



Adsorption of Cr(VI) onto cationic surfactant-modified activated carbon

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ABSTRACT

Highly toxic oxyanions, such as hexavalent chromium (Cr(VI)), have caused adverse effects on human health. This study evaluated the feasibility of using cationic surfactant-modified activated carbon (AC) to remove Cr(VI). To modify activated carbon using a cationic surfactant, AC was mixed with a surfactant solution of 0.5 critical micelle concentration (CMC), at which concentration the surfactant molecules exist as mono-molecules. Adsorption kinetics and an isotherm model were used to study the adsorption characteristics of Cr(VI) onto MAC. The adsorption capacity of MAC for Cr(VI) was enhanced compared to that of AC. MAC modified by hexadecyltrimethylammonium had a higher adsorption capacity for the removal of Cr(VI) than that modified by cetylpyridinium. The modification of AC by a cationic surfactant enhanced both its Cr(VI) adsorption rate and its Cr(VI) adsorption capacity. The breakthrough point of MAC for Cr(VI) was 100 times greater than for the raw AC. As a result, MAC is a promising adsorbent to treat Cr(VI) in an aqueous stream.

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1. Introduction

The presence of heavy metals in a water system is hazardous to the environment and human beings due to their bioaccumulation in the food chain and persistence [1,2]. Therefore, the treatment of heavy metals in water and wastewater has become one of the most important environmental issues. Most heavy metals exist in a cationic form, but Cr(VI) combined with oxygen is anionic in natural aquatic system. Cationic heavy metals have been removed using precipitation, such as forms of $\text{Me}(\text{OH})_2$ by pH adjustment and MeS by sulfide precipitation [3]. However, the technique is not effective for removing Cr(VI).

Various techniques have been applied to remove Cr(VI) from the aqueous phase, including (bio)sorption [4–7], chemical reduction [4], and micellar-enhanced ultrafiltration [8–10]. Among these techniques, sorption has been widely used because it is cost-effective. An adsorbent containing a positive charge on the surface provides an adsorption site for the Cr(VI) because it is an anionic pollutant. Activated carbon, a representative adsorbent, has been widely used to remove diverse pollutants, including organic pollutants, reactive dyes, cationic heavy metals, and anionic metals from the aqueous phase and/or from the vapor phase, because it has huge surface area and various functional groups [11–13].

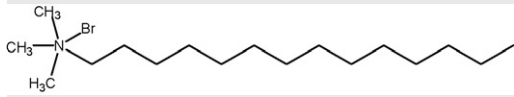
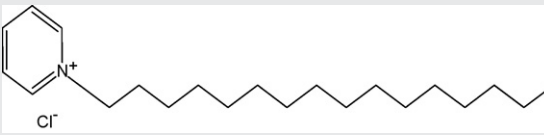
Activated carbon is well known to have a high adsorption capacity for hydrophobic organic pollutants because of its hydrophobic properties. However, the major mechanism for the adsorption of ionic pollutants is electrostatic interaction or ion exchange. Consequently, the surface charge is important for removing ionic pollutants. The surface-modification of activated carbon has been reported to increase the surface charge and enhance its adsorption capacity for ionic pollutants [11–13].

Surfactants are chemicals that have molecules with a hydrophobic tail and a hydrophilic head, and have been applied to modify the surface properties of a solid surface [8–11]. In a cationic surfactant/activated carbon/water system, the surfactant adsorbs onto the surface of the activated carbon due to hydrophobic interaction, then the hydrophilic part of the surfactant tends toward the aqueous phase [11,12]. That means the activated carbon has a net positive charge on the surface. Consequently, the surface of the AC is reshuffled to be cationic. There have been numerous studies on the adsorption of Cr(VI) onto bioadsorbents. However, the major functional groups of biosorbents are the carboxylic and amine groups, which have positive charges, making them suitable for the adsorption of cationic metals [4,5].

