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Sulfidogenic fluidized bed treatment of real acid mine drainage water

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ABSTRACT

The treatment of real acid mine drainage water (pH 2.7–4.3) containing sulfate (1.5–3.34 g/L) and various metals was studied in an ethanol-fed sulfate-reducing fluidized bed reactor at 35 °C. The robustness of the process was tested by increasing stepwise sulfate, ethanol and metal loading rates and decreasing feed pH and hydraulic retention time. Highest sulfate reduction rate (4.6 g/L day) was obtained with feed sulfate concentration of 2.5 g/L, COD/sulfate ratio of 0.85 and HRT of 12 h. The corresponding sulfate and COD removal efficiencies were about 90% and 80%, respectively. The alkalinity produced in sulfidogenic ethanol oxidation neutralized the acidic mine water. Highest metal precipitation efficiencies were observed at HRT of 24 h, the percent metal removal being over 99.9% for Al (initial concentration 55 mg/L), Co (9.0 mg/L), Cu (49 mg/L), Fe (435 mg/L), Ni (3.8 mg/L), Pb (7.5 mg/L) and Zn (6.6 mg/L), and 94% for Mn (7.21 mg/L).

1. Introduction

Metal-containing acid mine drainage (AMD) is created by the interaction of air and water with sulfides, such as pyrite (FeS_2), found in overburden piles and also in mine shafts consisting of sub-commercial grade mining material left over from the mining operations.

Other sulfide minerals are oxidized in a similar way as pyrite, releasing metals and sulfate in solution and therefore, AMD may contain several metals such as Cu, Fe, Zn, Al, Pb, As and Cd at high concentrations. AMD is acidic in nature and generally has low organic carbon content. If uncontrolled, AMD flows into local streams, lakes and rivers, contaminating soils and destroying plant and animal biota. The formation of acidic wastewaters can continue even tens and hundred years after mine closure if the conditions remain favorable (Szczepanska and Twardowska, 1999).

Sulfate reducing bioreactors are becoming an alternative to conventional chemical processes for the treatment of acidic and metal-containing wastewaters due to high efficiency (Sahinkaya, 2009). In the presence of organic compounds, sulfate is microbially reduced to hydrogen sulfide under anaerobic conditions and heavy metals (especially, Cu, Pb, Zn, Cd, Ni and Fe) form stable precipitates with the produced sulfide. Moreover, produced bicarbonate increases the pH of the wastewater. This way, metals and sulfate are concomitantly removed and pH can be increased to neutral values in a single reactor (Kaksonen et al., 2003a,b; Nagpal et al., 2000a,b).

Ethanol is a good substrate for sulfate reducing bacteria and suitable for large scale applications (Kaksonen et al., 2003a; Nagpal et al., 2000a). Under sulfidogenic conditions, ethanol is first converted to acetate and in the second step acetate may further be oxidized to CO_2. In this case, acetate oxidation is obligatory to produce alkalinity (reactions (1) and (2)) as the first step (conversion of ethanol to acetate) does not produce alkalinity (Sahinkaya, 2009). Some SRB oxidize organic substrates completely to CO_2, while others incompletely to acetate (Sahinkaya, 2009). It is well known that acetate may accumulate in the reactor at high loadings, which may decrease the sulfide and alkalinity production (Kaksonen et al., 2004; Sahinkaya and Yucesoy, in press; Bayrakdar et al., 2009). Hence, in the case of ethanol supplementation, the loading rate should be carefully adjusted not to accumulate acetate and cease alkalinity production:

$$2CH_3CH_2OH + SO_4^{2-} \rightarrow 2CH_3COO^- + HS^- + H^+ + 2H_2O \qquad (1)$$

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \qquad (2)$$

Most of the studies on the treatment of metal-containing wastewater using bioreactor processes have been conducted with synthetic AMD water containing few metals for the sake of simplicity, whereas, real AMD may contain a number of metals, which makes biotreatment of real AMD more challenging. In this context, this study aims at evaluating the efficiency of an ethanol supplemented sulfidogenic fluidized bed reactor (FBR) for the treatment of real AMD water containing high concentrations of sulfate and various metals, and high acidity.

