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Synthesis of an innovative calcium-alginate magnetic sorbent for removal of multiple contaminants

S.F. Lim [a], J. Paul Chen [a,b,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore
[b] Division of Environmental Science and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore

Abstract

A new calcium-alginate magnetic sorbent has been prepared by an electrostatic extrusion technique. The sorbent has the calcium alginate as a bio-polymeric shell and iron oxides as magnetic cores. It is characterized by a multifunctional property: ease in separation via magnetic force, and effective adsorption of arsenic(V) and copper ions. It has been found that the equilibrium time of copper and arsenic(V) can be attained in less than 3 and 25 h, respectively. The maximum adsorption capacities of arsenic and copper ions are 6.75 and 60.24 mg/g, respectively, which are much higher than those of commercial adsorbents. Solution pH plays a key role in adsorption. The adsorption of arsenic increases as the pH is decreased. On the other hand, higher pH can enhance adsorption of copper ions.

Keywords: Calcium-alginate magnetic particles; Arsenic; Copper; Adsorption

1. Introduction

Water serves as a backbone for our human survival and development. The occurrence of water-related health risk is associated with pollution in water supplies. Water-related diseases, acute, and chronic exposure to chemicals are public health issues on local, national, regional and international levels [1]. The presence of heavy metals in drinking water has posed a serious environmental problem.

Various physicochemical processes have been developed for removal of inorganic contaminants from aqueous solutions. Chemical precipitation, ion-exchange, electrocoagulation, membrane filtration, and sorption process are commonly used. Sorption process has advantages of ease in operation, good performance, and relatively low cost. Numerous papers show that the technology is effective for treatment of contaminants with similar chemical properties (e.g., cationic or anionic). For instance, calcium alginate has great adsorption capacities for copper, lead, and zinc [2–5]. However, it is less effective in removal of anionic contaminants. On the other hand, iron oxides have demonstrated a good adsorption capacity for arsenic, an important anionic contaminant; they are not able to adsorb cationic contaminants effectively. Normally, the reported sorbents cannot simultaneously remove both cationic and anionic inorganic compounds.

The aim of the study was to develop a sorbent with greater affinities for both arsenic and copper ions and ease in separation. An innovative calcium-alginate magnetic sorbent was first prepared by environmental friendly substances such as alginate and iron oxides. The size of the sorbent was controlled by using an electrostatic extrusion method. The characterization of the sorbent was conducted. The effects of pH on the adsorption were assessed. Adsorption kinetics was investigated and the adsorption isotherms were determined. The results from this work will be used for the preliminary understanding of the process, which leads to further development of sorption modeling tools.

2. Materials and methods

2.1. Materials

Copper nitrate trihydrate, nitrate acid, polyethylene glycol, and sodium hydroxide from Merck (Germany), and sodium alginate, calcium chloride dehydrate, sodium nitrate, disodium

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* Corresponding author at: Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore. Fax: +65 6872 5483/+1 831 303 8636.
E-mail addresses: esecjp@nus.edu.sg, jchen.enve97@gtalumni.org (J.P. Chen).

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hydrogen arsenate heptahydrate, ferrous chloride tetrahydrate, and ferric chloride from Fluka (Switzerland) were used. All other chemicals were purchased from Sigma–Aldrich (Singapore). All chemicals were of analytical grades. Nitrate acid and sodium hydroxide solutions in various concentrations were used for pH adjustments.

2.2. Preparation of sorbent

Synthetic magnetite was first prepared according to an approach described by Cornell and Schwermann [6]. The size of magnetic sorbent was controlled by an electrostatic extrusion method [3]. The sodium-alginate solution with the metal oxides dripped through a needle which was connected to the high voltage power generator. The size of the droplets was determined by the voltage of the generator. The droplets with desired sizes dripped into a calcium chloride solution, where the beads were formed. The beads were then washed by the deionized water, collected, and dried using a freeze dryer.

2.3. Characterization of sorbent

The diameter of the randomly selected particles was measured by a laser diffraction using a Coulter LS230 Particle Size Analyzer (Beckman Coulter, UK). A NOVA 300 BET Analyzer (Quantachrome, U.S.A.) was used to determine the specific surface area of the magnetic particles. Before the adsorption process, the magnetic particle samples were purged with pure nitrogen over night at a temperature of 323 ± 0.2 K to remove any contaminants that may be present in the particles.

2.4. Adsorption experiment

All the batch sorption experiments were carried out for single-species arsenic(V) and copper. In each experiment, the metal solution was first prepared and the sorbent was subsequently added into the solution. The concentrations of metal ions were measured by an inductively coupled plasma emission spectrometer (ICP-ES; Perkin-Elmer Optima 3000, U.S.A.). The experimental temperature was controlled at 293 K.

Two adsorption kinetic experiments were conducted to obtain information on the equilibrium time for the single-species sorption process of arsenic(V) and copper by the sorbent. In the experiments, a solution of pH 5 was adjusted initially. The samples were taken at appropriate time intervals and the concentrations were determined by ICP-ES.

A series of batch adsorption equilibrium experiments was carried out for the determination of adsorption isotherm and pH effects. The solution pH was controlled between 5 and 6 in the isothermal adsorption experiments. The flasks were rotated on a rotary shaker for 48 h to reach equilibrium. At the end of the experiments, the samples were taken for the analysis of the concentrations.

In the pH effects experiments, the sorbents were added into the conical flasks containing metal solutions with various initial pHs. All the flasks were shaken on a rotary shaker with the rotation speed of 200 rpm for 48 h. The solution pH was measured by a pH meter (Orion 525A). The metal concentrations were measured by ICP-ES.

3. Results and discussion

3.1. Physical properties of calcium-alginate magnetic sorbent

The calcium-alginate magnetic sorbent was prepared by the electrostatic extrusion technique. Table 1 shows the optimum instrumental parameter used for the synthesis of the sorbent. The particle produced has a mean diameter of 309.6 μm. The specific surface area is 312.94 m^2/g. The sorbent has shown a great magnetic property. When a permanent magnet is placed near a conical flask, the magnetic sorbents are immediately attracted on the wall. It is demonstrated that the ease in magnetic separation can be achieved in both dry and wet conditions.

The calcium-alginate magnetic particles were exposed to solutions with pH ranging from 1 to 13 for 72 h. It was observed that the sorbent swelled at pH above 11. No significant change in the size was found at pH ranging 1–9. It is thus advisable to avoid using the particles in alkaline conditions.

3.2. Adsorption behavior

The success in preparation of the magnetic particles provides an alternative for the treatment of toxic ionic contaminants in aqueous solutions. A series of adsorption studies was conducted by the sorbent. The model contaminants in the study were arsenic(V) and copper(II) due to their high toxicity in water environment.

3.2.1. Adsorption kinetics

Two adsorption kinetic experiments were performed with the results shown in Fig. 1. Adsorption of arsenic(V) occurs rapidly initially followed by a slightly slower process. The equilibrium can be attained within 25 h, which is much faster than for the sorbents reported for removal of anionic contaminants. The copper adsorption occurs rapidly in the first hour followed by a slightly slow sorption process. The copper adsorption equilibrium time is 3 h which is compatible with many biosorbents [5].

3.2.2. Adsorption isotherms

The adsorption isotherm describes the equilibrium relationship between the adsorbent and the adsorbate. The experimental data of adsorption isothermal study are given in Fig. 2.

Table 1
Operational parameters of electrostatic extrusion for the synthesis of calcium-alginate magnetic particle

Applied voltage	8 kV
Electrode spacing	4 cm
Flow rate	10 mL/min
Needle size	26G 0.5 in. (0.45 mm × 13 mm)