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Biotreatment of As-containing simulated acid mine drainage using laboratory scale sulfate reducing upflow anaerobic sludge blanket reactor

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ABSTRACT

Heavy metal contamination of water sources can occur from the discharge of acid mine drainage (AMD). This study assessed sulfidogenic treatment of As-, Fe-, Zn-, Ni- and Cu-containing AMD in an upflow anaerobic sludge blanket (UASB) reactor, operated for approximately 500 days. Sulfate reducing granules were successfully enriched with synthetic wastewater and sulfate concentration decreased from 2000 mg/L in the influent to 100–200 mg/L in the effluent. The pH increased from 3–4 to 6–8 as a result of biogenic alkalinity production. Arsenic removal was not detected in the absence of heavy metals, possibly due to the high dissolved sulfide concentration. In the presence of heavy metals, and at low dissolved sulfide concentrations, As removal efficiency increased to 98–100% likely due to the formation of arsenopyrite (FeAsS) or the adsorption of As on metal sulfide precipitates. Fe, Cu, Ni and Zn removal efficiencies approached 99% in the presence of dissolved sulfide. When hydrogen sulfide generation was insufficient to precipitate all of the metals, Fe was detected in the UASB effluent. The results showed that As-, Fe-, Zn-, Ni- and Cu-containing AMD can be effectively treated by sulfate reducing granules in UASB reactors.

1. Introduction

Arsenic may be released into water due to the oxidation of arsenic bearing sulfide minerals during the processing of gold and other metal ores (Azcue and Nriagu, 1995; Smedley et al., 1996; Williams et al., 1996). Arsenopyrite-bearing sulfide ores may be oxidized, releasing As and sulfate according to the following Reaction (1) (Eary, 1992; Gemici et al., 2008).

$$\mathrm{FeAsS} + 3.5\mathrm{O}_2 + \mathrm{H2O} \rightarrow \mathrm{Fe}^{3+} + \mathrm{SO}_4^{2-} + \mathrm{H}_2\mathrm{AsO}_4^- \qquad (1)$$

Iron oxidizing bacteria, such as *Acidithiobacillus ferrooxidans*, can oxidize Fe^{2+} to Fe^{3+} which oxidizes arsenopyrite and releases As species according to Reaction (2) (Komnitsas and Pooley, 1991; Natarajan, 2008).

$$\mathrm{FeAsS} + 13\mathrm{Fe}^{3+} + 8\mathrm{H}_2\mathrm{O} \rightarrow 14\mathrm{Fe}^{2+} + \mathrm{SO}_4^{2-} + 13\mathrm{H}^+ + \mathrm{H}_3\mathrm{AsO}_4 \qquad (2)$$

The released As may contaminate surface and ground waters. Effective technologies are needed to prevent the contamination, which has been reported in many countries, including Japan, Spain, India, Bangladesh, China, Chile, Argentina, Mexico, Taiwan, Vietnam, United States, and Turkey (Herrera et al., 2007). Regulatory agencies have published the maximum contaminant level (MCL) for arsenic in drinking water to protect human health. The World Health Organization (WHO), U.S. Environmental Protection Agency (EPA) and Republic of Turkish Ministry of Health established an allowable limit of 10 μg/L for drinking water (Elcik et al., 2013).

Typical arsenic concentrations in uncontaminated natural waters are between 1 μg/L and 10 μg/L. However, As concentrations in AMD range from 100 μg/L to 72000 μg/L with the highest value reported in Zimbabwe Duke mining area (Williams, 2001).

Due to the potential for combined removal of acidity, metals and sulfate, processes based on biological sulfate-reduction appear to be the most promising (Altun et al., 2014). The process is based on biological hydrogen sulfide and alkalinity production by sulfate reducing bacteria (SRB) (Reaction (3)) and the precipitation of metals with the biogenic hydrogen sulfide (Reaction (4)).

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$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (3)$$

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+ \quad (4)$$

where organic matter (CH_2O) represents the electron donor and M^{2+} denotes the metal, such as Zn^{2+}, Cu^{2+}, Ni^{2+}, or Fe^{2+}. Although there are several studies on sulfidogenic AMD treatment, very few studies are available in the literature on sulfidogenic treatment of As-containing waters (Luo et al., 2008; Battaglia-Brunet et al., 2012; Altun et al., 2014). Therefore, further studies are required to optimize the operation of sulfidogenic bioreactors for the treatment of As-containing AMD in order to protect water contamination by As. Sulfidogenic upflow anaerobic sludge blanket (UASB) reactors have been successfully used for the treatment of acidic metal-containing waters in full scale (de Vegt and Buisman, 1995, 1996; de Vegt et al., 1997, 1998; Boonstra et al., 1999; Kaksonen and Puhakka, 2007). However, the use of sulfidogenic granular bioreactors for the treatment of As-containing AMD has not been extensively explored. This study aimed at investigating As removal from AMD using sulfidogenic granules in an UASB reactor. Also, the removal efficiencies of Fe, Cu, Zn and Ni together with As were investigated under varying operational conditions. Hence, the results of the study may be used for optimizing full scale AMD treatment for As removal.

