

Adsorption Characteristics of As(V) onto Cationic Surfactant-Modified Activated Carbon

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Abstract

Arsenic at abandoned mine sites has adversely affected human health in Korea. In this study, the feasibility of using cationic surfactant-modified activated carbon (MAC) to remove As(V) was evaluated in terms of adsorption kinetics, adsorption isotherms, and column experiments. The adsorption of As(V) onto MAC was satisfactorily simulated by the pseudo-second-order kinetics model and Langmuir isotherm model. In column experiments, the breakthrough point of AC was 28 bed volumes (BV), while that of MAC increased to 300 BV. The modification of AC using cationic surfactant increased the sorption rate and sorption capacity with regard to As(V). As a result, MAC is a promising adsorbent for treating As(V) in aqueous streams.

Keywords: Arsenic, Adsorption kinetics, Adsorption isotherm, Surfactant-modified activated carbon

1. Introduction

Mining has supplied us with large amounts of minerals and other valuable substances. However, contaminants from mining waste have considerably deleterious effects on human health. In addition, ecosystems that include agricultural soil, groundwater, and surface water have been contaminated by abandoned mines.¹⁻³⁾ In particular, mine wastes contain heavy metals such as As, Cr, Zn, Cu, Pb, Cd, and Ni, which are nondegradable and pose a risk to ecosystems and human health.¹⁻³⁾ At abandoned mining sites, agricultural water, surface water, and ground water are contaminated with heavy metals leaching from mine tailing. This issue assumes particular seriousness when contaminated groundwater is used as residential drinking water. Heavy metals in a water system are hazardous to the environment and human population owing to their persistence and bioaccumulation through the food chain.^{2,3)} Therefore, the treatment of heavy metals in groundwater or surface water is one of the most important environmental issues for abandoned mine sites. Heavy metals mostly exist in a cationic form, but As combined with oxygen is anionic in a natural aquatic system. Inorganic As

exists as arsenite (As(III)) and arsenate (As(V)) in natural systems. Generally, As(III) is more toxic than As(V), but As(III) oxidizes to As(V) in the presence of natural oxidants such as manganese oxide.⁵⁾ As of January 2006, the United States Environmental Protection Agency had reduced the arsenic guideline for public drinking water from 50 ppb to 10 ppb.

Cationic heavy metals have been removed by precipitation, e.g., the precipitation of $\text{Me}(\text{OH})_2$ by pH adjustment and the precipitation of MeS by sulfide addition.⁶⁾ However, the technique is not effective in removing anionic metals such as As(III) and As(V).^{7,8)} A common treatment for arsenic removal in the aqueous phase is adsorption using biomass, activated carbon (AC), iron oxide, or iron-coated materials.^{5,7-14)} AC is ineffective in removing inorganic pollutants from the aqueous phase even though it is very effective in removing organic pollutants. The surface modification of ACs has been applied to enhance the adsorption capacity for inorganic contaminants.¹⁴⁻¹⁶⁾ The introduction of an ionic functional group onto the surface of ACs increases the adsorption capacity of AC for various inorganic pollutants.¹⁴⁻¹⁷⁾

A cationic surfactant can be used to modify the surface properties of AC to enhance the sorption capacity for anionic pollutants.¹⁵⁻¹⁷⁾ The hydrophobic group of the surfactant is adsorbed onto AC and the hydrophilic head is directed toward the aqueous phase. Consequently, the surface of AC is reorganized to be

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cationic.

In this study, we evaluated the feasibility of cationic surfactant-modified AC (MAC) for the removal of As(V) from an aqueous stream in terms of adsorption kinetics, adsorption isotherms, and column experiments.

2. Materials and Methods

2.1. Materials

As(V) stock solution was prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma, USA) in deionized water. Granular AC, made from charcoal and having a mesh size of 8-20 mesh, was purchased from Aldrich (USA). The cationic surfactant used in this study was hexadecyltrimethylammonium bromide (HDTMA, Sigma, USA). The chemical structure and properties are summarized in Table 1.

2.2. Modification of AC

Ten grams of AC was added to the solution of HDTMA at a concentration of 0.1611 g/L, which corresponds to the 0.5 critical micelle concentration (CMC). Above the CMC, the surfactant forms micelles that remain in the bulk zone. Therefore, a concentration of 0.5 CMC was selected to maximize the amount of surfactant adsorbed onto 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. We use the notations 1MAC, 2MAC, and 3MAC to denote MAC obtained by one, two, and three cycles of surfactant modification, respectively.

