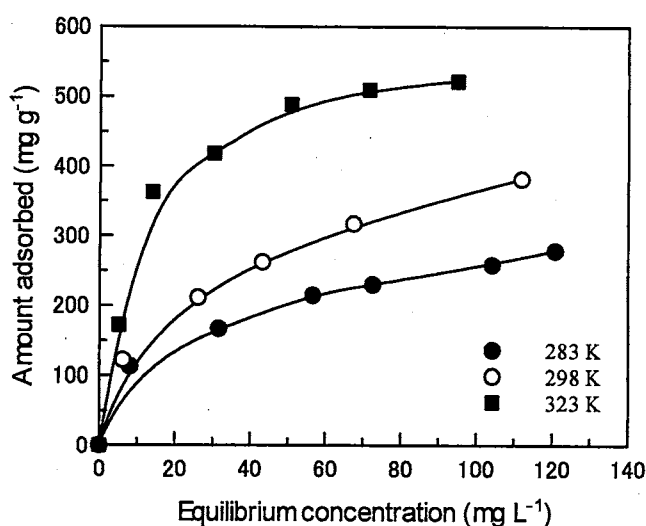
Fig. 1 Adsorption isotherms for Cr(VI) on UBTLs at different temperatures ($W_s = 0.1g\ L^{-1}$, $t = 15$ days and pH = 2.00).

Table 1. Langmuir parameters for sorption of Cr(VI) on UBTLs at different temperatures

Temperature (K)	q_m (mg g^{-1})	b (L mg^{-1})	R^2 (-)
283	345	0.034	0.994
298	455	0.041	0.995
323	588	0.084	0.999

298 K and pH = 2.00 is 455 mg g^{-1}, comparable to that of activated carbon (241-459 mg g^{-1}) (Martiner *et al.*, 1995). The equilibrium amount adsorbed is found to increase with an increase in temperature, indicating the endothermic nature of the process. The values of separation factor, R_L (<0.9) also indicate the favorable adsorption at low pH and at high temperature.

Kinetics of Adsorption

The adsorption kinetics of Cr(VI) on UBTLs follows two steps mechanism; very rapid initial sorption for a few hours to one day, followed by a long period of much slower uptake to approach the equilibrium for 10–15 days. It was found that the initial rate of adsorption increases with an increase in initial concentration of Cr(VI) but does not follow simple first or second order kinetics. The Lagergren's pseudo-first order rate equation is applicable for the initial rapid step but the overall adsorption kinetics follows Ritchie's pseudo-second order rate equation (1) (Ho and McKay, 2000) better than the Lagergren's pseudo-first order rate equation:

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

where, q_t = the amount adsorbed at time t and q_e = the equilibrium amount adsorbed. Ho's

pseudo-second order rate equation was derived by assuming that two surface sites could be occupied by one divalent adsorbate ion whereas in my experimental conditions adsorbate species is mainly monovalent ion ($HCrO_4^-$) with less amount (<2%) of divalent ion ($Cr_2O_7^{2-}$). Such kinetic behavior suggests that the $HCrO_4^-$ ion is initially adsorbed on one surface site but interacts with more surface sites at longer times. The pseudo-second order rate constant and equilibrium amount adsorbed were determined for different concentrations of Cr(VI), pHs, doses and particle sizes of UBTLs, temperatures and presence of foreign ions; cation and anion.

Adsorption Mechanism

Transport mechanism: Kinetically, initial rapid step and second slow step were analyzed using different model equations. Generally adsorption of a solute from solution is to be 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 *et al.*, 2002). Verification of different transport models suggested that the initial rapid step is reaction-controlled and slow step is intraparticle-diffusion-controlled.

