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Performance of sulfidogenic anaerobic baffled reactor (ABR) treating acidic and zinc-containing wastewater

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ABSTRACT

The applicability of anaerobic baffled reactor (ABR) was investigated for the treatment of acidic (pH 4.5–7.0) wastewater containing sulfate (1000–2000 mg/L) and Zn (65–200 mg/L) at 35 °C. The ABR consisted of four equal stages and lactate was supplemented (COD/SO_4^{2-} = 0.67) as carbon and energy source for sulfate reducing bacteria (SRB). The robustness of the system was studied by decreasing pH and increasing Zn, COD, and sulfate loadings. Sulfate-reduction efficiency quickly increased during the startup period and reached 80% within 45 days. Decreasing feed pH, increasing feed sulfate and Zn concentrations did not adversely affect system performance as sulfate reduction and COD removal efficiencies were within 62–90% and 80–95%, respectively. Although feed pH was steadily decreased from 7.0 to 4.5, effluent pH was always within 6.8–7.5. Over 99% Zn removal was attained throughout the study due to formation of Zn-sulfide precipitate.

1. Introduction

The exploitation of sulfide minerals results in oxidation of exposed iron and sulfur compounds, and thus, in the production of acidic metal and sulfate-containing wastewaters (e.g. acid mine drainage water (AMD)) (Nagpal et al., 2000a,b; García et al., 2001). Conventionally, hydroxide precipitation is the most commonly applied method for the treatment of metal containing waters. The production of high quantities of sludge is the main disadvantage of the method. Also, sulfate removal is only possible when Ca^{2+} containing chemicals, such as lime, are used for neutralization. However, stringent discharge legislations will dictate more efficient sulfate removal and recovery of valuable metals from waters, which are possible with the use of active bioreactor processes (Kaksonen and Puhakka, 2007).

In the treatment of AMD and metal containing industrial wastewater, sulfate-reducing bioreactors are becoming an alternative to conventional chemical treatment (Kaksonen and Puhakka, 2007; Liamleam and Annachhatre, 2007; Hoa et al., 2007; Costa et al., 2007). With the supplementation of organic compounds, sulfate is microbially reduced to H_2S under anaerobic conditions and heavy metals form stable precipitates with produced H_2S. Moreover, produced bicarbonate increases the pH of the wastewater (Eqs. (1) and (2)). This way, metals and sulfate are concomitantly removed and pH can be increased to neutral values in a single reactor (Eqs. (1) and (2)). The precipitate can be used for metal recovery (Kaksonen et al., 2003).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (1)$$

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

In the literature, several studies have shown that sulfate reducing suspended (Moosa et al., 2002, 2005; Sahinkaya, 2008) and attached growth (Steed et al., 2000; Kaksonen et al., 2003; Sahinkaya et al., 2007; Hoa et al., 2007) bioprocesses can be effectively used for AMD treatment. However, it is well known that with the biofilm type reactors higher removal rates at short hydraulic retention time (HRT) can be achieved compared to suspended growth reactors. For example Kaksonen et al. (2003), showed that at 35 °C fluidized-bed reactor (FBR) treatment of metal-containing wastewater results in almost complete precipitation of Zn and Fe at loading rates of over 600 and 300 mg/L d, respectively. However, accumulation of metal precipitates within biofilm reactors makes metal recovery difficult (Sahinkaya, 2008).

The anaerobic baffled reactor (ABR) is a modification of up-flow anaerobic sludge blanket (UASB) reactor and it is a staged reactor where biomass retention is enhanced by forcing the water flow through several compartments (Kaksonen and Puhakka, 2007). In ABRs, the over and underflow of liquid reduces bacterial washout, which enables it to retain active biological solids without the use of any fixed media. The other significant advantage of ABR is that partial separation of bacteria in different compartments occurs, which prevents most of the biomass to expose adverse environmental

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Table 1
Operational conditions of the reactor.

Parameter	Period I	Period II	Period III	Period IV	Period V	Period VI	Period VII	Period VIII
Days	0–46	46–62	62–91	91–131	131–191	191–244	244–284	284–304
Feed sulfate concentration (mg/L)	1000	1000	1000	2000	2000	2000	2000	2000
Feed Lactate concentration (mg COD/L)	670	670	670	1340	1340	1340	1340	1340
Feed Zn concentration (mg/L)	0	65	130	130	200	200	200	200
Feed pH	6.5–7.0	6.5–7.0	6.5–7.0	6.5–7.0	6.5–7.0	5.5	5.0	4.5

conditions, such as low pH and high metal concentrations (Uyanik et al., 2002a,b; Vossoughi et al., 2003). Vossoughi et al. (2003) studied the performance of ABR at COD/SO_4^{2-} ratios of 16.7–6. They reported that methanogenic archeae (MA) and sulfate reducing bacteria (SRB) can coexist in the same reactor and COD removal efficiency slightly increased with increasing sulfate concentration. The maximum sulfate-reduction efficiency was 86–97% and at high sulfate concentrations, the conversion efficiency in the first compartment was low and most of the sulfate was reduced in the following compartments. Although several studies have shown that ABRs are very effective in anaerobic wastewater treatment and biomass granulation (Uyanik et al., 2002a,b; Sallis and Uyanik 2003; She et al., 2006), few studies (Barber and Stuckey, 2000; Vossoughi et al., 2003) have explored its sulfate-reduction potential. Also, the potential of ABRs for the biotreatment of sulfate and metal-containing wastewaters has not been studied (Kaksonen and Puhakka, 2007).

