



## 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  $\text{MeS}$  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].

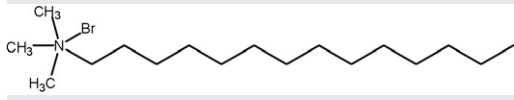
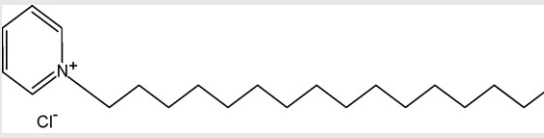
Activated carbon is well known to have a high adsorption capacity for hydrophobic organic pollutants because of its hydrophobic properties. However, the major mechanism for the adsorption of ionic pollutants is electrostatic interaction or ion exchange. Consequently, the surface charge is important for 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  $\text{Na}_2\text{CrO}_4$  (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  $0.1677 \text{ g/L}$  and  $0.1611 \text{ g/L}$ , 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  $70^\circ\text{C}$  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  $100 \text{ mg/L}$  Cr(VI). Each mixture was agitated at  $20^\circ\text{C}$  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  $28 \text{ cm}^3$  were filled with AC or MAC. The flow rate was  $20 \text{ ml/h}$  created by a Masterflex L/S pump (Coleparmer, USA) and the initial concentration of Cr(VI) was  $5.0 \text{ mg/L}$ . 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  $540 \text{ nm}$  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  $258 \text{ nm}$  and the HDTMA was estimated by a total-nitrogen analysis using the standard method, with the UV/VIS spectrophotometer at  $220 \text{ nm}$ . 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 ( $\text{mg/g}$ ) 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 ( $\text{g}$ ).

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  $K_1$  ( $\text{h}^{-1}$ ),  $K_2$  ( $\text{h g/mmol}$ ), and  $K_p$  ( $\text{mmol h/g}$ ) 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

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