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2. Methods

2.1. Bioreactor

A laboratory scale FBR (Fig. 1) inoculated with anaerobic digester effluent was used in the study. Concentrated anaerobic digester effluent was injected to the reactor to have an initial volatile suspended solids content of 1 g in the FBR. After the injection of the anaerobic consortia, the reactor was run in recirculation mode for 2 days without feeding to let the biomass to attach on the carrier material. The FBR was maintained in a temperature controlled room and operated at about 35 °C. The active bed volume of the FBR was 300 mL. Activated carbon (particle size range of 0.5–1 mm) was used as biomass carrier and bed fluidization was 15–20%. During the reactor operation of around 220 days, we did not observe significant abrasion of the media due to inter-particle collision caused by liquid flow. For both reactors, the recirculation flow rate was between 60 and 70 mL/min, giving the recirculation ratio of 150–300 depending on the feed flow rate. The reactor can be considered as completely mixed due to high recirculation rate. Similarly, Chung et al. (2006) stated that a recirculation ratio of 150 promoted completely mixed conditions.

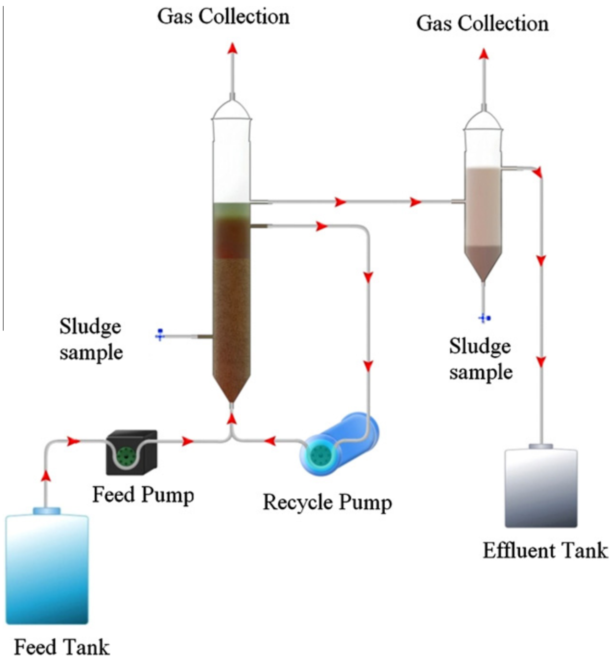

Fig. 1. Schematic diagram of fluidized bed reactor.

The FBR was fed with AMD water collected from a copper mine area near Elazığ, Turkey. The AMD water was collected three times (between August 2009 and May 2010) during around one year to determine the variation in the composition and to study the robustness of the FBR.

Ethanol was supplemented as a carbon and electron source for sulfate reducing bacteria (SRB). For the first 64 days (period 1), as a start-up strategy, the FBR was fed with a metal deficient synthetic wastewater containing 2000 mg/L sulfate to enrich sulfate reducing bacteria (SRB) (Table 1). After start-up (period 1), in period 2, the FBR was fed with AMD1 to adapt SRB to the real AMD as AMD1 was the most dilute AMD. The pH and sulfate concentrations and metal concentrations of the AMD1, 2 and 3 were presented in Tables 1 and 2, respectively. In periods 3 and 4, the FBR was fed with AMD2, which was the most concentrated AMD. In order to see the impact of COD/sulfate ratio on the reactor performance, COD/sulfate ratio was kept at 0.67 and 0.85 during

Table 1
Operational conditions of FBR.

Parameter	Periods						
	1	2	3	4	5	6	7
Days	0–64	64–74	74–100	100–134	134–163	163–188	188–220[a]
Feed	Synthetic	AMD1	AMD2	AMD2	AMD3	AMD3	Simulated AMD2
Feed sulfate (mg/L)	2000	1500	3360	3360	2500	2500	3500
Feed ethanol (mg COD/L)	1340	1005	2180	2900	1950	2150	2975
COD/sulfate	0.67	0.67	0.67	0.85	0.78	0.85	0.85
HRT (h)	24	24	24	24	16	12	24
Feed pH	6.5–7	4.3	3.04	3.04	2.7	2.7	3

[a] Except for days 191–196 when metal deficient water was used to recover the FBR.

Table 2
Average influent metal concentrations (mg/L) for each period.

