Research article

Arsenate removal from aqueous solution using synthetic siderite

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ABSTRACT

The study was carried out to evaluate the feasibility of synthetic siderite for As(V) removal from aqueous solution. Batch experiments were performed to investigate effects of various experimental parameters such as contact time (10 min–8 h), initial As(V) concentration (0.5–60.0 mg/L), temperature (15, 25, 35 and 45 °C), pH (2.0–10.0) and the presence of competing anions on As(V) adsorption on the synthetic siderite. Kinetic data reveal that the uptake rate of As(V) was rapid at the beginning and 90% adsorption was completed within 10 min at 45 °C and equilibrium was achieved within 3 h. The adsorption process was well described by pseudo-second-order kinetics model. The adsorption data better fitted Langmuir isotherm at low temperatures (i.e., 15 and 25 °C), while Freundlich isotherm at relatively high temperatures (35–45 °C). The maximum adsorption capacity calculated from Langmuir isotherm model was up to 31 mg/g. Thermodynamic study indicates an exothermic nature of adsorption and a spontaneous and favorable process. The optimum pH for As(V) removal was broad, ranging from 3.0 to 10.0. The As(V) adsorption was impeded by the presence of SiO_3^{2-}, followed by PO_4^{3-} and NO_3^-. The adsorption process appeared to be controlled by the chemical process. The high As uptake may attribute to both coprecipitation of As with goethite and lepidocrocite forming during the reaction and subsequent adsorption of As on these minerals.

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1. Introduction

High As groundwaters have been found in many countries, including Bangladesh, West Bengal, Argentina, China, Mexico, the United States, Chile and Japan [1,2]. Many high-As groundwaters have been used for drinking water. Long-term exposure to As in drinking water has caused a variety of chronic health problems, including skin diseases (pigmentation, dermal hyperkeratosis, skin cancer), cardiovascular, neurological, hematological, renal and respiratory diseases, as well as lung, bladder, liver, kidney and prostate cancers [3]. In order to protect public health, the World Health Organization has set a provisional guideline limit of 10 μg/L for As in drinking water [4], which was subsequently adopted by the European Union [5] and the United States [6]. The lowering of As drinking water standard requires effective and cheap technologies for As removal from the As drinking water.

Among a variety of technologies (including precipitation-coagulation, membrane separation, ion exchange, lime softening and adsorption), adsorption and coagulation are believed to be the cheapest As removal methods. Although coagulation with iron and aluminium salts is more effective, the requirement of skilled operator and the introduction of contaminants into the water limit its application in small community and household levels. Since solid adsorbents are easy to handle and are appropriate for use in country side where high As groundwater mostly occurs, adsorption has received much attention on As removal. Iron containing substances have been widely investigated to remove As from aqueous solution due to their high specific surface area, including Mn-substituted Fe oxyhydroxide [7], granular ferric hydroxide [8] ferrihydrite [9], goethite [10], zero valent iron [11], Ce(IV)-doped Fe oxide [12], natural hematite and natural siderite [13]. Although natural siderite has been found to be a potential adsorbent for As removal, the kinetic rates for As adsorption are relatively low [2,13]. In comparison with the natural siderite having been aged for a long-term period, synthetic siderite has much more active sites on the surface. However, a review of the literature shows that little has been done to evaluate the applicability of synthetic siderite for remediation of As from high As drinking water.

This study investigates the feasibility of the synthetic siderite for As(V) removal from aqueous solution. The main objectives are (i) to understand the As(V) adsorption kinetics, (ii) to evaluate the impact of temperature, pH and coexisting anions on the As(V) removal kinetics and/or capacities; and (iii) to describe and explain some important thermodynamic parameters.

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2. Materials and methods

2.1. Materials

All reagents used in this study, including ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and ammonium hydrocarbonate (NH_4HCO_3), were of analytical grade. Stock As(V) solution (1000 mg/L) were prepared from sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$, Fluka Chemical) using deionized water. All glasswares and sample bottles were rinsed with 10% HNO_3 for at least 24 h, soaked with tap water, and finally rinsed with deionized water three times.

Artificial siderite was synthesized with ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and ammonium bicarbonate (NH_4HCO_3). Ferrous carbonate was precipitated by mixing 1 M Fe^{2+} with 2 M HCO_3^- at room temperature. The precipitate was filtered with 0.45 μm membrane. After rinsed with deionized water for three times, the artificial siderite was air-dried for 24 h and ground to powder (200 mesh). The product was then kept in a desiccator.

2.2. Batch experiments

The batch experiments to study the removal of As from solution were carried out by reacting 50 mL of As solution in 100 mL polyethylene bottles with 0.10 g of the adsorbent. The bottles were immersed in a shaking water bath at predetermined temperature (15, 25, 35, 45 °C). The shaker speed was controlled at 150 rpm. After a predetermined contact time, the aqueous samples in each bottle were decanted and centrifugated at 4500 rpm for 5 min, and then filtered through a 0.45 μm cellulose acetate filter. The supernatant was analyzed for dissolved Fe and total As. Unless specified otherwise, the concentration of the As species was expressed as the element (As).