Analysis of Adsorbed UBTLs

SEM and EDX Studies on Adsorbed Surface: Scanning electron microscopic observation and EDX (energy dispersive X-ray) point analysis of the equilibrium-adsorbed UBTLs surface showed that the adsorbed chromium is not-homogeneously distributed on the UBTLs surface; a large amount of chromium is located in the cavities on the surface, compared with top places; which was confirmed by EDX elemental analysis. Such distribution might be due to the heterogenic nature of UBTLs surface. Again, the SEM & EDX observations of the UBTLs surface for different adsorption times showed that the chromium species initially adsorbed at the top places on the surface gradually migrate to the surface cavities with increasing contact time and forms the granular arrangement at the cavities. Figure 2 shows the SEM micrograms of half day-and 15 days-adsorbed UBTLs surface at top (T) and cavity (C) places. There is some chromium (EDX analysis) at the top places of half day-adsorbed UBTLs which almost disappears for 15 days-adsorbed UBTLs. Again, the granular arrangements of chromium are located in the cavity of 15 days adsorbed UBTLs which is empty for half day-adsorbed UBTLs. This observation is the direct evidence for the validity of intraparticle diffusion model for the slow step of adsorption process.

FTIR: Fourier transform infrared spectroscopic studies on UBTLs unadsorbed and adsorbed with different times show that the stretching vibration of O-H group in UBTLs shifts the position to the higher frequency (from 3330 to 3340 cm^{-1}) with increasing adsorption time. The shifting of stretching vibrational frequency of O-H group to the higher frequency with increasing amount adsorbed indicates that the chromium interacted with -OH groups results in the decreasing intra-or inter-molecular hydrogen bonding capacity in cellulose units. Moreover, a new peak appeared at 510 cm^{-1} for one day-adsorbed UBTLs corresponds to the stretching vibration of Cr-O which shifted to 498 cm^{-1} for 15 days-adsorbed UBTLs.
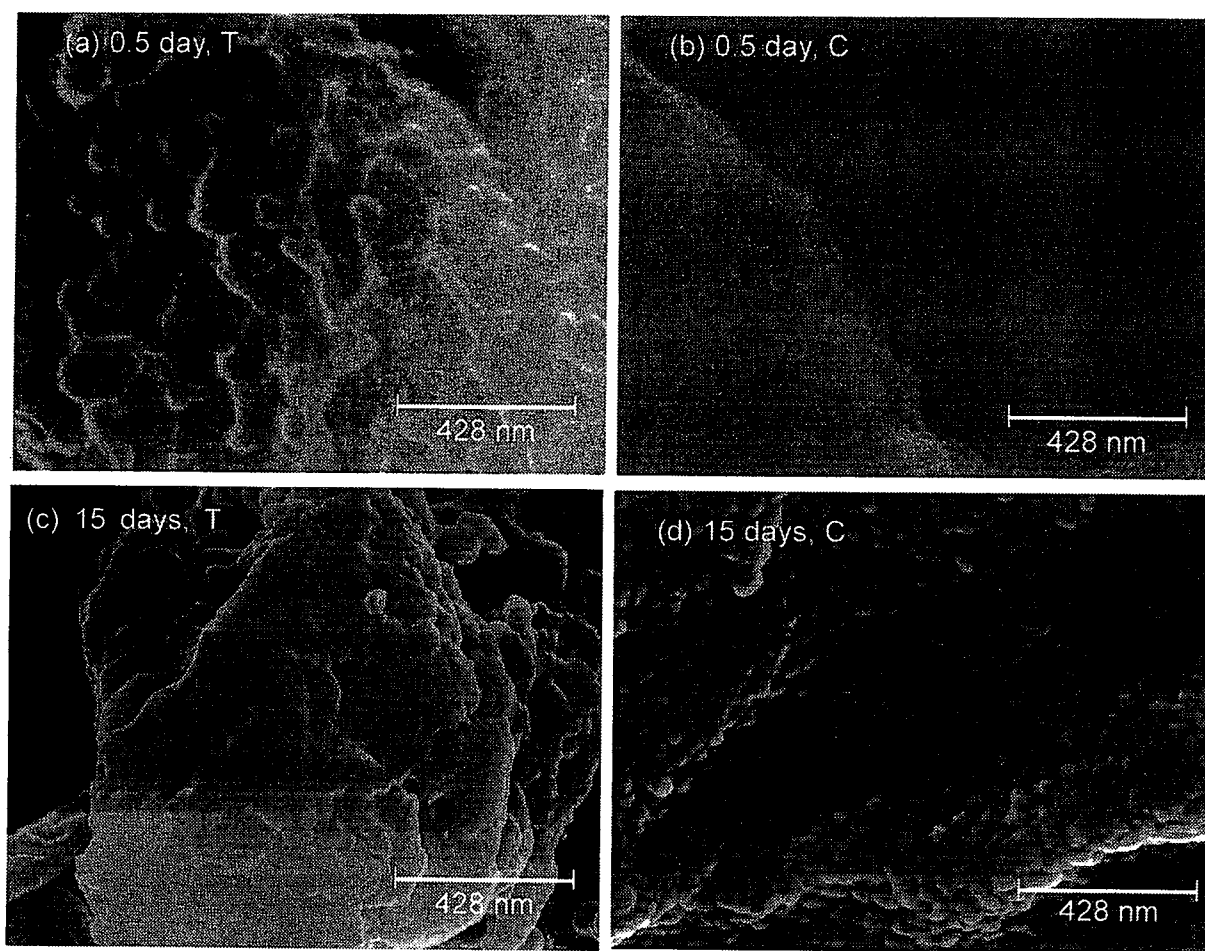
Fig. 2 SEM micrograms of halfday-and 15 days-adsorbed UBTLs (×70,000).