Periods	Days		Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
2 (AMD 1)	64–74	Conc.	0.16	236	0.002	2.19	0.03	3.98	2.27	1.89	368	6.48	10.69	0.77	0.99	3.01
		Stdv.	0.01	3	0.00	0.30	0.01	0.30	0.20	0.12	7	1.10	1.20	0.05	0.02	0.30
3 (AMD 2)	74–100	Conc.	55.36	120	0.01	9.05	0.09	45.48	435	19.54	366	7.21	13.11	3.79	7.48	6.64
		Stdv.	0.17	2	0.01	0.48	0.05	1.03	49	0.37	0.10	2.61	1.04	0.13	3.37	0.83
4 (AMD 2)	100–134	Conc.	53.05	111	0.01	8.26	0.08	49.17	354	18.35	368	5.23	9.91	3.66	4.93	5.27
		Stdv.	3.13	4	0.01	0.66	0.04	2.90	14	1.11	4	0.37	0.73	0.17	ND	0.31
5 (AMD 3)	134–163	Conc.	39.40	122	0.00	5.34	0.07	38.47	164	16.58	248	3.72	9.28	2.50	ND	3.90
		Stdv.	2.26	7	0.00	0.08	0.01	1.06	19	1.32	16	0.03	0.01	0.03	ND	0.17
6 (AMD 3)	163–188	Conc.	44.98	116	0.00	6.01	0.18	39.69	139	15.85	245	2.97	13.73	1.69	5.39	2.57
		Stdv.	1.70	5	0.01	0.17	0.08	0.90	5	0.41	25	1.68	2.20	1.43	4.63	2.20
7 (AMD 2)	188–220*	Conc.	17.61	48	0.00	7.11	0.10	45.65	260	26.23	253	6.86	13.04	3.52	9.01	7.43
		Stdv.	28.37	72	0.01	0.88	0.08	3.16	88	9.70	9	2.24	ND	0.70	0.54	2.88

* Except for days 191–196 when metal deficient water was used to recover the FBR.

periods 3 and 4, respectively, by varying ethanol concentration. During periods 5 and 6, AMD3 was fed to the reactor. Ethanol was supplemented to have COD/sulfate ratios 0.78 and 0.85 during periods 5 and 6, respectively. Hydraulic retention time (HRT) kept at 24 h in the beginning of the study was decreased to 16 and 12 h in periods 5 and 6, respectively. Lastly in period 7 synthetic wastewater simulating the most concentrated AMD (AMD2) was fed to the reactor to study the robustness of the process at an HRT of 24 h (Table 1).

2.2. Analytical techniques

The feed solution was sampled once a week and the FBR liquid samples were periodically drawn from the recycle line of the FBRs. Before the measurements of sulfate, chemical oxygen demand (COD), acetate, soluble metals and sulfide, the samples were centrifuged at 3000*g* for 10 min using Hettich Rotofix 32 centrifuge. 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 (APHA, 1999). COD and alkalinity were also measured according to Standard Methods (APHA, 1999). Before COD measurements, sample pH was decreased below 2.0 with concentrated H_2SO_4 and the sample was purged with N_2 gas around 5 min to remove H_2S from the sample. For metal measurements sample was first filtered through 0.45 μm polyethersulfone membrane syringe filters and then acidified with concentrated HCl to pH around 1.0. For total metal concentration measurements, samples were first acidified with concentrated HCl, then, samples were filtered through 0.45 μm to remove biomass and other particles. Metal concentrations were measured with an Inductively Coupled Plasma (ICP) combined with atomic emission spectroscopy. All measurements were done at least in duplicate. Mean values and standard deviations were presented.

Electron flow from ethanol oxidation to sulfate reduction was calculated assuming 0.67 mg COD is required to reduce 1.00 mg sulfate based on reactions (1) and (2). The following equation was used in the electron flow calculations;

$$\%\ \text{Electron flow} = 100[0.67(\text{SO}_{4,0} - \text{SO}_{4,\text{e}})]/(\text{COD}_0 - \text{COD}_\text{e}) \qquad (3)$$

where, $SO_{4,0}$ and $SO_{4,e}$ are influent and effluent sulfate concentrations (mg/L), and COD_0 and COD_e are influent and effluent COD concentrations (mg/L), respectively.

3. Results and discussion

3.1. Sulfate reduction and COD oxidation

Time course variations of influent and effluent sulfate concentrations and removal efficiency were presented in Fig. 2. In the first period, the FBR was fed with a metal deficient synthetic wastewater containing 2000 mg/L sulfate. The COD/sulfate ratio was kept at 0.67. The effluent sulfate concentration decreased linearly until day 50 reaching around 300 mg/L corresponding to 85% sulfate reduction. Similarly, sulfate reduction rate increased linearly and reached about 2 g/L day at the end of first period (Fig. 3). Unlike sulfate, COD removal started with high efficiency and during period 1 averaged 95% (Fig. 2).