This study evaluated the feasibility of using cationic surfactant-modified activated carbon for the removal of Cr(VI) from aqueous streams. The specific purposes of the study were to: (1) confirm the adsorption rate (adsorption kinetic) and capacity (adsorption isotherm) through the adsorption models, and (2) evaluate the feasibility of cationic surfactant-modified activated carbon by column experiments.

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Table 1
Chemical structure of cationic surfactant.

HDTMA (hexadecyltrimethylammonium bromide)	CPC (cetylpyridinium chloride)
	

2. Materials and methods

2.1. Materials

Cr(VI) stock solution was prepared by dissolving Na_2CrO_4 (Sigma, USA) in deionized water. Granular activated carbon made from charcoal, with a size of 8–20 mesh, was purchased from Aldrich (USA). The activated carbon has $844.09 \text{ m}^2/\text{g}$ of surface area and $540.25 \text{ m}^2/\text{g}$ of micropore area. The cationic surfactants used in this study were cetylpyridinium chloride (CPC, Sigma, USA) and hexadecyltrimethylammonium bromide (HDTMA, Sigma, USA). Their chemical structures and properties are summarized in Table 1.

2.2. The AC modification

Ten grams of activated carbon was added to a solution of HDTMA or CPC at a concentration of 0.1677 g/L and 0.1611 g/L , respectively. These concentrations correspond with the 0.5 critical micelle concentration (CMC). Above the CMC, a surfactant forms a micelle that is very stable and remains in the bulk zone. Therefore, 0.5 CMC was selected to maximize the amount of surfactant adsorbed onto the AC. The mixture was agitated for 12 h and then filtered using 5B filter paper (Advantec, Japan). The filtered AC was dried in an oven at 70°C for 5 h. The raw AC and surfactant-modified AC were called AC and MAC, respectively.

2.3. Batch test

Adsorption kinetic tests were carried out by adding 0.5 g of AC or MAC to a 250 ml Erlenmeyer flask containing 50 ml of solution at a concentration of 100 mg/L Cr(VI). Each mixture was agitated at 20°C and 150 rpm for 6 h. After the desired time interval, each mixture was sampled and filtered using 5B filter paper. Adsorption isotherm tests were carried out under exactly the same conditions as the adsorption kinetic tests, except the concentration of the Cr(VI) solution was $10\text{--}200 \text{ mg/L}$. All of the experiments were performed in triplicate.

2.4. Column experiment

Glass columns with a bed volume of 28 cm^3 were filled with AC or MAC. The flow rate was 20 ml/h created by a Masterflex L/S pump (Coleparmer, USA) and the initial concentration of Cr(VI) was 5.0 mg/L . For the column experiment, three times-coated MAC by HDTMA was used. The column experiments were executed at room temperature and the initial pH was 7.0.

2.5. Analysis

The residual concentration of Cr(VI) in the filtrate was measured using a standard method. This method consists of measuring the absorbance using a UV/VIS spectrophotometer (HS 3300, Humas, Korea) with 540 nm of a sample of filtrate to which a small amount of 1,5-diphenylcarbazide (Sigma, USA) has been added [4,5]. To identify the residual concentration after the adsorption of the surfactant onto the AC, the CPC was analyzed using the UV/VIS

spectrophotometer at 258 nm and the HDTMA was estimated by a total-nitrogen analysis using the standard method, with the UV/VIS spectrophotometer at 220 nm . The pH of each solution was measured using a pH/ISE meter (735P, Istek, Korea).

2.6. Models for adsorption kinetics and isotherm

The amount of Cr(VI) adsorbed onto the activated carbon was calculated by the following equation:

$$q_e = \frac{C_0 - C_e}{M} \quad (1)$$

where q_e is the amount of Cr(VI) adsorbed per unit mass of activated carbon (mg/g) at equilibrium, C_0 and C_e are the initial and equilibrium concentrations of Cr(VI), respectively, and M is the mass of the activated carbon (g).

