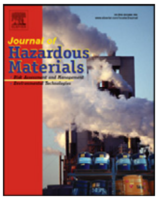
Journal of Hazardous Materials 250–251 (2013) 469–476

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Arsenite adsorption on cryogels embedded with iron-aluminium double hydrous oxides: Possible polishing step for smelting wastewater?

Prashanth Suresh Kumar, Linda Önnby*, Harald Kirsebom

Department of Biotechnology, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

HIGHLIGHTS

- Double hydrous oxides were synthesized as adsorbents and incorporated into cryogels.
- Removal of As(III) was evaluated for smelting wastewater in continuous mode.
- As(III) adsorption was possible without pre-oxidation and pH adjustment.
- Results indicate chemisorption of As(III) on the adsorbents.
- As(III) concentrations reached below the EU emission limit for industrial wastewater.

ARTICLE INFO

Article history:
Received 8 October 2012
Received in revised form 11 February 2013
Accepted 13 February 2013
Available online 20 February 2013

Keywords:
Arsenic
Arsenite
Adsorption
Cryogels
Double hydrous oxides

ABSTRACT

Arsenic is among the most toxic elements and it commonly exists in water as arsenite (As(III)) and arsenate (As(V)) ions. As(III) removal often requires a pre-oxidation or pH adjustment step and it is a challenge to adsorb As(III) at circumneutral pH. In this study, iron-aluminium double hydrous oxides were synthesized and incorporated into cryogels. The resulting composite cryogels were evaluated for As(III) adsorption. Initial experiments indicated that the adsorbent showed similar adsorption kinetics for both As(V) and As(III) ions. The adsorption of As(III) best fit the Langmuir isotherm and the maximum adsorption capacity was 24.6 mg/g. Kinetic modeling indicated that the mechanism of adsorption was chemisorption, making the adsorbent–adsorbate interactions independent of charge and hence allowing the adsorbent to function equally efficient across pH 4–11. A Swedish smelting wastewater was used to evaluate the adsorption performance in continuous mode. The studies showed that the adsorbent was successful in reducing the arsenic concentrations below the European Union emission limit (0.15 mg/l) in a smelting wastewater collected after two precipitation processes. The arsenic removal was obtained without requiring a pH adjustment or a pre-oxidation step, making it a potential choice as an adsorbent for As(III) removal from industrial wastewaters.

1. Introduction

Water contamination from arsenic is a well-known environmental concern which still needs great attention. Arsenic is notoriously known for its toxicity. Apart from causing skin pigmentation, muscular weakness and neurological disorders; chronic exposure is known to cause skin, lung, liver and kidney cancers [1,2]. In aqueous systems, inorganic arsenic predominantly exists as oxyanions of arsenate (H_3AsO_4) and arsenite (H_3AsO_3), having oxidation states of +5 and +3, respectively [3]. Arsenite (As(III)) ions are more mobile and toxic when compared to arsenate (As(V)) ions [4]. The WHO guideline for maximum contaminant level of arsenic in drinking water has been set to 0.01 mg/l [5].

The existence of arsenic is further expressed in certain areas (e.g. Southeast Asia, USA, China, Europe etc.) due to the presence of arsenic in the geological location [3,6–8], where arsenic can be released due to weathering processes [4]. In Sweden, a dominating part of the overall arsenic pollution can be traced to mining and smelting activities which includes the extraction, production and processing of metals–e.g. arsenic is released in the wastewater from extraction of copper [9]. Present treatment technologies for the smelting company relevant to this study include two different precipitation steps, where most existing metal ions are effectively removed. Arsenic, however, still prevails at concentration levels higher than desired (between 1 and 2 mg/l). Therefore, it was suggested that an adsorbent should be developed and added to the existing treatment system as a polishing step, since adsorption is known to be the preferential method of treatment when low arsenic

---

* Corresponding author. Tel.: +46 709 207975/46 222 4818; fax: +46 46 222 47 13.

E-mail addresses: Prashanth.Suresh@biotek.lu.se (P. Suresh Kumar), Linda.Onnby@biotek.lu.se (L. Önnby), Harald.Kirsebom@biotek.lu.se (H. Kirsebom).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.02.022

concentrations are involved [2]. Unlike the arsenic limit for drinking water, the permissible limits of arsenic can considerably differ for industrial wastewater discharges. It is of practical significance that an adsorbent performs well in realistic wastewater conditions, which always offer more challenging conditions that affect the adsorption process. The intention was moreover to possibly reduce the arsenic concentrations below 0.15 mg/l which is the industrial wastewater emission limit (EU framework water directive) set by the European Union [10].

Various metal oxides have been used as adsorbents for arsenic [2,3] and it has often proved more difficult to remove As(III) ions than As(V) ions [11]. This is generally because As(III) has a pKa_1 value of 9.2 and hence is present in the neutral form at circumneutral pH and thus electrostatic attraction with the adsorbents do not occur [12,13]. To overcome this difficulty, alternative methods of As(III) removal have included a pre-oxidation step or a pH adjustment [14,15].

In this study, iron-aluminium double hydrous oxides (Fe-Al particles) were synthesized as adsorbents to remove As(III) from synthetic as well as realistic industrial wastewater conditions. Although iron hydroxides have often been used for arsenic removal [16], the coprecipitation of iron hydroxides and aluminium hydroxides increases the point of zero charge and the surface area of the adsorbent, and it also decreases the dissolution rate of iron from the adsorbent [12]. The Fe-Al particles were prepared using a bi-phase sol–gel method [17] and further incorporated in cryogels (Fe-Al-Cryo). Cryogels are macroporous polymers prepared in solutions at subzero temperatures which can be used for immobilization of particles to enable easier recovery and a possible regeneration of the adsorbents after their use [18]. Cryogels have shown to possess good mass transfer characteristics, enabling solutions of high flow rates to be passed through them with low resistance [19].