In period 2, the most dilute real AMD water (AMD1) was fed to the reactor to adapt the microorganisms. The AMD1 contained 1500 mg/L sulfate and relatively lower metal concentrations and lower acidity compared to AMD2 and AMD3 (Tables 1 and 2). Ethanol was externally supplied to have COD/sulfate ratio of 0.67 (Table 1). During this period, sulfate and COD removal efficiencies were close to 85% and 97%, respectively. In period 3, the most concentrated AMD water (AMD2) was fed to the reactor. The AMD2 was characterized by low pH (around 3), high sulfate (3400 mg/L) and high metal concentrations (around 450 mg/L Fe). In period 3, feed COD/sulfate ratio was kept at a stoichiometric value of 0.67. The sulfate reduction efficiency decreased to around 70% and effluent sulfate concentration increased to around 1000 mg/L (Fig. 2) in period 3. In the period 4, the feed COD/sulfate ratio was increased to 0.85 and as a result the sulfate reduction

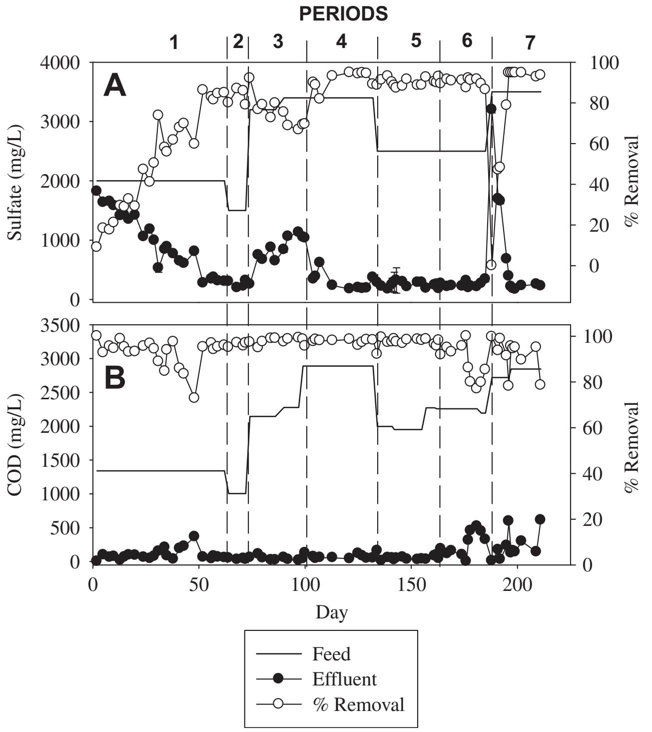

Fig. 2. Feed and effluent sulfate and COD concentrations and % removal in sulfidogenic FBR treating mine water.

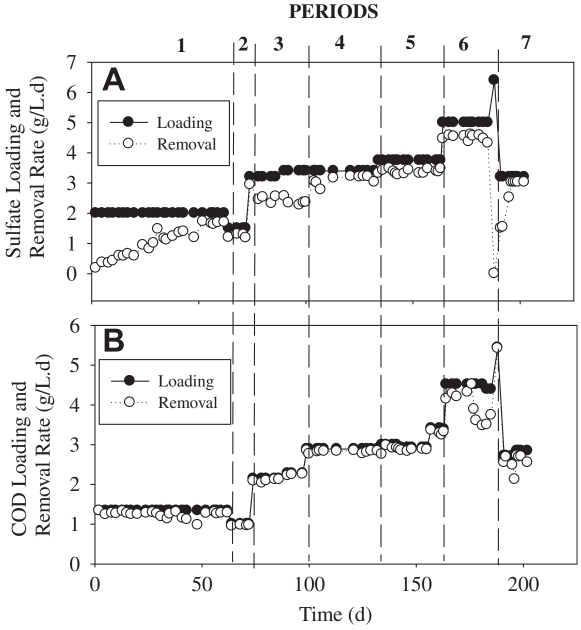

Fig. 3. Sulfate and COD loading and removal rates in sulfidogenic FBR treating mine water.

Table 3
Average effluent soluble metal concentrations (mg/L) for each period.

