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Adsorption of As(V) by boehmite and alumina of different morphologies prepared under hydrothermal conditions

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HIGHLIGHTS

- Hierarchical boehmite and alumina were synthesized by a simple hydrothermal method.
- Use of different aluminum salts induced different morphologies in the materials.
- The synthesized materials were superior in As(V) adsorption to commercial alumina.

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ABSTRACT

Morphology-controlled materials at the micro- and nanoscale levels are of great significance to the design and application of materials. Stable and well-dispersed boehmite and alumina with different morphologies were fabricated under hydrothermal conditions. The nitrate, chloride, and sulfate aluminum salts yielded nanoplate, microspindle, and microsphere morphologies, respectively. Calcination of the prepared boehmite samples yielded alumina samples with retention of the morphologies. In comparisons of samples with identical morphologies, alumina exhibited better uptake of As(V) than boehmite; the As(V) concentration was analyzed by the standard molybdenum blue method. The adsorption capabilities of the morphologically controlled materials are ranked microspindle > microsphere > nanoplate. The impacts of process parameters, such as reaction time; initial As(V) concentration; solution pH; competing ions (Ca^{2+}, Mg^{2+}, NO_3^-, PO_4^{3-}), which are common in most aquatic ecosystems; and co-contaminants (Cr(VI), Pb(II)), on removal efficiencies were examined. A well-defined mesostructure, superior surface area, chemical and electrostatic interaction, and surface charge distribution over the aluminol surface sites could be factors in the uptake of As(V). The design and synthesis of functional hierarchical micro- and nanostructured materials with the desired adsorptive properties, which are suitable for water treatment applications, can be achieved through environmentally benign hydrothermal fabrication.

1. Introduction

Novel technological innovations for the design and synthesis of morphology-controlled materials have received great attention and are among the most exciting and promising fields (Cölfen and Mann, 2003). For example, boehmite (AlOOH) and alumina (Al_2O_3) are being used in catalysis, separation, adsorption, and biomedical applications (Webster et al., 2005; Yu et al., 2009; Cai et al., 2011; Li et al., 2011; Zhang et al., 2011). Boehmite, a hydrated form of alumina, is used as a precursor in the preparation of alumina. Significant attempts have been made in the development of solution-phase methods for the synthesis of micro- and nanostructured boehmite; among these, hydrolysis and precipitation are the most common methods. However, boehmite can form less-ordered structures and can be poorly crystallized (El-Katatny et al., 1998; Guzmán-Castillo et al., 2001; Okada et al., 2002); therefore, synthesis of stable, well-dispersed particles with controlled morphology and crystallinity by

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environmentally benign, simple procedures is a great challenge (Mathieu et al., 2007; Cai et al., 2009).

Hydrothermal synthesis, a relatively new method, has better control over the crystallinity and morphology of the materials than the hydrolysis and precipitation methods. Recently, hydrothermal routes to synthesize boehmite have been investigated by adjusting the reaction parameters; for example, two-dimensional nanoplatelets and one-dimensional nanowires were prepared without the addition of templates/seeds by manipulating the acidity of the reaction solution (Chen et al., 2007). The impact of anion type on the hydrothermal treatment of aluminum hydroxide gel was evaluated as well. The growth mechanism of boehmite created nanorods in the presence of NO_3^- and Cl^-, nanowires were formed in the presence of SO_4^{2-} under acidic conditions, and nanoplates were produced under alkaline conditions, irrespective of the anion type (He et al., 2009). The effects of counterions on particle morphology were also studied under hydrothermal conditions. Aluminum nitrate and trisodium citrate yielded cantaloupe-like and microsphere structures of boehmite (Feng et al., 2008). Morphological variants of boehmite (nanoflakes, flower-like structures, and hollow microspheres) were observed using aluminum nitrate and urea as raw materials in sulfate-mediated transformations (Cai et al., 2010). An additive-free hydrothermal approach was developed for the synthesis of lamellar boehmite from aluminum nitrate and urea (Wu et al., 2013a). Likewise, a morphology control concept named the anion competition method was introduced to obtain lamellar assemblies through hollow microsphere morphologies of boehmite by altering the relative proportion of anions; for example, aluminum sulfate was introduced as an additional concomitant raw material to the aluminum chloride/aluminum nitrate–urea hydrothermal processes to form the anion competition systems (SO_4^{2-}-Cl^- and SO_4^{2-}-NO_3^-) (Wu et al., 2013b). Microspheres of boehmite were also synthesized via tartrate- and citrate-mediated synthetic methods (Cai et al., 2009, 2013; Han et al., 2013). Additionally, an additive-free and time-saving microwave hydrothermal route was described for the synthesis of boehmite microspheres from aluminum sulfate and urea (Wu et al., 2014). However, reports concerning morphology-controlled syntheses of boehmite and alumina with the adsorptive properties desired in water treatment applications are still limited.