Raman scattering: Raman spectroscopic studies were carried out on three different samples of 0.5, 7 and 15 days-Cr(VI)-adsorbed UBTLs to identify adsorbed species of chromium and their changes with time. Significant Raman bands are observed at 894.5 cm^{-1} for half day-adsorbed UBTLs, 894.5 and 866 cm^{-1} for 7 days-adsorbed UBTLs and 861 cm^{-1} for 15 days-adsorbed UBTLs. Comparing these bands with the standard samples' bands cited in literatures (Ramsey *et al*, 2001) showed that 894.5 cm^{-1} band is for symmetric stretching vibration of Cr=O in $HCrO_4^-$, and the band at 866 and 861 cm^{-1} are probably for the symmetric stretching of $Cr^{III}-O-Cr^{VI}$ (858 cm^{-1}) but neither symmetric stretching of Cr=O of $Cr_2O_7^{2-}$ (904 cm^{-1}) nor of CrO_4^{2-} (847 cm^{-1}). The above observations suggest that the $HCrO_4^-$ ions are first adsorbed on the UBTLs surface under the experimental condition, which are partly changed to Cr(III) compounds with increasing contact time.

XPS: To make clearer identification of chromium compounds as well as the oxidation state of chromium on the adsorbed UBTLs, X-ray Photoelectron Spectroscopic studies were performed after 6 months of adsorption. The XPS spectra show two peaks at binding energy of 577.2 eV ($Cr2p^{3/2}$) and 587 eV ($Cr2p^{1/2}$) for every one of 0.5, 7 and 15 days Cr(VI) adsorbed UBTLs. The absence of any peak near 579 eV indicated that all

UBTLs samples contain trivalent chromium. These results mean that all the adsorbed hexavalent chromium are gradually reduced to Cr(III) on the UBTLs surface with the keeping time.

Again, the XPS study shows that four types of carbons (C-C, C-O, C-2O and C-3O) exist in the adsorbed UBTLs, which suggests that the adsorbed Cr did not make any direct bond with carbon. The variation of carbon composition with adsorption time also shows that the percentage of C-2O increases with increasing adsorption time, indicating the interaction of Cr with C-2O: i.e., the formation of new Cr-O-C structure.

Electrochemical approach to mechanism

According to the electrochemical approach, solid surface becomes charged when dispersed in aqueous solutions. Adsorption of most ions is dependent on surface charge. Since the adsorbate Cr(VI) is a ionic species, the surface charges of UBTLs before and after adsorption were measured to investigate the variation of surface charge with adsorption. The point of zero charge (PZC) and point of zero net proton charge (PZNPC) of unadsorbed UBTLs were determined by acid-base titration method. The experimental value the PZC is 4.15 ($pH_{PZC} = 4.15$) and indicates that at pH = 4.15, the positive and negative charges on the UBTLs surface are zero ($\sigma_0 = 0$), and when the pH value lower or upper than 4.15, the UBTLs surface becomes negative or positive, respectively. The determined value of PZNPC, 4.35, indicates that at pH = 4.35, surface proton charge of the UBTLs is zero ($\sigma_H = 0$), and when the pH value upper or lower than 4.35, the UBTLs surface becomes negative or positive, respectively, by deprotonation/protonation.