Periods	Days		Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
2 (AMD 1)	64–74	Conc.	0.07	189	0.00	0.05	0.08	0.11	0.57	27.82	325	2.85	54.17	0.01	0.02	0.21
		Stdv.	0.04	51	0.00	0.04	0.05	0.08	0.31	11.17	170	3.10	26.56	0.01	0.02	0.09
3 (AMD 2)	74–100	Conc.	0.06	121	0.00	0.01	0.05	0.02	0.46	19.60	240	3.23	23.25	0.00	0.02	0.04
		Stdv.	0.05	32	0.00	0.03	0.03	0.04	0.23	3.98	46	1.58	14.44	0.01	0.02	0.06
4 (AMD 2)	100–134	Conc.	0.06	109	0.00	0.00	0.00	0.00	0.28	17.97	379	0.30	11.21	0.00	0.00	0.00
		Stdv.	0.01	10	0.00	0.00	0.00	0.00	0.06	1.75	65	0.38	1.07	0.00	0.01	0.00
5 (AMD 3)	134–163	Conc.	0.14	120	0.00	0.00	0.00	0.00	0.31	18.22	278	0.35	10.30	0.00	0.00	0.00
		Stdv.	0.14	7	0.00	0.00	0.01	0.00	0.07	1.75	17	0.06	0.26	0.01	0.00	0.00
6 (AMD 3)	163–188	Conc.	0.20	115	0.01	0.02	0.02	0.03	0.11	15.52	265	1.14	12.63	0.03	0.05	0.52
		Stdv.	0.02	6	0.00	0.00	0.00	0.01	0.37	0.45	10	0.15	0.71	0.01	0.01	0.38
7 (AMD 2)	188–220*	Conc.	0.23	106	0.01	0.02	0.03	0.03	0.71	29.11	284	1.03	12.56	0.03	0.06	0.98
		Stdv.	0.22	87	0.00	0.00	0.01	0.01	1.15	11.04	30	0.09	0.23	0.01	0.01	0.94

* Except for days 191–196 when metal deficient water was used to recover the FBR.

efficiency increased to around 90%. Similarly, sulfate reduction rate increased with increasing feed COD/sulfate ratio (Fig. 3). During this period COD removal efficiency was also quite high and close to 97% (Figs. 2 and 3). Therefore, increasing COD/sulfate ratio had a positive effect on sulfate reduction efficiency. According to previous studies the yield coefficient of SRB was between 0.05 and 0.15 mg volatile suspended solids (VSS)/mg sulfate reduced (Kaksonen et al., 2003a,b; Sahinkaya, 2009). Due to biomass growth on COD, less COD was available for sulfate reduction. Additionally, sulfate reducers may compete with methanogenic archaea and fermetative bacteria. Hence, it is not surprising to observe higher sulfate reduction efficiency at slightly higher than stoichiometric COD/sulfate ratio of 0.67.

In period 5, AMD3 was fed to the reactor. As the sulfate concentration of AMD3 was lower than AMD2, the HRT of the reactor was decreased from 24 to 16 h in period 5. Hence, in period 5 the sulfate loading rate (3.75 g/L day) was slightly higher than that of period 4 (3.36 g/L day) (Fig. 3). The COD loading rates in the periods 4 and 5 were kept constant at 2.9 g/L day. Hence, the COD/sulfate ratio in period 5 was 0.78 (Table 1). In period 5, the sulfate and COD removal efficiencies were about 90% and 95%, respectively, corresponding to about 3.4 and 2.8 g/L day sulfate and COD removal rates, respectively (Fig. 3). In period 6, the COD/sulfate ratio increased to 0.85 and HRT was decreased to 12 h giving sulfate and COD loadings of 5 and 4.3 g/L day, respectively (Fig. 3). In this period, the sulfate reduction efficiency did not change and was around 90%. However, COD removal efficiency decreased from 95% (period 5) to around 80%, possibly due to the shorter HRT used. The highest sulfate reduction rate of 4.6 g/L day was observed during period 6. The maximum sulfate reduction rate in an ethanol-fed fluidized bed reactor treating synthetic AMD was reported as about 4 g/L day (Kaksonen et al., 2003a, 2004). In another study, Sahinkaya and Yucesoy (in press) reported the maximum sulfate reduction rate as around 3 g/L day in an anaerobic baffled reactor treating Cu and Zn containing synthetic AMD. Hence, the sulfate reduction rate in the real AMD treating FBR was slightly higher than those observed in bioreactors treating synthetic AMD water.