2.3. Batch Test

An adsorption kinetics test was carried out by adding 0.5 g of AC or MAC to 50 mL of solution at a concentration of 10 mg/L As(V) in a 250-mL Erlenmeyer flask. The mixture was agitated at 20°C and 150 rpm for 6 h. The pH of the solution was adjusted to 4.0 using 0.1 N HCl to simulate wastewater obtained from a mining site. After a desired time interval, the mixture was sampled and filtered using 5B filter paper. Adsorption isotherms were determined for exactly the same condition as that for the adsorption kinetics test, with the exception that the concentration range for As(V) solution was 1-100 mg/L. All experiments were performed in triplicate.

2.4. Column Test

Glass columns with a bed volume (BV) of 27.74 cm³ were filled with 10 g of AC or MAC, respectively. The glass column

was 11 mm in inner diameter and 300 mm in length. The flow rate used was 20 mL/h, the pump used was a Masterflex L/S pump (Cole-Parmer, USA), the initial concentration of As(V) was 1.5 mg/L, and the pH was adjusted to 4.0 to simulate an acidic environment. For the column experiment, the column was filled with 3 MAC. The column experiments were conducted at room temperature.

2.5. Analysis

Anodic stripping voltammetry (PDV6000, MTI, Australia) was used to determine the concentration of As(V).⁵⁾ The residual concentration after the adsorption of surfactant onto AC and HDTMA was estimated by total-nitrogen analysis using the standard method with a UV-Vis spectrophotometer at 220 nm. The pH of each solution was measured using a pH/ion selective electrode meter (735P, Istek, Korea).

The amount of As(V) adsorbed onto AC was calculated by the following equation:

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

where q_e is the amount of As(V) adsorbed per unit mass of AC (mg/g) at equilibrium; V_l is the volume of the solution (L); C_0 and C_e are the initial and equilibrium concentrations of As(V) (mg/L), respectively; and M is the mass of AC (g).

The As(V) adsorption kinetic data are correlated with the adsorption kinetic models¹⁵⁻¹⁹⁾:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

Pseudo-first order kinetic model (2)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Pseudo-second order kinetic model (3)

where q_e and q_t are amount of Cr(VI) adsorbed onto activated carbon at the equilibrium and time t , respectively, K_1 (h⁻¹) and K_2 (h · g/m mole) are adsorption rate constants at each model.

The experimental data were fitted with the well-known adsorption isotherm model as follows¹⁵⁻¹⁷⁾:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$$

Langmuir adsorption model (4)

Table 1. Chemical structure and properties of HDTMA

Chemical structure	Molecular weight	Critical micelle concentration	Aggregation number
	364.45	0.92 mM	170

$$q_e = K_F C_e^{1/n}$$

Freundlich adsorption model (5)

where q_{\max} is the solid-phase concentration corresponding to complete monolayer coverage of adsorption sites; K_L is a constant related to the free energy of adsorption; and the constants K_F and n in the Freundlich model are parameters related to the strength of the adsorptive bond and bond distribution, respectively.²⁰⁾

The empty bed contact time (EBCT, min) can be calculated as followings²¹⁾:

$$EBCT = \frac{V_r}{Q}$$

(6)

where V_r is the fixed-bed volume and Q is the volumetric flow rate. The total mass of As introduced into the column during the experiment can be determined as following:

$$M_{total} = \frac{C_0 Q t_{total}}{1000}$$

(7)

where C_0 is the inlet concentration of As(mg/L), and t_{total} is the total flow time(min). The column capacity for As adsorption at a given flow rate and inlet concentration of As can be calculated as follows:

$$C_{cap} = \frac{Q}{1000} \int_0^{t_{total}} (C_0 - C) dt$$

(8)

where C is the outlet concentration of As(mg/L). The total adsorption efficiency of As during the experiment can be calculated as follows:

$$R = \left[\frac{C_{cap}}{M_{total}} \right] \times 100$$

(9)

The mass of As adsorbed per unit mass of MAC in the column can be determined as following:

$$q_a = \frac{C_{cap}}{M_{MAC}}$$

(10)

where M_{MAC} is the mass of MAC in the column (g)

3. Results and Discussion

3.1. Adsorption Kinetics of As(V)

Fig. 1 shows the adsorption kinetics of As(V) on AC and MAC. At an initial concentration of 10 mg/L, the adsorption of As(V) onto MAC reached equilibrium within 30 min. The pseudo-

second-order model satisfactorily simulated the kinetics of adsorption of As(V) onto MAC (data not shown). The pseudo-second-order rate expression has been used to describe chemisorptions involving valency forces through the exchange of electrons.^{18,19)} This type of kinetics indicates that the major mechanism governing the adsorption of As(V) onto MAC is ion exchange or electrostatic interaction. As the number of modifications increased from 0 to 1 to 2 to 3, the rate of adsorption of As(V) was 3.5 times that of AC for 1MAC, 8 times for 2MAC, and 48 times for 3MAC. Consequently, the modification of AC using cationic surfactant increased the adsorption rate of As(V).