The Cr(VI) adsorption kinetic data were correlated with the adsorption kinetic models:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (\text{pseudo-first order kinetic model}) \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (\text{pseudo-second order kinetic model}) \quad (3)$$

$$q_t = K_p t^{1/2} \quad (\text{intra-particle diffusion model}) \quad (4)$$

where q_e and q_t are the amounts of Cr(VI) adsorbed onto the activated carbon at equilibrium and time t , respectively, and K_1 (h^{-1}), K_2 (h g/mmol), and K_p (mmol h/g) are the adsorption rate constants for each model.

The Cr(VI) adsorption isotherm data were correlated with the theoretical models of Langmuir and

Freundlich:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (\text{Langmuir adsorption model}) \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (\text{Freundlich adsorption model}) \quad (6)$$

where q_{\max} is the solid phase concentration corresponding to the complete monolayer coverage of the adsorption sites, K_L is a constant related to the free energy of adsorption, and the constants K_F and n of the Freundlich model are parameters related to the strength of the adsorptive bond and bond distribution, respectively [1]. The Freundlich model describes the heterogeneous surface energies by multilayer adsorption and the Langmuir model explains the monolayer adsorption on the adsorption site [6].

3. Results and discussion

3.1. Adsorption kinetics of Cr(VI)

HDTMA or CPC was not detected in the aqueous phase after the modification of the AC. This means all the surfactant molecules in the aqueous phase were adsorbed on the AC. Fig. 1(a) and (b) shows the adsorption kinetic of Cr(VI) on the AC and MAC by the HDTMA

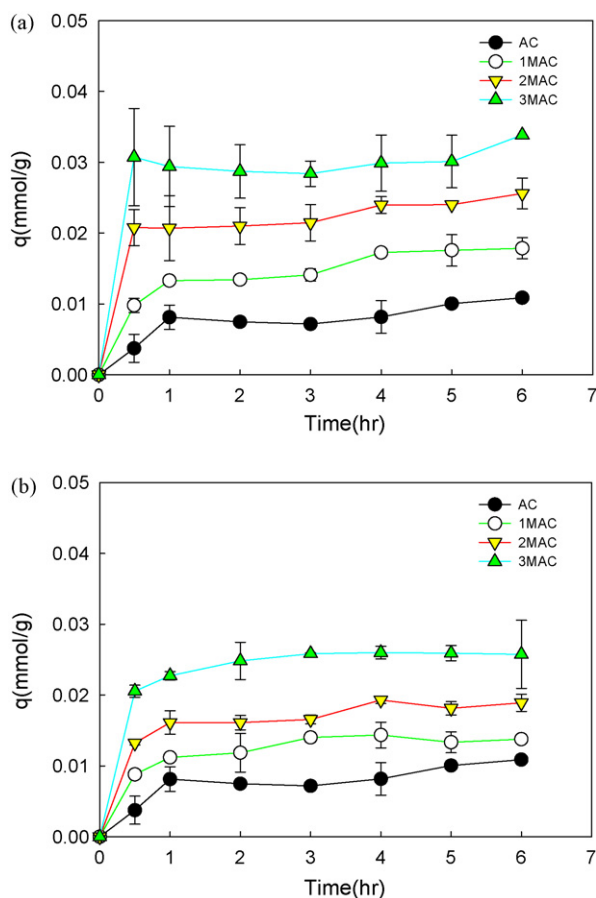


Fig. 1. Adsorption kinetic of Cr(VI) on AC and MAC (a) MAC by HDTMA; (b) MAC by CPC. Initial concentration of Cr(VI): 100 mg/L; activated carbon: 0.5 g; temperature: 20 °C; agitation rate: 150 rpm.