Protonation capacity and site density of unadsorbed UBTLs were also determined by acid-base titration method and Freundlich isotherm equation, and the values were compared with the adsorption capacity of UBTLs to Cr(VI). The numerical value of Freundlich constant (k_F) has a good correlation with the adsorption capacity of UBTLs to Cr(VI). From the comparison it would be possible to say that the protonated surface hydroxyl groups of UBTLs control the adsorption of Cr(VI) at the initial stage which follow the total site density on the equilibrium stage. Again, the ratio of protonation capacity to site density with adsorption capacity indicates that during first one day one Cr ion attaches with 1.41 protonated sites whereas for 15 days of adsorption one Cr ion attaches with 1.44 total surface sites on UBTLs. It would be possible because the electrode potential of chromium is higher than hydrogen, again the reduction potential of Cr(VI) to Cr(III) is 1.35 eV. Thus the adsorption of Cr(VI) on UBTLs is initially controlled by protonation process and on the equilibrium stage is controlled by the total surface charge. From the above investigations, the mechanism for the adsorption of Cr(VI) on UBTLs can be described in Fig. 3.

Desorption and Recollection of Chromium

Desorption studies with different concentrations of NaOH show that 2M NaOH solution is suitable for desorption of almost all chromium within 24 hours with decomposition of UBTLs. Since the UBTLs is very cheap,there is no need for further use. The desorbed solution contains high concentration chromium which can be easily collected by reduction and precipitation process.
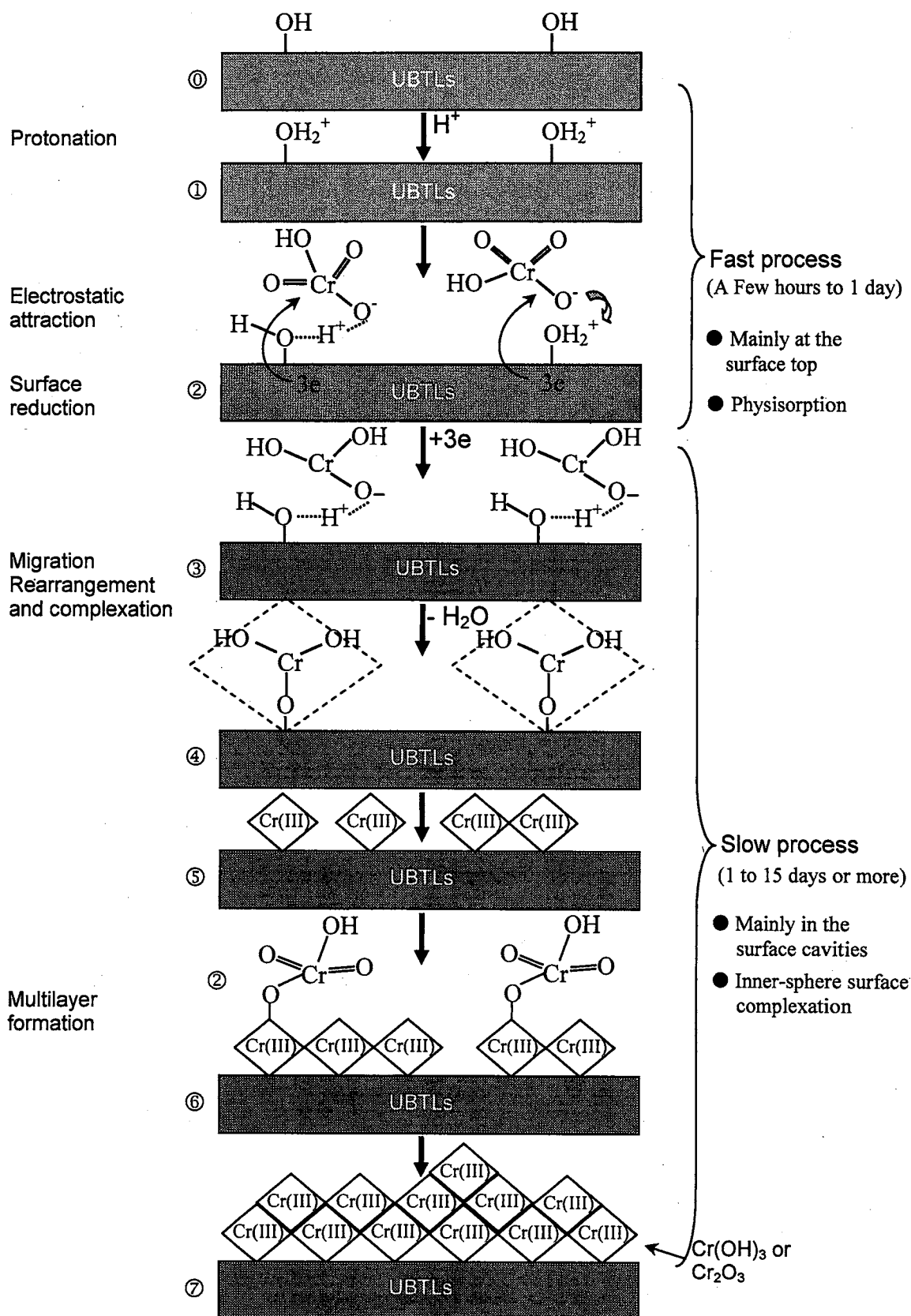
Fig. 3 Mechanism of Cr(VI) adsorption on used black tea leaves at pH = 2.00