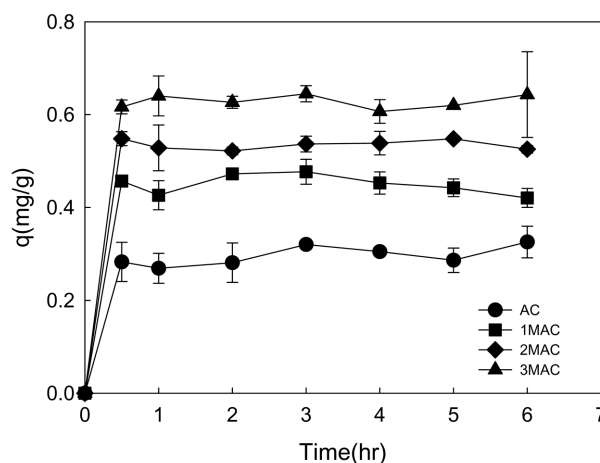


Fig. 1. Adsorption kinetic of As(V) on AC and MAC. (Concentration of As(V): 10mg/l; MAC: 0.5 g; Temperature: 20°C; Agitation speed: 150rpm)

2.2. Adsorption Isotherm of As(V)

Fig. 2 shows the adsorption isotherms of As(V) for AC and MAC. The maximum adsorption capacity increased from 0.016 mmol/g for AC to 0.021, 0.023, and 0.025 mmol/g for 1MAC, 2MAC, and 3MAC, respectively. The increase in the number of positively charged sites due to HDTMA⁺ enhanced the adsorption of As(V). The As(V) adsorption data show a good correlation with the results of the theoretical Langmuir and Freundlich models. The Freundlich model describes the heterogeneous surface energies in multilayer adsorption, and the Langmuir model explains monolayer adsorption at the adsorption site. The characteristics of As(V) adsorbed onto MAC and AC follow the Langmuir model slightly more than they do the Freundlich model. This means that the adsorption of As(V) onto MAC is site-specific and leads to the formation of an As(V)-HDTMA⁺ complex. The model parameters are summarized in Table 2. Even though the adsorption capacity of MAC for As(V) was enhanced by modifying AC with a cationic surfactant, there was no significant increase in the adsorption capacity with the number of modifications. In conclusion, the cationic surfactant improved the adsorption capacity of AC for As(V).

The affinity between As(V) and the MAC adsorbent can be predicted using the Langmuir parameter KL , which is obtained from the dimensionless separation factor RL using the following equation:

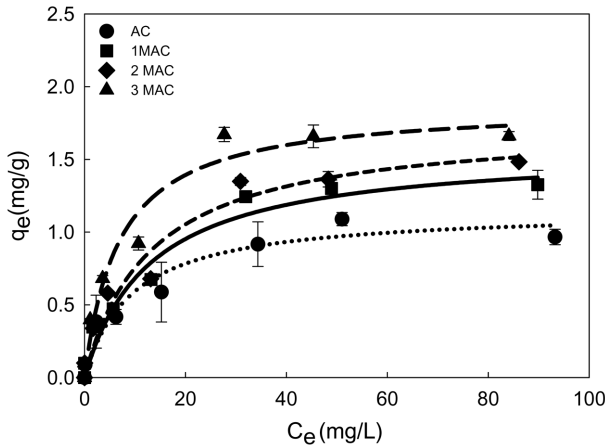


Fig. 2. Adsorption isotherm of As(V) on AC and MAC. Concentration range: 1-100 mg/L; Dose of MAC: 10.0 g/L; Temperature: 20°C; Agitation speed: 150 rpm.

Table 2. Parameters for Langmuir and Freundlich adsorption models of As(V) adsorption on modified activated carbon

Absorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	K_L	r^2	K_F (mg/g)	n	r^2
AC	1.13	0.112	0.93	0.275	3.246	0.91
1MAC	1.57	0.081	0.96	0.311	2.892	0.95
2MAC	1.69	0.087	0.96	0.333	2.837	0.96
3MAC	1.87	0.145	0.97	0.494	3.320	0.94

$$R_L = \frac{1}{1 + K_L C_0} \quad (11)$$

where C_0 is the initial concentration of As(V) (mg/L) and (K_L) is the Langmuir isotherm constant. Kundu and Gupta used mathematical calculations to show that R_L indicates the shape of the isotherm.¹³⁾ $R_L < 1$ indicates favorable adsorption and $R_L > 1$ indicates unfavorable adsorption. Fig. 3 shows the separation factor for As(V) adsorbed onto MAC. The values of R_L were found to be between 0 and 1, which indicates highly favorable adsorption with increased adsorption efficiency at higher As(V) concentration and greater number of modifications.