and CPC, respectively. Regardless of the amount of modification and the kind of surfactants, the adsorption of Cr(VI) reached equilibrium within 1 h. As the amount of modification increased, the amount of Cr(VI) adsorbed increased. This result shows that sequential modification enhanced the adsorption of the surfactant onto the AC and that this increase in surfactant adsorption caused an increase in the adsorption of Cr(VI). The Cr(VI) adsorption rate onto MAC-HDTMA increased from 110.44 h g/mmol of AC to 127.63 h g/mmol for 1MAC, 171.16 h g/mmol for 2MAC and 197.89 h g/mmol for 3MAC (Table 2). In the case of the MAC modified by the CPC, the adsorption rate tendency was similar to the MAC-HDTMA. The adsorption rate was enhanced from 110.44 h g/mmol for AC to 347.74 h g/mmol for 1MAC, 257.99 h g/mmol for 2MAC, and 570.65 h g/mmol for 3MAC (Table 2).

Originally, the AC had few positively charged functional groups on the surface, but in the presence of the cationic surfactant,

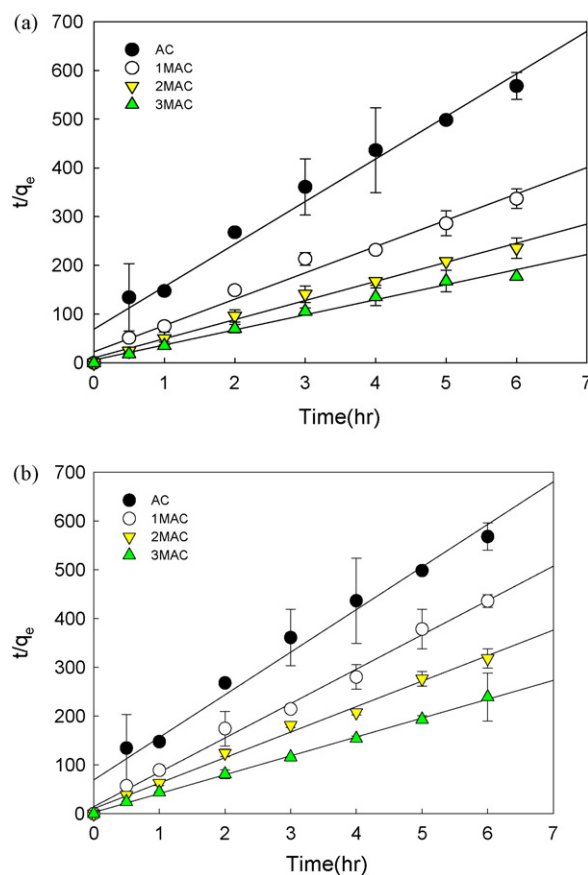


Fig. 2. Pseudo-second order model for adsorption of Cr(VI) on AC and MAC. (a) MAC by HDTMA, (b) MAC by CPC.

the adsorption of CTA⁺ and CP⁺ on the surface of the AC introduced positive adsorption sites there. The adsorption rates of Cr(VI) on MAC-HDTMA or MAC-CPC were faster than with the AC due to the electrostatic interaction between the Cr(VI) and the head group of the positive charge. At equilibrium, the amount of Cr(VI) adsorbed onto the MAC-HDTMA was more than that for the MAC-CPC (Figs. 1 and 2). The adsorption of Cr(VI) onto the MAC depended on the chemical structure of the cationic surfactant because the pyridinium cationic head group in CPC is more bulky than the trimethylammonium cationic head group in HDTMA. The electron-rich pyridinium group might inhibit the access of Cr(VI) to the cationic part in CPC compared to the trimethylammonium group in HDTMA.

The adsorption kinetic followed the pseudo-second order model described in Eq. (3). The kinetic parameters for the adsorption kinetic models are summarized in Table 2. Fig. 2(a) and (b) shows the fitting results of the experimental data to the models. Baral et al. reported that the pseudo-second model was fitted well in

Table 2
Kinetic parameters for the adsorption of Cr(VI) onto modified activated carbon.