Lastly in period 7, a synthetic AMD simulating AMD2 was fed to the FBR to study the robustness of the process. Between days 188 and 191, the HRT of the FBR was 12 h giving sulfate loading rate of 7 g/L day. At such a high loading rate and low pH (3), the reactor performance sharply decreased and sulfate reduction efficiency decreased to less than 5% (Figs. 2 and 3). Similarly, sulfide concentration decreased to around zero (Fig. 4). In order to recover the process, between days 191 and 196, a synthetic metal deficient wastewater (pH 7.0 and 3500 mg/L sulfate) was fed to the reactor with an HRT of 24 h. During this period, the reactor quickly recovered and both sulfate and COD removal efficiencies reached to around 95%. On day 197, synthetic wastewater simulating AMD2 with pH of 3.0 was fed to the reactor at an HRT of 24 h. Between days 197 and 211, the sulfate reduction rate reached to about 95%. Hence, HRT should be around 24 h to efficiently treat AMD2.

In the present study, no efforts were made to determine whether sulfate reduction follows zero or first order kinetics. However, the data obtained by Kaksonen et al. (2004) with an ethanol-fed sulfidogenic FBR indicate that the sulfate reduction would not follow zero order kinetics as the relationship between sulfate reduction rate and HRT was not linear. Sulfate reduction rate likely depends on several variables, such as sulfate, ethanol, dissolved sulfide and biomass concentrations and pH.

3.2. Alkalinity and sulfide production

According to reactions (1) and (2), sulfidogenic oxidation of ethanol to acetate does not produce alkalinity and acetate oxidation is

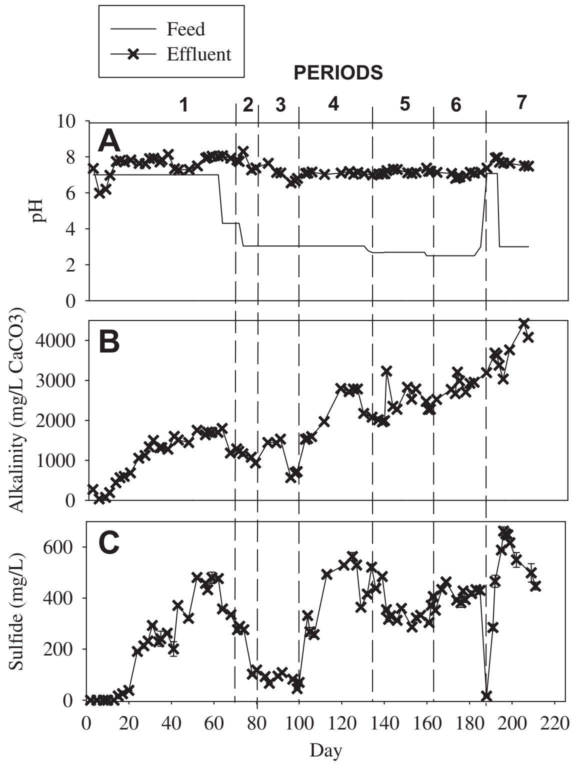

Fig. 4. Feed and effluent pH, and effluent alkalinity and dissolved sulfide concentrations in sulfidogenic FBR treating mine water.

necessary to produce sufficient alkalinity to increase the pH of AMD to neutral values. Alkalinity and pH variations for the feed and effluent of the FBR were as illustrated in Fig. 4. The effluent pH of the reactor was close to 8.0 throughout the reactor operation although the feed pH was decreased to about 3.0 after period 3. The effluent alkalinity increased with increasing sulfate loading and decreasing metal loads (Figs. 2 and 3 and Table 2).

For the first 20 days, dissolved sulfide was not detected in the FBR although sulfate reduction occurred at low efficiencies (Figs. 2 and 4). The reason of that was the adsorption of sulfide by activated carbon used as carrier material (Xiao et al., 2008). After day 20, sulfide concentration increased sharply reaching 500 mg/L. In period 3, sulfide concentration decreased to lower than 100 mg/L with the feeding of AMD2. The reason of this decrease was due to high metal concentration in AMD2 and low sulfate reduction efficiency during period 3 as discussed previously. Sulfide concentration increased sharply in period 4 with the increase of sulfate reduction efficiency and remained between 400 and 500 mg/L for the rest of the period 4. The sulfide concentration transiently dropped to zero on day 188 due to increased sulfate loading rate to 7 g/L day. After the FBR recovered, sulfide concentration increased to about 600 mg/L. The high sulfide and alkalinity production shows that FBR suits well for the treatment of acidic metal- and sulfate-containing wastewater.

