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Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking water

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Abstract

A novel type adsorbent was prepared by in situ precipitation of $Fe(OH)_3$ on the surface of activated Al_2O_3 as a support material. The iron content of the adsorbent was $0.31 \pm 0.003\%$ m/m (56.1 mmol/g); its mechanical and chemical stability proved to be appropriate in solutions. The total capacity of the adsorbent was 0.12 mmol/g, and the pH of zero point of charge, $pH_{zpc} = 6.9 \pm 0.3$. Depending on the pH of solutions, the adsorbent can be used for binding of both anions and cations, if $pH_{eq} < pH_{zpc}$ anions are sorbed on the surface of adsorbent (S) through $\{S-OH_2^+\}$ and $\{S-OH\}$ groups. A graphical method was used for the determination of pH_{iep} (isoelectric points) of the adsorbent and values of $pH_{iep} = 6.1 \pm 0.3$ for As(III) and $pH_{iep} = 8.0 \pm 0.3$ for As(V) ions were found. The amount of surface charged groups (Q) was about zero within the a pH range of 6.5–8.6, due to the practically neutral surface formed on the adsorption of As(V) ions. At acidic pH (pH 4.7), $Q = 0.19$ mol/kg was obtained. The adsorption of arsenate and arsenite ions from solutions of 0.1–0.4 mmol/L was represented by Langmuir-type isotherms. A great advantage of the adsorbent is that it can be used in adsorption columns, and low waste technology for removal of arsenic from drinking water can be developed.

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1. Introduction

The European Commission has recently published a new Directive (98/83/EC) on the quality of water intended for human consumption to achieve a common, high-quality standard and to protect public health. One of the new chemical guide values was concerned with arsenic, which was set at 10 µg/L. These legislative proposals are based on a reevaluation of chronic As toxicity to humans as detected in relatively large populations receiving potable water with elevated As levels over several decades. Arsenic concentrations >10 mg/L have been reported in water supplies throughout the world in places, like Bangladesh [1], West Bengal [2–4], Vietnam [5], Argentina [6], Taiwan [7], Mexico [8], and the United States [9,10].

In natural water inorganic arsenic is usually found in the form of As(III) as arsenite, and/or As(V) as arsenate. In the pH range of drinking water, the dominant arsenite species is neutral ($H_3AsO_3^0$; $pK_{a,1} = 9.2$) and the negatively charged anions ($H_2AsO_4^-$ and $HAsO_4^{2-}$; $pK_{a,1} = 2.91$ and $pK_{a,2} = 6.94$, respectively) are the principal arsenate species. Both arsenate and arsenite are subjected to chemically and/or microbially mediated redox and methylation reactions in waters [11,12].

Interactions of cations and anions with hydrous oxide surfaces are of importance in natural water systems. A potential removal process is adsorption on oxide/hydroxide surfaces, either formed in situ (by dosing of coagulants Fe^{3+}/Al^{3+} or by adding ferrous salt) or by providing a granulated adsorbent with sufficient capacity and affinity to $H_2AsO_4^-$ or $HAsO_4^{2-}$. Conventional approaches to the arsenic removal include coagulation, flocculation, and filtration with ferric salts, but reliability, safety, and residual treatments are not satisfactory for smaller treatment plants [13]. Arsenic ad-

sorption on amorphous aluminum and iron oxides was investigated as a function of solution pH, ionic strength, and redox state [14]. In this study in situ Raman and Fourier transform infrared (FTIR) spectroscopic methods were combined with sorption techniques, electrophoretic mobility (EM) measurements, and surface complexation modeling to study the interaction of As(III) and As(V) with amorphous oxide surfaces. The mechanisms of As sorption to these surfaces based on the spectroscopic, sorption, and EM measurements are as follows: arsenate forms inner-sphere surface complexes on both amorphous Al and Fe oxide, while arsenite forms both inner- and outer-sphere surface complexes on amorphous Fe oxide and outer-sphere surface complexes on amorphous Al oxide [14]. Adsorption on ferrihydrite occurs by ligand exchange of the As species for OH_2 and OH^- in the coordination spheres of surface structural Fe atoms [15]. While arsenate adsorption resulted in the net release of OH^- at pH 4.6 and 9.2, arsenite adsorption resulted in net OH^- release at pH 9.2 and net H^+ release at pH 4.6. The amount of H^+ or OH^- released/adsorbed As (mol/L) varied with the As surface coverage, indicating that different mechanisms of arsenic adsorption predominate at low versus high coverage. The results provide evidence that during arsenite adsorption at low pH, i.e., pH 4.6, the oxygen of the Fe–O–As bond remained partially protonated as Fe–O(H)–As [15]. In all of these experiments, different metal oxides have been prepared and used mainly in suspensions for understanding the phenomena of the equilibrium reactions between oxides and arsenic ions. However, in the purification technology, the precipitates cannot be advantageously used since large amounts of hazardous waste materials are produced daily and the disposal cost can be tremendous. There is a clear need for inexpensive, but reliable and efficient granular adsorbents for arsenic removal, based on the specific binding to ferric oxide surfaces.