The dissolved organic carbon content of metal-containing wastewater is very low and usually <10 mg/L (Johnson, 2000). Therefore, addition of a suitable carbon source and electron donor for sulfate reduction is necessary to promote biogenic H_2S production. SRB utilize several low molecular weight substrates, such as lactate, formate, acetate, ethanol and hydrogen. Some SRB oxidize organic substrates completely to CO_2, while others incompletely to acetate (Widdel, 1988). It is well known that lactate is a good substrate for most SRB and it can be used in bioreactor applications for the treatment of sulfate and metal-containing wastewaters (e.g. AMD) (Kaksonen et al., 2003).

Hence, this study aims at evaluating lactate-fed ABR potential for the biotreatment of acidic, Zn- and sulfate-containing synthetic AMD. To our knowledge, this is the first study on AMD treatment using a sulfidogenic ABR.

2. Methods

2.1. Bioreactor

A laboratory scale ABR was inoculated with an effluent of a full scale anaerobic digester located in Gaziantep, Turkey. Before inoculation, the sludge was sieved to remove coarse materials. The ABR was 20 cm wide, 80 cm long, 20 cm deep and constructed from glass, with a working volume of 20 L. Reactor was divided into four equal 5 L compartments by vertical baffles, each compartment having down-comer and riser regions created by further vertical baffle. The lower parts of down-comer baffles were angled at 45° in order to direct the flow evenly through the riser (Uyanik et al., 2002a,b). This produced effective mixing and contact between the feed and sulfate reducing bacteria (SRB) at the base of each riser. Each compartment was equipped with sampling ports that allowed drawing biological sludge, and liquid samples. To maintain anaerobic conditions, the sampling ports of the reactor and the fittings were sealed after inoculation. The reactor was maintained at 35 °C using a heater fan in a cabin. The produced methane gas was measured using gas-liquid displacement method and a safety bottle was used to avoid the vacuum of NaOH to the reactor. HRT was kept constant at 2 days throughout the study. To do this, the synthetic wastewater (pH 4.5–7.0 and 2000 mg/L sulfate) containing 2563 mg/L $MgSO_4 \cdot 7H_2O$; 1479 mg/L Na_2SO_4; 56 mg/L KH_2PO_4; 110 mg/L NH_4Cl; 11 mg/L Ascorbic acid, 50 mg/L yeast extract and 1340 mg COD/L lactate was fed to the reactor at a rate of 10 L/day. The composition of AMD may show great variation (Johnson, 2003) and we aimed to simulate a moderately acidic and Zn containing AMD. Lactate, which is one of the best organic source for SRB (Liamleam and Annachhatre, 2007; Kaksonen et al., 2003) was used as a carbon and electron source stoichiometrically to reduce sulfate to hydrogen sulfide and oxidize lactate completely to CO_2 and H_2O. Hence, throughout the study COD/SO_4^{2-} ratio was kept at 0.67. The feed solution was prepared daily. COD removal, Zn precipitation and sulfate reduction was not observed in the feed container.

2.2. Experimental procedure

The reactor performance was investigated at different feed organic, sulfate and Zn loadings for 304 days (Table 1). Firstly, the reactor was fed with an alkaline solution containing 1000 mg/L SO_4^{-2} without Zn (Period I, days 0–46) to enrich SRB. Then, the reactor performance was investigated at increased Zn, sulfate and organic loadings (Table 1) with decreasing pH.

The reactor feed, each compartment, and the effluent were sampled 3–4 times in a week for the measurement of pH, alkalinity, total volatile fatty acids (VFA), chemical oxygen demand (COD), sulfate, dissolved sulfide, and soluble Zn.

2.3. Analytical techniques

Before the measurement of sulfate, dissolved sulfide, soluble Zn and COD, samples were centrifuged using Hettich Rotofix 32 centrifuge at 4000 rpm for 10 min. Before centrifugation for sulfide measurement, the pH was increased to around 10 with 1 M NaOH and glass sample tube was sealed using a Teflon crimp cap not to cause any loss of sulfide. Total sulfide was analyzed spectrometrically using a Shimadzu UV-1601 Spectrophotometer following the method described by Cord-Ruwisch (1985). A turbidimetric method was used to measure sulfate concentrations. COD and alkalinity were also measured according to Standard Methods (APHA, 1999). Before COD measurements, sample pH was decreased to below 2 with concentrated H_2SO_4 and the sample was purged with N_2 gas around 5 min to remove H_2S from the sample. Total VFA concentration was measured following the procedure described by Alvarez et al. (2007). For soluble Zn measurements sample was first filtered through 0.45 μm polyethersulfone membrane syringe filters and then acidified with concentrated HCl to pH below 2. For total Zn concentration measurements, samples were first acidified with concentrated HCl to solubilise Zn particles. Then, samples were filtered through 0.45 μm to remove biomass and other particles. Zn concentration was measured with an atomic absorption spectrophotometer (Varian AA 140). Panalytical Axios-Advanced wavelength dispersive X-ray fluorescence spectrometer (XRF) was employed to analyze the elemental composition of sludge samples