Chemical Engineering Journal 180 (2012) 159–169

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Lepidocrocite and its heat-treated forms as effective arsenic adsorbents in aqueous medium

Eveliina Repo[a,*], Marko Mäkinen[a], Selvaraj Rengaraj[b,**], Gomathi Natarajan[c],
Amit Bhatnagar[d], Mika Sillanpää[a]

[a] Laboratory of Green Chemistry, Department of Energy and Environmental Technology, Faculty of Technology, Lappeenranta University of Technology, Patteristonkatu 1, FI-50100 Mikkeli, Finland
[b] Department of Chemistry, Sultan Qaboos University, Muscat, Oman
[c] Institute of Physics IA, RWTH Aachen, Sommerfeldstrasse 14, 52074 Aachen, Germany
[d] LSRE – Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto (FEUP), Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:
Received 24 August 2011
Received in revised form
10 November 2011
Accepted 10 November 2011

Keywords:
Adsorption
Arsenic
Lepidocrocite
Metal removal
Water treatment

ABSTRACT

The aim of this study was to investigate the adsorption potential of heat treated lepidocrocites (γ-FeOOH) towards As(III) and As(V) ions in aqueous solutions. Initially, mesoporous lepidocrocite was synthesized, treated at different temperatures, and characterized using various analytical techniques. During the heating, transformation of lepidocrocite into hematite was observed. The adsorption of As(III) and As(V) was studied by batch experiments and the effects of different operational parameters e.g., adsorbent dose, solution pH, contact time, and the initial concentration of As(III)/(V) (isotherms) were studied. Lepidocrocite treated at 250 °C exhibited >99% and 94% adsorption from 50 mg/L As(V) and As(III) solutions, respectively with an adsorbent dose of 2.5 g/L. The highest uptake capacity was obtained for As(III) (55 mg/g) on lepidocrocite without the heat treatment and for As(V) (38 mg/g) on lepidocrocite treated at 250 °C, which was assigned to be a mixture of maghemite and hematite. The adsorption kinetic data fitted well with the pseudo-second-order model and the BiLangmuir isotherm had the best applicability to describe the adsorption equilibrium.

1. Introduction

Arsenic contamination in groundwater and drinking water is one of the worst and the greatest threats to human health. Different forms of arsenic are found to be present in surface and groundwaters [1,2] depending on the pH and oxidation potential of the water [3]. Pentavalent arsenic (also known as arsenate (As(V)) occurs mainly as $H_2AsO_4^-$ at pH 3–7, whereas $HAsO_4^{2-}$ predominates in the pH range of 7–11. Trivalent arsenic (also known as arsenite (As(III)) is present as H_3AsO_3 (pH < 9) and $H_2AsO_3^-$ (pH 9–12). As(V) is more abundant in surface waters, while As(III) is present in groundwaters. Organic forms of arsenic e.g. monomethylarsinic acid (MMA) and dimethylarsinic acid (DMA) also exist, but these organic forms are often less toxic than the inorganic ones [4]. It has been reported that in some lake surface waters, up to 24% of the total amount of arsenic is in methylated forms [5]. Arsenic is classified as carcinogen and poses several health threats including different kinds of cancers and skin diseases [6]. In addition, the more abundant trivalent arsenic form is about 60 times more poisonous than the pentavalent one [7]. It has also been reported that As(III) is more difficult to remove from waters at neutral pH due to the non-ionic nature of the dominant form H_3AsO_3.

Realizing the harmful effects of arsenic on human health, there is an urgent need for its removal from water using an effective and robust technique. An efficient water treatment technology requires both safe and easy operation, high efficiency, and low cost [8]. Various technologies for arsenic removal from aqueous solutions have been examined so far with varying degree of success. Among them, adsorption technology offers satisfactory results because of simple design, easy to operate and removal of some other pollutants/contaminants present in the water being treated besides the target pollutant. The removal of arsenic on iron minerals has been studied extensively as iron oxides seem to be responsible of the attenuation of arsenic. Several iron bearing adsorbents have been tested for the arsenic removal from water including natural [9] and synthetic [10] siderite, goethite [11,12], modified goethite [13], granular ferric hydroxide [14], zerovalent iron fillings [15], iron oxide minerals [16–18], iron-oxide-coated polymers [19], and iron oxide nanoparticles [20,21].

---

* Corresponding author. Tel.: +358 40 355 3707; fax: +358 15 336 013.
** Corresponding author. Tel.: +358 40 355 3707.
E-mail addresses: eveliina.repo@lut.fi (E. Repo), rengaraj@squ.edu.om (S. Rengaraj).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.11.030

Iron oxide minerals are generally formed in natural waters and sediments at oxic–anoxic environment. Initially the solids formed are poorly crystalline with high specific surface area but, over time, transformation of these minerals occurs to form more crystalline forms, such as goethite or hematite. These iron oxides/hydroxides are found to be efficient arsenic adsorbents in natural environments. The interaction between arsenic and mineral surfaces is one of the important limiting factor of mobility and availability of arsenic species in aqueous environments. Various forms of iron oxides/hydroxides e.g. goethite have been studied extensively for arsenic removal. However, fewer reports are available dealing with the arsenic removal from water by other forms of iron minerals such as lepidocrocite. Lepidocrocite, (γ-FeOOH), is the γ form of iron oxyhydroxide, reported to appear during iron oxidation under several environments. It has been found to occur when metallic iron is immersed in aqueous aerated solutions at pH approaching neutral, as well as in atmospheric oxidation. In addition, lepidocrocite is formed when arsenic is removed by electrocoagulation process using iron electrodes [22]. Therefore, arsenic adsorption studies on lepidocrocite are also important. However, arsenic adsorption properties of this form have not been systematically studied. A recent article describes briefly both the synthesis of lepidocorite and the arsenic adsorption onto its surface. The focus of this article, however, was to clarify the anaerobic reduction products of pure and arsenic species of lepidocrocite by *Shewanella putrefaciens* [23].

