Journal of Hazardous Materials 269 (2014) 31–37

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Arsenic removal in a sulfidogenic fixed-bed column bioreactor

Muslum Altun[a,*], Erkan Sahinkaya[b], Ilknur Durukan[a], Sema Bektas[a], Kostas Komnitsas[c]

[a] Hacettepe University, Department of Chemistry, Beytepe, Ankara, Turkey
[b] Istanbul Medeniyet University, Bioengineering Department, Goztepe, Istanbul, Turkey
[c] Technical University of Crete, Department of Mineral Resources Engineering, Chania, Greece

HIGHLIGHTS

- Sulfidogenic treatment of As-containing AMD was investigated.
- High rate simultaneous removal of As and Fe was achieved.
- As was removed without adding alkalinity or adjusting pH.
- As and Fe removal mechanisms were elucidated.

ARTICLE INFO

Article history:
Received 24 August 2013
Received in revised form
13 November 2013
Accepted 21 November 2013
Available online 27 November 2013

Keywords:
Acid mine drainage
Sulfate reduction
Arsenic removal

ABSTRACT

In the present study, the bioremoval of arsenic from synthetic acidic wastewater containing arsenate (As^{5+}) (0.5–20 mg/L), ferrous iron (Fe^{2+}) (100–200 mg/L) and sulfate (2000 mg/L) was investigated in an ethanol fed (780–1560 mg/L chemical oxygen demand (COD)) anaerobic up-flow fixed bed column bioreactor at constant hydraulic retention time (HRT) of 9.6 h. Arsenic removal efficiency was low and averaged 8% in case iron was not supplemented to the synthetic wastewater. Neutral to slightly alkaline pH and high sulfide concentration in the bioreactor retarded the precipitation of arsenic. Addition of 100 mg/L Fe^{2+} increased arsenic removal efficiency to 63%. Further increase of influent Fe^{2+} concentration to 200 mg/L improved arsenic removal to 85%. Decrease of influent COD concentration to its half, 780 mg/L, resulted in further increase of As removal to 96% when Fe^{2+} and As^{5+} concentrations remained at 200 mg/L and 20 mg/L, respectively. As a result of the sulfidogenic activity in the bioreactor the effluent pH and alkalinity concentration averaged 7.4 ± 0.2 and 1736 ± 239 mg $CaCO_3$/L respectively. Electron flow from ethanol to sulfate averaged 72 ± 10%. X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were carried out to identify the nature of the precipitate generated by sulfate reducing bacteria (SRB) activity. Precipitation of arsenic in the form of As_2S_3 (orpiment) and co-precipitation with ferrous sulfide (FeS), pyrite (FeS_2) or arsenopyrite (FeAsS) were the main arsenic removal mechanisms.

1. Introduction

During the processing of gold and other metal ores, arsenic disengagement occurs, due to the oxidation of arsenic bearing minerals [1–3]. Arsenopyrite-bearing sulfide ores and tailings may also be oxidized in a similar way releasing As and sulfate according to the following reaction (R1) [4,5].

$$FeAsS + 3.5O_2 + H_2O \rightarrow Fe^{3+} + SO_4^{2-} + H_2AsO_4^- \quad (R1)$$

The presence of iron oxidizing bacteria, such as *Acidithiobacillus ferrooxidans*, accelerates the rate of arsenopyrite oxidation and the release of As species. The biological iron oxidation at low pH and the chemical dissolution of arsenopyrite are shown in the following reactions (R2) and (R3) [6,7]. Some of the Fe(III) may react with the dissolved arsenate resulting in the precipitation as scorodite, $FeAsO_4{\cdot}2H_2O$ (reaction (R4)) [5].

$$2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{A.\,ferrooxidans} 2Fe^{3+} + H_2O \quad (R2)$$

$$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_4 \quad (R3)$$

$$H_3AsO_4 + Fe^{3+} + 2H_2O \rightarrow FeAsO_4{\cdot}2H_2O + 3H^+ \quad (R4)$$

It has been reported that arsenic concentration ranges between 100 μg/L and 5000 μg/L in acidic leachates generated in areas where mining activities are carried out, while it normally resides between 1 μg/L and 10 μg/L in uncontaminated natural water.

* Corresponding author at: Hacettepe University, Department of Chemistry, Beytepe, Ankara, Turkey. Tel.: +90 4143470820.
E-mail address: muslumaltun@hotmail.com (M. Altun).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.11.047

Although fairly high levels of arsenic concentrations are observed in acid mine drainage (AMD), the highest value reported is 72 mg/L at Zimbabwe Duke mining area [8].

Arsenic contamination of ground- and surface waters due to acid mine drainage (AMD) formation has been reported in many countries, such as Japan, Spain, India, Bangladesh, China, Chile, Argentina, Mexico, Taiwan, Vietnam, United States, and Turkey [5,9].

Due to its potential for combined removal of acidity, metals and sulfate, biological sulfate-reduction appears to be the most promising AMD treatment and metals recovery method. The process is based on biological hydrogen sulfide and alkalinity production by SRB (reaction (R5)):

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (R5)$$

where organic matter (CH_2O) represents the electron donor.

The biogenic hydrogen sulfide results in the precipitation of dissolved metals as low solubility sulfides, as indicated in reaction (R6):

$$H_2S + M^{2+} \rightarrow MS_{(s)} + 2H^+ \quad (R6)$$

where M^{2+} denotes metal, such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} or Fe^{2+}.