3.3. Electron flow to sulfate reduction

Until day 30, methane production was observed in the FBR. Hence, much of the electrons produced from COD oxidation were utilized for methane production during the FBR start-up. The reason of ceasing methane production after the start-up period was likely due to the increased concentration of dissolved sulfide as it is more toxic to methanogenic archaea compared to sulfate reducers (Hulshoff Pol et al., 1998). Until day 20, dissolved sulfide concentration was very low and thereafter it sharply increased and reached about 200 mg/L on day 30 (Fig. 4C). The electron flow from ethanol oxidation to sulfate averaged 75 ± 14% (Fig. 5). The rest of electrons were most probably used for fermentative reactions and biomass growth as previous studies (Sahinkaya, 2009; Kaksonen et al., 2004) showed that 0.05–0.15 mg VSS was produced/mg sulfate reduced depending on reactor configuration and operational conditions. Similarly, Bayrakdar et al. (2009) and Sahinkaya and Yucesoy (in press) reported that the percent electron flow to sulfate reduction was slightly higher than 85% in sulfidogenic ABR. Sahinkaya (2009) reported this value as 83% in a sulfidogenic continuously stirred tank reactor (CSTR) treating acidic and Zn-containing wastewater. Kaksonen et al. (2004) reported the average electron donor utilized for sulfate reduction as 76 ± 10% in a mesophilic ethanol-fed FBR.

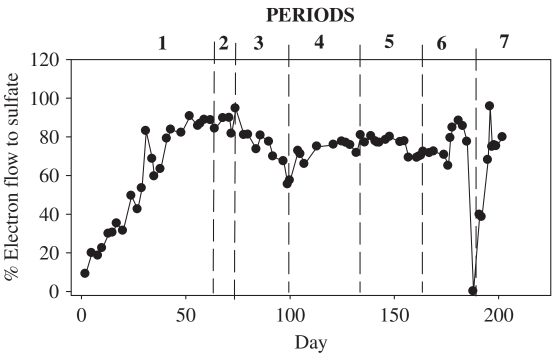

Fig. 5. Percent electron flow from ethanol oxidation to sulfate reduction in sulfidogenic FBR treating mine water.

3.4. Metal removal

Average influent, effluent soluble and effluent total metal concentrations were as presented in Tables 2–4, respectively. The concentrations of Ca, K, Mg and Na in the influent and effluent did not change appreciably throughout the reactor operation. During periods 3 and 4, the influent metal concentrations were very high due to the AMD2 feeding. Al, Co, Cu and Fe concentrations were quite high compared to other heavy metals. Although influent metal concentrations showed variation depending on the AMD being fed to the reactor, the effluent soluble and total heavy metal concentrations were quite low and the removal efficiencies were generally higher than 99% (Tables 3 and 4). Table 5 shows the average effluent soluble and total metal concentrations throughout the reactor operation. Results showed that quite low metal concentrations were obtained in the effluent of the reactor. Total effluent concentrations of Al, Cr, Fe and Ni were to some extent higher than those of soluble metal concentrations. This indicates difficulties in the settling of these metal–sulfide precipitates. The total and soluble effluent concentrations of Cd, Cu, Mn, Pb and Zn were quite similar.

The average effluent concentrations of Al, Fe, Mn and Zn were higher than those of many other metals (Table 5). This is likely due to higher solubility products (K_{sp}) of Al, Fe, Mn and Zn sulfides compared to those of e.g. the Cd, Cu and Pb sulfides (Table 5). The solubility products of Ni and Co sulfides are in the same range as Zn sulfides and vary depending on the form of the metal sulfide. The results of the present study are in agreement with our previous study, where we observed that the anaerobic baffled reactor

Table 4
Average effluent total metal concentrations (mg/L) for each period.