Arsenic (As) exists predominantly as pentavalent arsenate (As(V), AsO_4^{3-}) and trivalent arsenite (As(III), AsO_3^{3-}) in water (Mohan and Pittman, 2007). AsO_3^{3-} is the dominant oxyanion under reducing conditions; as a result, As(III) mostly occurs in suboxic groundwater whereas As(V) mainly exists in oxic water environments. The neutral and undissociated form of As(III) ($H_3AsO_3^0$), generally restricts the adsorption process, thus pre-oxidation of As(III) into As(V) has been suggested for effective uptake. Concern over arsenic's adverse effects on human health, principally carcinogenesis and related disorders (Tchounwou et al., 2003), has propelled efforts to identify and remediate arsenic from water sources. To this end, the United Nations Environmental Program agency (UNEPA) has classified activated alumina as one of the best available sorbent materials for the removal of As from contaminated waters. The Al-based materials are reported to remove arsenic from water matrices (Kim et al., 2004; Mohan and Pittman, 2007).

This research shows a promising strategy for the morphology-controlled synthesis of boehmite and alumina (microspindles, microspheres, and nanoplates) with potential water treatment applications, and to the best of our knowledge is the first report to investigate the adsorption of arsenic by hierarchical boehmite and alumina of different morphologies synthesized by a simple hydrothermal method. The objectives of this study are to gain insight into the effects of the counterions of aluminum salts on the morphology of the materials and to assess the performance of these materials in the adsorption of As(V). This study reports the tunable synthesis of potential adsorbents; these as-synthesized materials show distinct improvements in the removal of As(V) over the popular commercially available activated alumina (AA, which is used for comparison in this study). A comparative study of boehmite and alumina considers the effects of reaction parameter, adsorption reversibility, and commonly occurring competing ions and co-contaminants under natural water conditions.

2. Materials and methods

2.1. Reagents, materials, and solutions

All of the chemicals used in the study were reagent grade and were used as received without further purification. Aluminum nitrate, aluminum chloride, aluminum sulfate, urea, sodium arsenate, sodium chloride, sodium nitrate, disodium hydrogen phosphate, magnesium chloride, calcium chloride, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich Co. (USA). Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) was used to prepare the As(V) stock solution (100 mg L^{-1}) under weakly acidic conditions (e.g., 0.01 M HCl), and proper dilutions were made daily before use. Commercially available alumina (AA) was purchased from Daejung Chemical Co. (Korea). All solutions were prepared using 18 MΩ-cm water from a Millipore Milli-Q system. The pH values of the sample solutions were varied from pH 2 to 10 by adjustment with 1 N or 0.1 N HCl and NaOH solutions.

2.2. Syntheses of boehmite and alumina particles

The morphologies and sizes of the as-prepared inorganic materials could be easily tuned at the micro- and nanoscales through the composition and concentration of the metal precursor solutions and the amount of urea used. Boehmite and alumina (represented by prefix 'b' and 'a', respectively) with different morphologies, such as nanoplates, microspindles, and microspheres, were synthesized using a one-step hydrothermal method by simply adjusting the reaction parameters. Three precursor aluminum salts (aluminum nitrate, aluminum chloride, aluminum sulfate) and urea were used as raw materials.

In a typical synthesis, 293.1 mg $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 50 mL water, followed by the addition of 75.1 mg $(NH_2)_2CO$ to form a clear solution. The solution mixture was stirred vigorously for 10 min and was transferred to a Teflon-lined stainless steel autoclave (100 ml capacity). The hydrothermal vessel was heated to and maintained a temperature of 175 °C for the 180 min reaction time. After natural cooling, the samples were centrifuged at 4000 rpm for 10 min, were washed thrice with water to remove any adhering impurities, were dried at 80 °C for 600 min, and were stored for further experiments. This boehmite was labelled bN.

A similar synthetic procedure was extended to prepare boehmite samples from $AlCl_3$ and $Al_2(SO_4)_3$, which were labelled bC and bS, respectively. The synthesized boehmites (bN, bC, bS) underwent calcination at 450 °C for 1440 min, and the alumina products (aN, aC, aS) were thus obtained from the corresponding boehmites, as presented in the *supplementary data* (SD), Table S1.

2.3. As(V) sorption test

A suitable amount of adsorbent was immersed in an aqueous solution of As(V). The solution was continuously stirred (80 rpm) at room temperature for the desired time period to ensure the adsorption equilibrium. The concentration of As(V) was calculated from (Eq. (1)):