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. 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. At abandoned mining sites, agricultural water, surface water, and ground water are contaminated with heavy metals leaching from mine tailings. 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. 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. 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 Me(OH)2 by pH adjustment and the precipitation of MeS by sulfide addition. However, the technique is not effective in removing anionic metals such as As(III) and As(V). A common treatment for arsenic removal in the aqueous phase is adsorption using biomass, activated carbon (AC), iron oxide, or iron-coated materials. 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. The introduction of an ionic functional group onto the surface of ACs increases the adsorption capacity of AC for various inorganic pollutants.

A cationic surfactant can be used to modify the surface properties of AC to enhance the sorption capacity for anionic pollutants. 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...
2. Materials and Methods

2.1. Materials

As(V) stock solution was prepared by dissolving Na$_2$HAsO$_4$·7H$_2$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 cm$^3$ 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). 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:

$$q_e = \left( C_0 - C_e \right) \times \frac{V}{M}$$

where $q_e$ is the amount of As(V) adsorbed per unit mass of AC (mg/g) at equilibrium; $V$ 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 models:

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

Pseudo-first order kinetic model

$$\frac{t}{q} = \frac{1}{K_2 q_e} + \frac{1}{q_e}$$

Pseudo-second order kinetic model

where $q_e$ and $q$ are amount of Cr(VI) adsorbed onto activated carbon at the equilibrium and time $t$, respectively, $K_e$ (h$^{-1}$) and $K_2$ (g/m mole) are adsorption rate constants at each model.

The experimental data were fitted with the well-known adsorption isotherm model as follows:

$$q_e = \frac{q_m K_e C_e}{1 + K_e C_e}$$

Langmuir adsorption model

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Table 1. Chemical structure and properties of HDTMA

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Molecular weight</th>
<th>Critical micelle concentration</th>
<th>Aggregation number</th>
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<tr>
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<td>364.45</td>
<td>0.92 mM</td>
<td>170</td>
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</table>