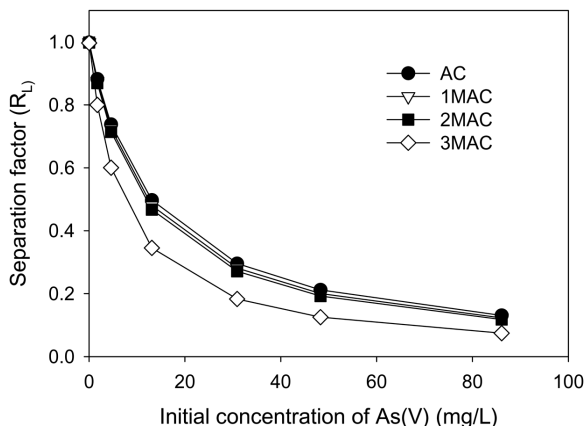


Fig. 3. Separation factor of As(V) adsorbed onto AC and MAC. Dose of MAC: 10.0 g/L; Temperature: 20°C; Agitation speed: 150 rpm.

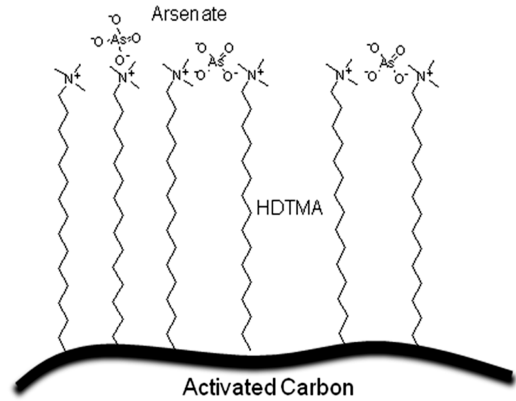


Fig. 4. Conceptual diagram on adsorption of As(V) onto HDTM-modified activated carbon.

Fig. 4 is a conceptual diagram of the adsorption of As(V) onto HDTM-modified AC. It is likely that HDTM+ adsorbed onto AC via hydrophobic interaction between the hydrophobic surface of AC and the hydrophobic tail of the surfactant. The positive charge of the cationic surfactant was directed toward the bulk solution. As a result, As(V) could be adsorbed onto MAC due to the positive charge introduced by the cationic surfactant.

3. Column Experiment

The feasibility of cationic surfactant-modified AC to treat As(V) in an aqueous stream was investigated in column experiments. The breakthrough curve is shown in Fig. 5. In the case of AC, As(V) was detected at 28 BV, while the breakthrough point of MAC for As(V) was 300 BV. Therefore, the lifetime of the adsorbent showed a 31-fold increase, which shows the feasibility of using MAC to remove As(V) from the aqueous phase. In AC, C_{cap} was 7.7 mg, while it was 13.7 mg in MAC, which is approximately 2 times higher than that of AC. The adsorption capacity at the breakthrough point was 1.82 mg/g, which is similar to that value obtained in the batch experiment. The total removal efficiency of As in MAC column was 81.5%, while the value for AC was 46.3%. Based on the experimental result, the MAC is a promising adsorbent for As.

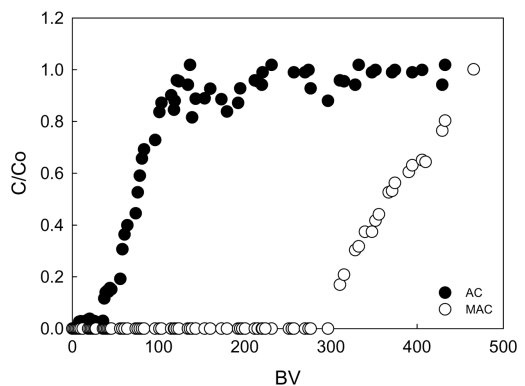


Fig. 5. Breakthrough curve of As(V) in the column packed with AC and MAC. Initial concentration of As(V): 1.5 mg/L; Empty bed contact time : 1.4 hr; Solution pH: 4.0.

4. Conclusion

We evaluated the feasibility of using cationic surfactant-modified AC for As(V) removal using hexadecyltrimethylammonium. Modification of AC enhanced the adsorption rate and capacity of As(V). The introduction of a positive functional group onto the surface of AC provides an adsorption site for As(V), and thus enhances the adsorption of As(V). Thus, cationic-surfactant modification of AC is a promising technology for enhancing the adsorption rate and capacity of AC for removal of As(V) from wastewater.

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