Comparison of Adsorption Capacity and Economics

To compare the adsorption capacity of UBTLs with that of activated carbon, some removal experiments were performed with commercial activated carbon (AC) under the same operational conditions as applied for UBTLs. Experimental data show that the maximum adsorption capacity, calculated from Langmuir equation, of AC is (q_m = 417 mg g^{-1}) smaller than that of UBTLs (q_m = 455 mg g^{-1}) at pH = 2.00 and T = 25 °C. Moreover, in case of AC, both of adsorption and reduction increase with decreasing the solution pH whereas adsorption increases and reduction decreases with decreasing of solution pH for UBTLs case, which is another superiority of UBTLs. Thus the UBTLs is better than commercial activated carbon for the removal of Cr(VI) from aqueous solution.

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学位論文審査結果の要旨

　提出学位論文について各審査委員が個別審査を行うと共に、平成18年2月6日開催の口頭発表を踏まえて、同日開催の論文審査委員会にて検討し、以下の通り判定した。

　本論文は、発展途上国で深刻な問題となっている廃水中の有害重金属Cr(VI)を、食品由来バイオマスである使用済み紅茶葉（UBTL）を収着材料として有効利用し、低コストの分離回収プロセスを開発するための基礎的研究であり、その要点は次の通りである。

　UBTLは比表面積が極めて小さいにも関わらず、特異的高収着能力を有することを見出し、それを利用した実用装置を開発するため、収着の動的挙動に及ぼす操作条件（pH、温度、濃度）の影響を系統的に明らかにし、収着操作の最適条件を探索している。さらに、収着動特性を種々の速度論モデルにより解析すると共に、各種の試料分析を実施し、収着の初期と中期以降とでは収着速度の支配過程が異なること、UBTLに収着されたCrが全て三価で、表面の微細凹みに粒状固相として偏在することを見出している。加えて、液中のCr(VI)が粒状固体を形成するに至る機構を解明、UBTLに収着されたCrをNaOH水溶液により脱離させ、固体のCr(OH)₃として効率的に回収するプロセスを提案している。

　このように、本研究は、発展途上国における重金属による水環境汚染を改善する技術開発に大きく貢献するものであり、本論文は博士（学術）の学位に十分値すると判断される。