Surfactant	Adsorbent	Pseudo-first order		Pseudo-second order		Intra-particle diffusion	
		K_1 (h^{-1})	r^2	K_2 (h g/mmol)	r^2	K_p (mmol h/g)	r^2
HDTMA	AC	0.403	0.56	110.44	0.94	0.0032	0.56
	1MAC	0.470	0.77	127.63	0.97	0.0041	0.85
	2MAC	0.325	0.43	171.16	0.97	0.0127	0.49
	3MAC	0.283	0.21	197.89	0.97	0.0199	0.27
CPC	1MAC	0.529	0.64	347.74	0.98	0.0054	0.66
	2MAC	0.450	0.61	257.99	0.99	0.0081	0.67
	3MAC	0.424	0.61	570.66	0.97	0.0139	0.51

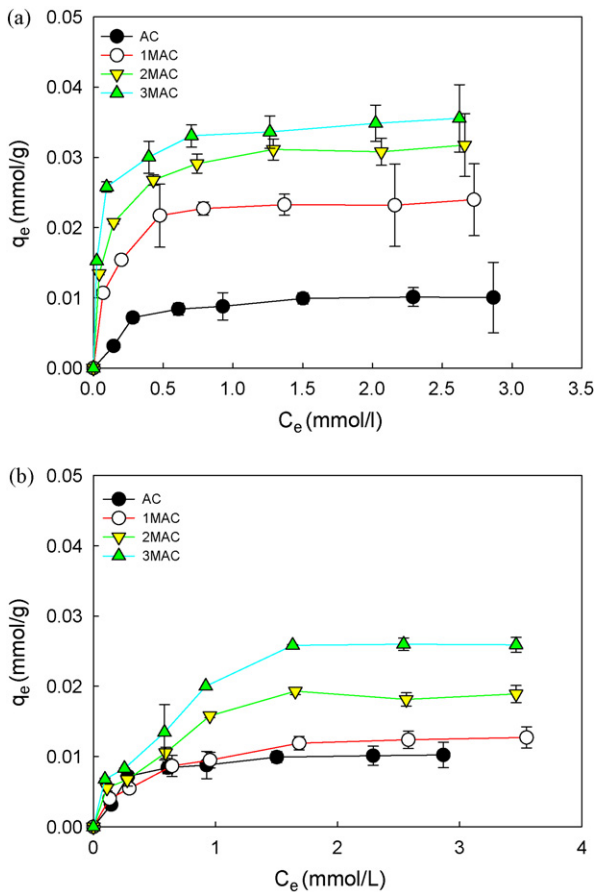


Fig. 3. Adsorption isotherm of Cr(VI) on AC and MAC (a) MAC by HDTMA; (b) MAC by CPC. Concentration range: 10–200 mg/L; MAC: 0.5 g; temperature: 20 °C; agitation rate: 150 rpm.

comparison with other models to explain the property of Cr(VI) adsorption onto calcined bauxite [7]. Choi et al. reported that the pseudo-second order model was suitable to explain the adsorption kinetic of anionic reactive dye (RB5) onto activated carbon in the presence of a cationic surfactant [11].

3.2. Adsorption isotherm of Cr(VI)

The results of the adsorption equilibrium of Cr(VI) on AC and MAC are shown in Fig. 3(a) and (b). The adsorption data was fitted with two adsorption isotherm models: the Langmuir and Freundlich isotherm equations described in Eqs. (5) and (6). The Cr(VI) adsorption characteristics of AC and MAC are better explained by the Langmuir isotherm model than by the Freundlich model. Several research groups have reported that the Langmuir model was more suitable for describing the adsorption isotherm of Cr(VI) onto