In our work a novel iron hydroxide-coated alumina adsorbent was developed from environmentally friendly raw materials. Precipitates of the $Fe(OH)_3$ were directly produced on the surface of support materials using an in situ precipitation method. The main features of adsorbents were determined as the pH value of the zero point of charge of the adsorbent (pH_{zpc}), the isoelectric point (pH_{iep}) in equilibrium solutions in the presence of As(III) and As(V) ions, the amount of surface charged groups, the surface charge, and the effect of pH on the adsorption of arsenic ions. The adsorbent/solution ratios, the ionic strength, the initial pH of the solutions, and arsenic concentrations were changed for the characterization of the adsorbent.

2. Experimental methods

2.1. Preparation of the adsorbent

The support of the adsorbent was granulated from Al_2O_3 powder made by Alum-Earth Plant at Almásfüzitő, Hun-

gary (Reg. No. K10). A fraction of the grain size ranging from 0.5 to 1.0 mm was activated at 450 °C over 4 h. The surface of the Al_2O_3 was covered by $Fe(OH)_3$ using an in situ precipitation method: Al_2O_3 was placed in an exsiccator and 10% m/m $FeCl_3$ was added in excess. An aspirator pump from the pores eliminated the air. After the bubbling was over, the excess $FeCl_3$ was poured off and $Fe(OH)_3$ was formed on the surface of the granules by NH_4OH solution. The material was air-dried and it is called $Al_2O_3/Fe(OH)_3$ adsorbent. The Fe content of the adsorbent was determined by atomic absorption spectrometric (AAS) method and was $0.31 \pm 0.003\%$ m/m (56.1 mmol/g). The mechanical and chemical stability of the adsorbent proved to be appropriate for use in columns. The total capacity of the adsorbent was 0.12 mmol/g. Mineralogical phases were identified by X-ray powder diffraction (Philips PW 1710) and χ-Al_2O_3 (45–50%), γ-Al_2O_3 (30%), and δ-Al_2O_3 (20%) were found with amorphous materials. The mineralogical structure of $Fe(OH)_3$ cannot be measured by XRD methods due to its amorphous form and the very low concentration. The BET surface area of the activated Al_2O_3 support and $Al_2O_3/Fe(OH)_3$ adsorbent proved to be 250 and 95.7 m^2/g, respectively, while the pore diameters were 4.7 and 11.1 nm. The difference in the specific surface area shows the perfect coverage of the $Fe(OH)_3$ on the support.

2.2. Equilibrium experiments

The pH_{iep} value of $Al_2O_3/Fe(OH)_3$ adsorbent in the presence of adsorbate ions was determined by potentiometric titration. Experiments consisted of 0.1, 0.25, 0.5, 1.0, and 2.5 g adsorbent/100 mL solutions with known concentration of anions as 1 and 4 mmol/L for As(III) and As(V) ions. A series of 8 flasks containing the same anions and different adsorbent concentration were adjusted to different pH values by the addition of $HClO_4$ or NaOH. Sodium perchlorate of 0.1 and 0.001 mol/L was added to each flask. Kinetic experiments were run and solutions were equilibrated in a controlled temperature shaker at 20 ± 0.5 °C (shaker-bath, Kutesz, Hungary). Samples were taken every 2 h, the equilibrium was found after 48 h, so 2 days were kept for further studies [16]. Following incubation, each sample was split into two fractions. One subsample was used for the determination of equilibrium pH. The other subsample was filtered (0.45 μm pore size) and the residual adsorbate concentration of the supernatant was determined. The pH values of equilibrium and initial solutions were measured by a pH meter (Radelkisz, Hungary) using a glass electrode with an RSD of 0.5%.

The interaction between the adsorbent and the arsenic ions was investigated and the solid/liquid ratio, concentration of As ions, ionic strength, and the initial pH value of solutions were changed. The pH_{zpc} of the adsorbent was determined in the presence of adsorbed ions by the measurement of the pH_{iep}. The pH_{iep} can be determined by the potentiometric method, which is suitable for both colloids and solid