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Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH)

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ABSTRACT

Relatively limited information is available regarding the impacts of temperature on the adsorption kinetics and equilibrium capacities of granular ferric hydroxide (GFH) for arsenic (V) and arsenic (III) in an aqueous solution. In general, very little information is available on the kinetics and thermodynamic aspects of adsorption of arsenic compounds onto other iron oxide-based adsorbents as well. In order to gain an understanding of the adsorption process kinetics, a detailed study was conducted in a controlled batch system. The effects of temperature and pH on the adsorption rates of arsenic (V) and arsenic (III) were investigated. Reaction rate constants were calculated at pH levels of 6.5 and 7.5. Rate data are best described by a pseudo first-order kinetic model at each temperature and pH condition studied. At lower pH values, arsenic (V) exhibits greater removal rates than arsenic (III). An increase in temperature increases the overall adsorption reaction rate constant values for both arsenic (V) and arsenic (III). An examination of thermodynamic parameters shows that the adsorption of arsenic (V) as well as arsenic (III) by GFH is an endothermic process and is spontaneous at the specific temperatures investigated.

1. Introduction

The presence of dissolved arsenic in groundwater has created significant concern on a global basis. Arsenic-contaminated groundwater affects millions of people in Bangladesh and in some regions of the Indian subcontinent (Kinniburgh and Smedley, 2000; Bagla and Kaiser, 1996). The source of dissolved arsenic in groundwater is primarily associated with oxidative weathering and geochemical reactions. Additionally, uncontrolled industrial waste discharges containing arsenic have an adverse effect. The presence of arsenic in water is extremely detrimental to human health (Smith, 1992; Davis et al., 1996). In order to protect public health, the US Environmental Protection Agency, the World Health Organization, and the European Commission have decided to lower the maximum contaminant level of arsenic in drinking water to $<10\,\mu g/L$. This stringent arsenic standard will inevitably require many utilities to upgrade their present systems or consider new treatment options.

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The chemistry of arsenic in aquatic systems is complex, and consists of oxidation–reduction, precipitation, adsorption, and ligand exchange. The principal aqueous forms of inorganic arsenic are arsenate [As (V)] and arsenite [As (III)], and their relative distributions are influenced by pH and redox conditions. In an oxidizing environment, the arsenate species predominates, and at a pH between 6 and 9, it exists as oxyanions of arsenic acid [$H_2AsO_4^-$ or $HAsO_4^{2-}$]. Under mildly reducing conditions, arsenite is thermodynamically stable and exists as a non-ionized arsenous acid [$H_3AsO_3^0$] at pH below 9. DeMarco et al. (2003) have discussed the chemistry of arsenic in aquatic systems and its ligand characteristics in detail.

A variety of arsenic treatment methods have been developed, including coprecipitation and adsorption (Hering, 1997; Raven et al., 1998; Meng et al., 2000; Gregor, 2001), precipitative softening (McNeill and Edwards, 1997), activated alumina, and ion exchange (Clifford et al., 2003). A detailed literature survey of past work is presented elsewhere (Banerjee et al., 1998). Although coprecipitation and adsorption with ferric and aluminum salts is one of the conventional methods, handling and disposal of the waste sludge is a significant problem of this process. At present, the applicability of the adsorption process using granular media is being explored. Results from several investigators (DeMarco et al., 2003; Driehaus et al., 1998; Pena et al., 2005) indicate that some of these adsorbents are very promising. However, a review of the literature shows that little has been done to determine the impacts of temperature on kinetics and capacities during the adsorption process. An understanding of the impact of temperature on the kinetics will benefit the development of an efficient arsenic treatment process. The objectives of this research were to gain an understanding of the adsorption process kinetics, to evaluate the impacts of temperature and pH on the arsenic removal kinetics and capacities, and to describe and explain some important thermodynamic parameters.

2. Methodology

2.1. Adsorbent

The adsorbent used in this research was granular ferric hydroxide (GFH) that was supplied by GEH—Wasserchemic (Germany). The material is predominantly akaganeite, a specific form of an iron oxide mineral (Amy et al., 2004). The individual particle size of this material ranges between 0.32 and 2.0 mm. GFH is characterized by its crystalline structure, large specific surface area, and high porosity. The characteristics and important properties of GFH are summarized in Table 1.

Table 1 – Properties of granular ferric hydroxide adsorbent[a]

Grain size (mm)	0.32–2.0
Bulk density (g/mL)	1.19 (wet)
pH_{ZPC}	7.6–7.8
Surface area	240–300 m^2/g
Porosity	72–77%
Moisture content	43–48%
Mineral identity (by XRD)	Akaganeite

[a] Amy et al. (2004).

2.2. Experimental procedures

Deionized distilled water was used to prepare synthetic water samples. Dibasic salts of sodium orthoarsenate and sodium arsenite were used as the sources of arsenic (V) and arsenic (III), respectively. Adsorption kinetics and isotherm experiments were conducted in a single solute system at a constant ionic strength (0.02 M of NaCl). All chemicals used were of laboratory reagent grade (99.99% pure). A non-adsorbable buffer, N, N-Bis (2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), was used to maintain a constant pH. BES does not interfere with arsenic adsorption (Banerjee et al., 2006).

The working solutions of arsenic (V) and arsenic (III) were prepared by diluting a sufficient volume of the respective stock solution to achieve the desired concentration. In order to study potential adsorption onto the surface of the vessel, the working solution was agitated for approximately 24 h. Before introduction of the GFH into the solution, several samples were withdrawn from the reactors at a predetermined time interval, and portions of those samples were analyzed to determine the concentrations of arsenic, as a function of time. No adsorptive losses of arsenic onto the reactor vessel were observed in these control experiments.

Experiments were conducted in a closed system consisting of a 1-L glass beaker that was placed inside a 1.5-L jacketed vessel. In order to minimize the effect of CO_2 and dissolved oxygen, the system was purged with nitrogen gas at a flow of 80 mL/min. The kinetic studies were conducted using about 250 mg/L of GFH media. The test solution containing either 100 μg/L of arsenic [V] or a similar concentration of arsenic [III] was then added to the reactor and allowed to equilibrate in a gyrating shaker equipped with a constant temperature bath. The kinetic studies were conducted at 20, 30, and 40 °C at pH 6.5 and 7.5, generally representative of the typical pH of natural waters. Samples were withdrawn at various time intervals. For each set of experiments, the last sample was collected after 24 h of contact. Our earlier work revealed that most of the arsenic was removed within the first 2h of contact, with equilibrium asymptotically approached after 24 h (Banerjee et al., 2003). Hence, a 24-h contact time is adequate for achieving an equilibrium condition.

The concentrations of arsenic in the treated and untreated samples were measured after filtration using a 0.45-μm disposable nylon filter. The combination of a pH electrode and a burette tip connected to an automatic titrator was used to maintain a constant pH condition in the reactor, by adding hydrochloric acid or sodium hydroxide. The concentrations of total arsenic were determined using inductively coupled plasma-mass spectroscopy, capable of detecting arsenic at concentrations as low as 1.5 μg/L. Since the studies were conducted using either arsenic (V) or arsenic (III), the total arsenic concentration in the samples represents that arsenic