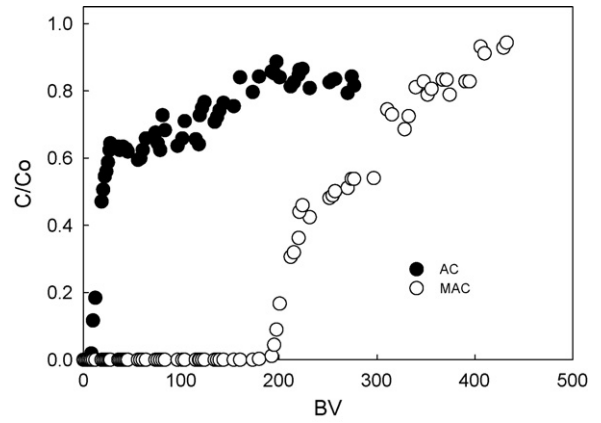


Fig. 4. Breakthrough curve of AC and MAC for Cr(VI). Concentration of Cr(VI): 10 mg/L; temperature: 20 °C; empty bed contact time.

adsorbents [8,9]. Bingol et al. reported that the Cr(VI) adsorption characteristics of cationic surfactant-modified yeast followed the Langmuir model [13]. The Langmuir model is based on monolayer adsorption. The adsorption of Cr(VI) onto MAC is a site-specific reaction because the adsorption mechanism is an electro-static interaction between the negative charge of the Cr(VI) and the positive charge of the MAC or AC.

From the fitting of the experimental data to the Langmuir model, the adsorption capacity of Cr(VI) onto MAC-HDTMA increased from 0.011 mmol/g for AC to 0.025 mmol/g, 0.032 mmol/g, and 0.035 mmol/g for 1MAC, 2MAC, and 3MAC, respectively (Table 3). The adsorption characteristics of Cr(VI) on MAC-CPC were similar to MAC-HDTMA. The adsorption capacity of MAC-CPC was enhanced from 0.011 mmol/g for AC to 0.014 mmol/g, 0.023 mmol/g, and 0.027 mmol/g for 1MAC, 2MAC, and 3MAC, respectively (Table 3). The MAC had more cationic adsorption sites than the original AC, and as the amount of modification increased, the adsorption capacity was enhanced by the electro-interaction between the Cr(VI) and the HDTMA+/CP+ adsorbed onto the AC. The Cr(VI)-HDTMA+ or Cr(VI)-CP+ complexation influenced the increase in adsorption capacity. The modification of the AC by HDTMA enhanced the adsorption capacity for Cr(VI) more than the AC modification by CPC. As described previously, the electron-rich pyridinium group blocked the access of Cr(VI) to the tertiary N in the group.

3.3. Column experiment

Fig. 4 shows the dynamic adsorption of Cr(VI) in columns packed with AC or MAC. In the case of the AC, the breakthrough of the Cr(VI) was nine bed volume (BV), while in the case of MAC it was 200 BV. Also, the surfactant was not observed in the effluent of the column. In batch adsorption experiments, the adsorption capacity of 3MAC was three times greater than AC, while the modification of the AC by HDTMA enhanced its adsorption capacity for Cr(VI) by 22 times

Table 3
Parameters for Langmuir and Freundlich adsorption models of Cr(VI) adsorption on modified activated carbon.

Surfactant	Absorbent	Langmuir isotherm			Freundlich isotherm		
		q_{\max} (mmol/g)	K_L	r^2	K_F (mmol/g)	n	r^2
HDTMA	AC	0.011	4.344	0.95	0.125	3.041	0.75
	1MAC	0.025	10.091	0.98	0.188	4.697	0.86
	2MAC	0.032	14.793	0.97	0.214	4.983	0.92
	3MAC	0.035	30.864	0.98	0.226	6.072	0.89
CPC	1MAC	0.014	2.259	0.99	0.009	3.137	0.97
	2MAC	0.023	1.923	0.97	0.014	2.881	0.93
	3MAC	0.032	1.619	0.97	0.018	2.660	0.94

in the column experiment. This may come from the lower reduction of Cr(VI) onto the surface of AC due to less contact time compared with batch experiment [5].