Here, the Fe-Al-Cryo was initially used in synthetic solutions of As(III) for preliminary studies regarding adsorption kinetics, adsorption capacities and pH. The adsorbent was further evaluated with two real wastewater samples. Firstly, the adsorption of As(III) was studied in the presence of pre-existing anions from a Swedish municipal wastewater which was spiked with 5 mg/l As(III). Furthermore, wastewater from a Swedish smelting company containing As(III) and other pollutants such as Sb, Hg and Cd, was treated with Fe-Al-Cryo in a continuous mode. The objective of this study is to possibly reduce the As(III) concentration in the smelting wastewater below 0.15 mg/l by using Fe-Al-Cryo without an additional pretreatment step.

2. Materials and methods

2.1. Chemicals

Acrylamide (AAm, >99%); aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$), ammonium persulfate (APS), arsenic trichloride ($AsCl_3$, 99.99%), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), hydrochloric acid (HCl, 37%), *N*,*N*'- methylenebisacrylamide (MBAAm) and *N*,*N*,*N*',*N*'–tetramethylethylenediamine (TEMED) were purchased from Sigma–Aldrich. Sodium hydroxide (NaOH) was bought from Merck. Arsenic atomic absorption standard (1000 μg/ml) and palladium nitrate ($Pd(NO_3)_2$) matrix modifier was obtained from AccuStandard.

2.2. Preparation of double hydrous metal oxides (Fe-Al particles)

The sol–gel particles were prepared with slight modifications of a method previously used [17]. Equimolar concentrations of $FeCl_3{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ (2 M in final suspension) were prepared by adding them to a 1 ml solution of 0.25% aqueous NH_3. An additional amount of 0.4 ml of 25% aqueous NH_3 was added to the mixture which thereafter was stirred thoroughly till a uniform suspension was obtained. The resulting suspension was added drop wise into a biphase system consisting of 25% ammonia and decane in a volume ratio of 1:1. The fine droplets passed through the decane into the 25% ammonia solution to form rigid spherical granules. The granules were thereafter filtered and washed thoroughly with membrane filtered deionized water (hereafter referred to as MQ-water). The filtrate was dried in an oven at 105 °C for 6 h.

The reaction for the adsorbent formation could be generalized as:

$$FeCl_3{\cdot}6H_2O + AlCl_3{\cdot}6H_2O + 6NH_3 + 6H_2O \rightarrow Fe(OH)_3{\cdot}Al(OH)_3 + 6NH_4Cl + 12H_2O \quad (1)$$

The obtained iron-aluminium hydrous oxide particles (Fe-Al particles) were ground and passed through a 106 μm test sieve. A suspension of these particles was observed under an optical microscope and it was observed that 90% of the Fe-Al-particles were less than 6 μm in size, with the maximum particle size being 31 μm (Fig. A1 in supplementary information).

2.3. Preparation of composite cryogel (Fe-Al-Cryo)

A 6% (w/v) monomer mixture was prepared in water by adding AAm: MBAAm in 7:1 molar ratio. Fe-Al particles (4% w/v) were added to this mixture. The solution was purged with nitrogen gas to remove oxygen from the system. APS and TEMED (1% w/w in respect to monomers) were added as the initiator and catalyst, respectively. The samples were prepared as 0.5 ml monoliths in an ethanol bath with polymerization taking place at −12 °C overnight. To minimize settling of Fe-Al particles, which occurs due to the high particle density, the sample tubes were pre cooled for 15 min. A few crystals of silver iodide were added to the tubes before addition of the sample solution. Silver iodide is insoluble and acts as a seed for promoting ice nucleation [20]. The samples were thereafter thawed and washed thoroughly before allowing them to dry overnight in an oven at 105 °C. The resulting composite cryogels were hereafter called Fe-Al-Cryo.

2.4. Characterization of Fe-Al-Cryo

Scanning electron microscopy (SEM) was used to study the distribution of the Fe-Al particles on the cryogel surface. Fe-Al-Cryo was freeze dried in a LABCONCO Lyph-Lock Freeze Dry System. The dried cryogel was cut into 2 mm thick discs. These discs were further sputter-coated with gold/palladium (40/60) and examined using a JEOL JSM-5000LV scanning electron microscope.

The average mass of the incorporated Fe-Al particles into the Fe-Al-Cryo was determined using thermogravimetric analysis (TGA). Fe-Al-Cryo and the plain cryogels (acting as control samples) were analyzed using a Q500 analyzer from TA Instruments. Thin sections of the samples were analyzed under N_2 during heating; initially from 0 to 150 °C for 30 min to evaporate water, and then from 50 to 700 °C to thermally decompose the polymer backbone of the cryogel. Sections from top, middle and bottom part of the Fe-Al-Cryo were analyzed regarding mass loading, the average value was used to determine the mass incorporated and further used as mass of Fe-Al particles per Fe-Al-Cryo in the adsorption studies.

The Brunauer–Emmett–Teller (BET) surface of the samples was calculated from nitrogen adsorption data measured using Micrometrics ASAP 2400 instrument. All the samples were dried and degassed at 21 °C. The BET surface area was calculated in the relative pressure range (P/P_o) of 0.05–0.3.