2. Materials and methods

2.1. Bioreactor

A laboratory scale glass column 30 cm in length with a 6 cm internal diameter was used as an UASB reactor. The reactor was filled with biomass granules obtained from a real scale UASB reactor treating paper industry wastewater. The column was filled with the granules up to half of its height. Total liquid and the granule bed volumes of the bioreactor were 800 mL and 400 mL, respectively. The reactor was covered with aluminum foil to prevent phototrophic bacterial activity. The active bed volume was considered for the calculation of hydraulic retention time (HRT). Throughout the study, synthetic wastewater was fed to the bioreactor using a peristaltic pump to obtain HRT of 0.5 d or 1.0 d (Table 1). The reactor was operated in a temperature controlled room at 30–32 °C and the influent container was refrigerated (4 °C) to prevent microbial growth.

2.2. Experimental set up

The bioreactor was operated for approximately 500 days under nine operating conditions (periods 1–9) (Table 1) using a synthetic influent containing (mg/L): 1480 Na_2SO_4, 2563 $MgSO_4 \cdot 7H_2O$, 56 KH_2PO_4, 111 NH_4Cl, and 11 ascorbic acid and ethanol as both a carbon and electron source (520–1040 mg/L ethanol (10.4–20.8 mmol/L) or 1000–2500 mg as chemical oxygen demand (COD)/L) (Table 1). The reactor was operated in the absence of heavy metals for 120 days to enrich sulfate reducing granules (period 1). In the second period, the influent solution was supplemented with 1 mg/L As(V) in the form of KH_2AsO_4 and its concentration was increased stepwise in the subsequent periods, reaching 5 mg/L in period 4 (Table 1). In period 5, heavy metals (Fe, Cu, Ni and Zn) in sulfate forms were added to the influent to determine their impact on As removal efficiency. In the 6th period, As(V) concentration in the influent was increased to 10 mg/L. In period 7, HRT was increased to 1.0 day to mitigate the heavy metal toxicity to sulfate reducers. In period 8, Fe, Cu, Ni and Zn concentrations in the influent were increased to determine the impact of high concurrent metal concentrations on sulfidogenic As removal. In the last period, the influent COD concentration was decreased to 1000 mg/L to decrease the dissolved sulfide concentration in the bioreactor and to evaluate its impact on As removal. Throughout the bioreactor operation, the influent pH was maintained at 3.0–4.0 (Table 1) using concentrated sulfuric acid.

2.3. Sampling and analytical methods

The UASB influent and effluent were regularly sampled for sulfate, COD, metal (Fe, Cu, Ni and Zn) and metalloid (As) analysis. The effluent samples were also analyzed for pH, alkalinity and dissolved sulfide concentrations. Samples were centrifuged at 3000 g for 10 min (HettichRotofix 32) and then filtered using syringe filters (0.45 μm) prior to sulfate, dissolved sulfide, COD and total As analyses. For total metal analysis, samples were first acidified using concentrated H_2SO_4 to pH below 2 and then filtered using syringe filters (0.45 μm). For soluble metal analysis, samples were first filtered and then acidified. Sulfate concentrations were measured using a turbidimetric method (APHA, 2005). Alkalinity was measured on unfiltered samples by titrating the solution to a pH 4.5 endpoint with 0.1 N HCl (APHA, 2005). The total dissolved sulfide concentrations were measured using a spectrophotometric method (Cord-Ruwisch, 1985). A microdigestion and subsequent titration method was used for the COD measurements (APHA, 2005). Prior to COD measurements, the samples were acidified with concentrated H_2SO_4 and then purged with nitrogen gas for 5 min in order to remove dissolved sulfide. Total arsenic was measured using Perkin–Elmer Analyst 400 graphite furnace atomic absorption spectrometer equipped with a graphite tube atomizer and programmable auto sampler. Fe, Cu, Ni and Zn concentrations were measured using inductively coupled plasma (ICP) combined with atomic emission spectroscopy (AES, Perkin Elmer Optima 5300).

Percent electron flow from ethanol oxidation to sulfate reduction was calculated according to Eq. (5), in which biomass growth was ignored.

Table 1
Hydraulic retention time (HRT) and influent composition of the sulfidogenic upflow anaerobic sludge blanket reactor.

Periods	1	2	3	4	5	6	7	8	9
Time (d)	0–122	122–143	143–185	185–252	252–280	280–330	330–407	407–435	435–472
HRT (d)	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0
pH	3.5–4	3.5–4	3.5–4	3.5–4	3.5–4	3.5–4	3–3.5	3–3.5	3–3.5
Sulfate (mg/L)	2000	2000	2000	2000	2000	2000	2500	2500	3000
COD (mg/L)	2700	2700	2700	2700	2700	2700	2000	2000	1000
COD/Sulfate (mg COD/mg sulfate or mmol ethanol/mmol sulfate)	1.35	1.35	1.35	1.35	1.35	1.35	0.8	0.8	0.33
As(V) (mg/L)	0	1	2	5	5	10	10	10	10
Fe (mg/L)	0	0	0	0	100	130	130	250–300	250–300
Cu (mg/L)	0	0	0	0	10	15	15	30	30
Ni (mg/L)	0	0	0	0	5	10	10	15	15
Zn (mg/L)	0	0	0	0	25	25	25	50	50