4. Conclusion

This study investigated the adsorption characteristics of Cr(VI) on modified activated carbon by two cationic surfactants, HDTMA and CPC. Modification enhanced the adsorption rate and adsorption capacity of AC for Cr(VI). As the amount of modification increased, the adsorption capacity increased because the modification introduced more positive groups on the AC. The adsorption capacity of the MAC by a cationic surfactant was 3–5 times higher than that of the AC. Modification of the AC by a cationic surfactant enhanced the adsorption rate. The adsorption kinetic followed a pseudo-second order kinetic model. The Langmuir model was suitable for describing the adsorption characteristics of the Cr(VI) onto MAC because Cr(VI) adsorption is a site-specific reaction.

The adsorption capacity of Cr(VI) for the AC modified by HDTMA with the trimethylammonium group as a cationic head group was greater than that for the AC modified by CPC with the pyridinium group as a cationic head group. In conclusion, it is feasible to use cationic surfactant-modified activated carbon to remove anionic Cr(VI) because there are a greater number of positively charged adsorption sites compared to AC. Moreover, anionic pollutants may be effectively removed because the adsorption rate and maximum adsorbed amount increased.

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References

- [1] L. Khesami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies, *J. Hazard. Mater.* 123 (2005) 223–231.
- [2] C.A. Basar, C. Aydiner, S. Kara, B. Keskinler, Removal of CrO₄ anions from waters using surfactant enhanced hybrid PAC/MF process, *Sep. Purif. Technol.* 48 (2005) 270–280.
- [3] M. Zaw, M.T. Emmett, Arsenic removal from water using advanced oxidation processes, *Toxicol. Lett.* 133 (2002) 113–118.
- [4] D. Park, Y.-S. Yun, J.-H. Jo, J.-M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, *Water Res.* 39 (2005) 533–540.
- [5] D. Park, Y.-S. Yun, D.-S. Lee, S.-R. Lim, J.M. Park, Column study on Cr(VI)-reduction using the brown seaweed *Ecklonia* biomass, *J. Hazard. Mater.* 137 (2006) 1377–1384.
- [6] T. Karthikeyan, S. Rajgopal, M. Lima Rose, Chromium(VI) adsorption from aqueous solution by Hevea Brasilensis sawdust activated carbon, *J. Hazard. Mater.* 124 (2005) 192–199.
- [7] S.S. Baral, S.N. Das, P. Rath, G.R. Chaudhury, Chromium(VI) removal by calcined bauxite, *Biochem. Eng. J.* 34 (2007) 69–75.
- [8] K. Baek, B.-K. Kim, H.-J. Cho, J.-W. Yang, Removal characteristics of anionic metals by micellar-enhanced ultrafiltration, *J. Hazard. Mater.* 99 (2003) 303–311.
- [9] K. Baek, J.-W. Yang, Cross-flow micellar-enhanced ultrafiltration for removal of nitrate and chromate: competitive binding, *J. Hazard. Mater.* 108 (2004) 119–123.
- [10] K. Baek, J.-W. Yang, Simultaneous removal of chlorinated aromatic hydrocarbon, nitrate, and chromate using micellar-enhanced ultrafiltration, *Chemosphere* 57 (2004) 1091–1097.
- [11] H.-D. Choi, M.-C. Shin, D.-H. Kim, C.-S. Jeon, K. Baek, Removal characteristics of reactive black 5 using surfactant-modified activated carbon, *Desalination* 223 (2008) 290–298.
- [12] H.-D. Choi, J.-M. Cho, K. Baek, J.-S. Yang, J.-Y. Lee, Influence of cationic surfactant on adsorption of Cr(VI) onto activated carbon, *J. Hazard. Mater.* 161 (2009) 1565–1568.
- [13] A. Bingol, H. Ucin, Y.K. Bayhan, A. Karagunduz, A. Cakici, B. Keskinler, Removal of chromate anions from aqueous stream by a cationic surfactant-modified yeast, *Bioresour. Technol.* 94 (2004) 245–249.