Recent reviews describe various adsorbents used for arsenic removal from water [24–26]. It is important to note here that many factors may affect the selection of a suitable arsenic adsorbent depending on the adsorbent–adsorbate interaction, thus making the selection a complex task.

The aim of this study was to assess the potential of the synthetic lepidocrocite before and after heat treatment for arsenic (As(III) and As(V)) removal from aqueous solutions. The synthesized samples were characterized by different techniques in order to gain an insight on the physicochemical properties and their role in arsenic adsorption. The adsorption studies were conducted under various experimental conditions, such as solution pH, adsorbent dose and contact time. The data from the experiments were fitted with different equilibrium and kinetic models to identify the adsorption mechanisms. The results have been thoroughly discussed which would help in the better understanding of arsenic adsorption mechanism by the studied adsorbents.

2. Experimental

2.1. Materials

All the chemicals used in this study were of analytical grade and acquired from Merck. Stock solutions of 1000 mg/L were prepared by dissolving appropriate amounts of As(III) and As(V) oxides (As_2O_3 or As_2O_5) at first in 25% NaOH following instant neutralization with 2 M HCl and dilution with deionized water. Sample solutions ranging from 1 to 500 mg/L were prepared from the stock solutions. Adjustment of pH was made with 0.1 M NaOH and 0.1 M HCl.

2.2. Synthesis of lepidocrocite

The lepidocrocite was synthesized according to the procedure reported by Hall et al. [27]. In a typical synthesis, iron(II) chloride tetrahydrate (20 g) was dissolved in deionized water (500 mL). This solution was filtered, and the filtrate was added to a solution of hexamethylene tetramine (urotropin) (28 g) dissolved in deionized water (100 mL). A solution of sodium nitrite (7 g) in deionized water (100 mL) was then added with constant stirring. The mixture was heated to 60 °C and left to stand for 3 h, with occasional agitation. The precipitate formed was then washed with warm water until no chloride ions remained, before being dried at 65 °C. The deep-orange γ-FeOOH was ground with a mortar and pestle until a fine powder was produced. The resulting samples were calcined at different temperatures (120 °C, 250 °C, 350 °C, 450 °C and 550 °C) for 2 h, for further studies. The obtained products were named according to the heat treatment temperature (for example, L-120 denotes lepidocrocite treated at 120 °C).

2.3. Characterization

Autosorb-1-C surface area and pore size analyzer (Quantachrome, UK) was used to determine the surface properties of synthesized lepidocrocites. The Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model were used for specific surface area calculation and porosity measurement, respectively. The morphologies and microstructures were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The structural analysis of the samples was performed using a Bruker (D5005) X-ray diffractometer (XRD) equipped with graphite monochromatized Cu Kα radiation (λ = 1.540, 56 Å). The ratio between Fe and O within the sample was analyzed using an energy-dispersive X-ray spectrophotometer installed in the scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was conducted with a Sigma Probe (ThermoVG, U.K.) X-ray photoelectron spectrometer, of which the source is Al Kα radiation (1.486 eV). The photoemitted electrons from the sample were analyzed in a hemispherical energy analyzer at a pass energy of $E_p = 20$ eV. All spectra were obtained with an energy step of 0.1 eV and a dwell time of 50 ms. A software package (Avantage Thermo VG) was used to analyze the XPS data. Zetasizer Nano Series model ZEN 3600 (Malvern, UK) was employed to measure the isoelectric points of lepidocrocites. These measurements were performed in 1 mM KCl. Fourier transform infrared spectroscopy (FTIR) (Nicolet Nexus 8700, USA) was used to characterize lepidocrocite surfaces before and after arsenic adsorption.

2.4. Batch adsorption studies

Batch experiments were conducted at ambient temperature by varying adsorbent dose (0.5–3 g/L), pH (3–11), contact time (10 min to 48 h), and arsenic concentration (1–500 mg/L). Agitation of the system under investigation was carried out on a rotary shaker type ST5 (CAT M.Zipperer GmbH, Staufen, Germany) with agitation speed of 50 rpm. At the designated time, the adsorbent was separated from aqueous solution using 0.45 μm polypropylene syringe filter.

2.5. Chemical analysis

After dilution with 2% HNO_3, the samples were analyzed by an inductively coupled plasma optical atomic emission spectrometry (ICP-OES) model iCAP 6300 (Thermo Electron Corporation, USA). Changes in the As concentrations due to adsorption were analyzed at wavelength of 189.042 nm. The minimum detectable concentration of As ions by this equipment was 12.7 μg/L. The quantity of the adsorbed metal per unit mass of Lepidocrocite (mg/g) was calculated as follows:

$$q_e = \frac{(C_i - C_e)}{M} V \tag{1}$$

where C_i and C_e are the initial and the equilibrium concentrations (mg/L), while M is the weight of the adsorbent (g) and V is the volume of the solution (L).