The effect of contact time (10 min–8 h) was examined at 25 and 45 °C with initial As(V) concentrations of 10.0 mg/L. Adsorption isotherm studies were conducted by varying initial As(V) concentrations (0.5–60.0 mg/L) at different temperatures (i.e., 15, 25, 35, and 45 °C). The effect of solution pH was investigated by adjusting solution pH from 2.0 to 10.0 using 0.05 M HCl and 0.01 M NaOH solutions with an initial As(V) concentration of 1.0 mg/L. To determine the effect of other competitive anions on As adsorption, batch tests were performed using solutions of 1.0 mg/L As(V) containing 0.5, 1, 2, 5, 10 and 20 mg/L of P (as PO_4^{3-}), N (as NO_3^-), S (as SO_4^{2-}) or Si (as SiO_3^{2-}), separately. After a 3 h reaction time, the suspension was filtered through a 0.45 μm cellulose acetate filter and analyzed for total As, as described above.

2.3. Analytical methods

Solution pH was monitored by a standard pH meter (Sartorius, PB-10). Dissolved Fe and As was analyzed by ICP-MS (7500C, Agilent). The mineral composition of the adsorbents was determined by X-ray diffraction analysis (XRD), using a URD-6 powder diffractometer (Co Kα radiation, graphite monochromator, 2θ range 2.6–70°, step 0.01°, counting time 5 s per step). Morphological analysis of the pristine and used adsorbent was performed by scanning electron microscopy (SEM) using Zeiss SUPRA 55 microscope (at 15 kV) with energy-dispersive X-ray analyses.

3. Results and discussion

3.1. Effect of contact time

The As(V) adsorption kinetic study was carried out with adsorbent dosage of 2 g/L and initial As concentration of 10.0 mg/L at 25 and 45 °C, respectively. Results are shown in Fig. 1. It demonstrates that adsorbed As significantly increased with an increase
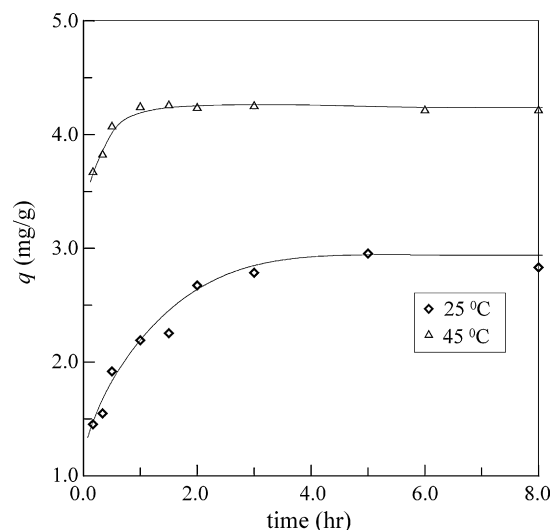

Fig. 1. Effect of contact time on As(V) adsorption on the synthetic siderite (initial As(V) concentration = 10.0 mg/L, adsorbent dosage = 2 g/L).

in contact time. The adsorption rate was rapid at the initial stage (10 min–1.0 h) and gradually slowed down afterwards. The slower adsorption was likely due to the decrease in adsorption sites on the surface of the adsorbents [14,15]. About 90% As was removed in 10 min at 45 °C, while only 40% at 25 °C. Arsenic concentration was kept relatively constant at contact times >1.0 h at 45 °C. The adsorption equilibrium was generally achieved within 1.0 h. In comparison, adsorption equilibrium time was a little higher at 25 °C. The kinetic data show that As removal mainly occurred within 3.0 h and there was no significant change in residual As concentrations after this time up to 8.0 h. It means that an equilibrium of As adsorption was roughly attained after 3.0 h at 25 °C, which is much shorter than As(V) adsorption on the natural siderite [2,13]. Adsorption experiments in other batches were conducted with the contact time of 3.0 h. It should be noted that the adsorption capacities calculated from the kinetic experiments do not reflect the actual capacities because the experiments were conducted in the presence of a large excess of surface sites. The actual adsorption capacity can be estimated from isotherm results, which are discussed later.

Results also reveal that the uptake rates of As(V) increased with increasing temperature. Tyrovola et al. observed a similar trend when they used zero-valent iron for the removal of As(V) and As(III) [16]. Other investigators also reported that the As removal rate and the capacity of the adsorbents increased with increasing temperature (e.g., Mn-substituted Fe oxyhydroxide [7], granular ferric hydroxide [8], red mud [17], activated alumina [18]).

3.2. Adsorption kinetic modeling

3.2.1. Pseudo-second-order model

An appropriate kinetic model is often used for quantifying the changes in adsorption with time. Traditionally, the pseudo-first-order Lagergren equation is applied to adsorption kinetics [8,19]. However, a recently introduced pseudo-second-order equation was employed to analyze the kinetic data since it allows evaluating effective adsorption capacity, initial adsorption rate and the rate constant of the kinetic model without any parameters beforehand [20]. The pseudo-second-order Lagergren equation is shown as Eq. (1) [19].

$$\frac{t}{q} = \frac{1}{q_e}t + \frac{1}{K_2 \cdot q_e^2} \tag{1}$$