Although there are several studies on sulfidogenic AMD treatment, very few studies are available in literature on sulfidogenic arsenic treatment. In the study of Battaglia-Brunet et al. [10] arsenic removal was investigated in a fixed bed sulfidogenic bioreactor in which glycerin or hydrogen gas, as electron sources, and 100 mg/L of As(V) were fed. Results showed that if the reactor is fed with glycerin, very low sulfate removal rates are obtained at pH 5 and the produced sulfide is just sufficient to remove arsenic as As_2S_3. However, when hydrogen gas was introduced in the reactor, sulfide concentration increased and resulted in dissolution of the precipitated As_2S_3. It is known that As_2S_3 may dissolve at high pH and hydrogen sulfide concentration according to reaction (R7):

$$3/2As_2S_3\,(\text{amorphous}) + 3/2H_2S \rightarrow H_2As_3S_6^- + H^+$$
$$\log K = -5.0 \quad (R7)$$

However, the co-presence of Fe and As in AMD may lead to the formation of arsenopyrite (FeAsS) and the removal efficiency of As in a sulfidogenic bioreactor may increase and become possible even at neutral pHs and high concentrations of sulfide [11]. It is also known that the generated FeS may precipitate during sulfidogenic AMD treatment and also adsorb arsenic [12]. Therefore, further studies are required for the sulfidogenic treatment of As containing AMD using highly efficient bioreactors in order to protect drinking water contamination from As.

This study aims at investigating As removal from AMD in a sulfidogenic continuously fed fixed-bed bioreactor. The performance of the bioreactor was investigated in the presence or absence of Fe under varying operating conditions.

2. Materials and methods

2.1. Bioreactor

A laboratory scale glass column with dimensions of 5 cm (diameter) × 30 cm (length) was used as a fixed bed up-flow anaerobic bioreactor (Fig. 1). The column was packed with commercially available sand (particle diameter 1–1.5 mm) as biomass attachment medium (400 mL). The sand was washed with 10% nitric acid followed by rinsing with deionized water to eliminate possible contamination with organic matter which could be attached on the surface of the particles. The bioreactor was inoculated with

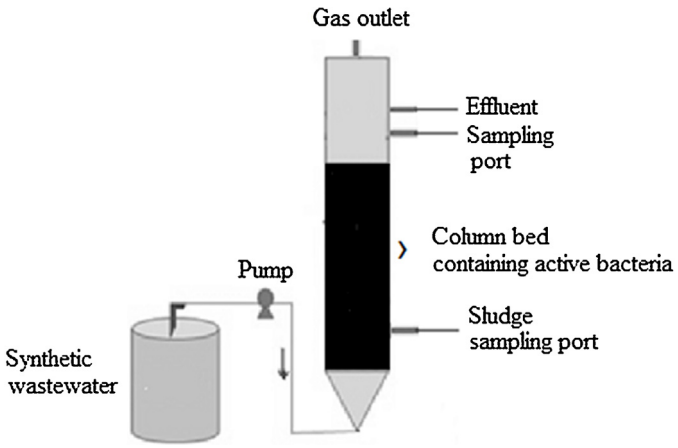

Fig. 1. A laboratory scale fixed bed up-flow anaerobic glass bioreactor with dimensions of 5 cm (diameter) × 30 (length).

50 mL sludge containing active SRB obtained from a sulfate reducing anaerobic baffled reactor [13]. The reactor was covered with aluminum foil to prevent phototrophic bacterial activity. The active bed volume was considered for the calculation of HRT. Throughout the study, synthetic solution was fed to the bioreactor using a peristaltic pump at a flow rate of 1 L/day corresponding to 9.6 h HRT. The reactor was operated in a temperature controlled room at 30–32 °C and the feed container was refrigerated (4 °C) prior to use to prevent bacterial growth.

3. Experimental

The bioreactor operated for 245 days under eight separate operating periods (Table 1) using a synthetic feed containing 1.480 g/L Na_2SO_4, 2.563 g/L $MgSO_4{\cdot}7H_2O$, 56 mg/L KH_2PO_4, 111 mg/L NH_4CI, 11 mg/L ascorbic acid and ethanol as carbon and electron source (1560 mg COD/L). In the first period (0–66 days), As(V) and Fe(II) free influent was fed to the bioreactor in order to enrich the ethanol oxidizing SRB. In the second period, As(V) was supplemented to the synthetic feed and ascorbic acid was excluded from the influent solution in order to prevent As(V) reduction. Stock solution of 1000 mg/L As(V) was prepared using $Na_2HAsO_4{\cdot}7H_2O$ in deionized water. In the periods 2–6, As(V) concentration in the synthetic feed was gradually increased from 0.5 mg/L to 20 mg/L, while the influent pH was kept constant at 4. In the periods 7–9, $FeSO_4{\cdot}7H_2O$ supplemented to the synthetic feed in order to evaluate the impact of Fe presence on As removal under sulfidogenic conditions. In the periods 7 and 8, Fe(II) concentration in the influent was 100 and 200 mg/L, respectively. In these periods the influent pH was decreased to 3.5 using HCl (Table 1). Throughout the study, influent sulfate concentration and HRT were kept constant at 2000 mg/L and 9.6 h, respectively.

Influent and effluent of the bioreactor were sampled once and three times a week, respectively, for sulfate, dissolved sulfide (only in effluent), alkalinity, COD, pH and total As and Fe measurements. All chemicals were purchased from Merck, Germany.

3.1. Analytical methods

Prior to sulfate, dissolved sulfide, COD and total As and Fe measurements, samples were centrifuged at 3000 × *g* for 10 min (HettichRotofix 32) and then filtered using syringe filters (0.45 μm). Sulfate concentration was measured using a turbidimetric method [14]. Total dissolved sulfide concentration was measured using a spectrophotometric method [15]. COD was measured using a micro digestion and subsequent titration method according to APHA and