Periods	Days		Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
3 (AMD2)	74–100	Conc.	17.09	106.34	0.01	0.77	0.40	0.05	7.19	17.97	232.20	3.27	20.55	0.52	0.03	2.45
		Stdv.	28.61	13.58	0.01	1.41	0.72	0.06	1.60	0.80	38.32	1.11	17.86	0.96	0.03	4.23
4 (AMD2)	100–134	Conc.	5.11	54.78	0.00	0.07	0.01	0.00	3.35	16.26	349.94	0.28	11.07	0.06	0.00	0.63
		Stdv.	10.72	19.97	0.00	0.16	0.03	0.00	2.07	0.95	67.28	0.50	2.38	0.15	0.01	1.27
5 (AMD3)	134–163	Conc.	2.58	66.41	0.00	0.02	0.00	0.00	5.73	16.34	275.10	0.23	9.41	0.02	0.00	0.11
		Stdv.	1.13	19.78	0.01	0.01	0.00	0.00	3.02	1.51	66.20	0.14	0.47	0.03	0.00	0.07
6 (AMD3)	163–188	Conc.	1.70	69.47	0.01	0.04	0.03	0.03	2.71	12.97	216.85	0.81	10.83	0.06	0.06	0.23
		Stdv.	1.18	0.55	0.01	0.03	0.02	0.03	2.11	0.91	17.18	0.30	1.36	0.05	0.04	0.12
7 (AMD2)	188–220[a]	Conc.	1.67	96.26	0.01	0.07	0.04	0.10	6.31	22.43	243.87	1.06	11.23	0.08	0.08	0.24
		Stdv.	1.16	88.01	0.00	0.05	0.01	0.17	4.80	7.47	27.42	0.54	0.81	0.03	0.03	0.24

[a] Except for days 191–196 when metal deficient water was used to recover the FBR.

Table 5
Average soluble and total effluent metal concentrations throughout the reactor operation, the discharge standards given by Turkish Water Pollution Control Regulation (TWPCR), and solubility products for various metal sulfides and hydroxides (Dean, 1999).

	Soluble effluent (mg/L)	Total effluent (mg/L)	TWPCR for 2-h composite samples (mg/L)	Solubility product (mol/L)	
				S^{2-}	OH^-
Al	0.13 ± 0.07	5.63 ± 6.56		2×10^{-7}	1.3×10^{-33}
Cd	0.00 ± 0.00	0.01 ± 0.00	0.2[a]	8.0×10^{-27}	7.2×10^{-15}
Co	0.02 ± 0.02	0.19 ± 0.32		4.0×10^{-21} (α-CoS) 2.0×10^{-25} (β-CoS)	5.9×10^{-15}
Cr	0.03 ± 0.03	0.10 ± 0.17	2		2×10^{-16}
Cu	0.03 ± 0.04	0.04 ± 0.04	5	6.3×10^{-36}	2.2×10^{-20}
Fe	0.41 ± 0.22	5.06 ± 1.94	3	6.3×10^{-18}	4.9×10^{-17}
Mn	1.13 ± 1.25	1.48 ± 1.26		2.5×10^{-10} (MnS amorphous) 2.5×10^{-13} (MnS crystalline)	1.9×10^{-13}
Ni	0.01 ± 0.02	0.15 ± 0.21		3.2×10^{-19} (α-NiS) 1.0×10^{-24} (β-NiS) 2.0×10^{-26} (γ-NiS)	5.5×10^{-16}
Pb	0.03 ± 0.02	0.03 ± 0.03	0.5	8.0×10^{-28}	1.4×10^{-15}
Zn	0.73 ± 0.39	0.73 ± 0.98	3	1.6×10^{-24} (α-ZnS) 2.5×10^{-22} (β-ZnS)	3×10^{-17}

[a] For 24 h composite sample.

effluent Zn concentration was always higher than Cu concentration (Sahinkaya and Yucesoy, in press). The solubility product of Al sulfide is relatively high (2×10^{-7}), compared to that of Al hydroxide (1.3×10^{-33}) (Dean, 1999), indicating that Al may have precipitated in the FBR as hydroxide rather than sulfide. The removal of Mn was the most difficult compared to other heavy metals. The removal efficiency varied between 55% and 94% (Table 6). The solubility products of Mn sulfides (2.5×10^{-13}–2.5×10^{-10}) and Mn hydroxide (1.9×10^{-13}) are relatively high. Average values of FBR effluent metal concentrations were compared with the discharge values given by Turkish Water Pollution Control Regulation (TWPCR) (Table 5). Almost all effluent metal concentrations were lower than the discharge standards given by TWPCR. However, total effluent Fe concentration exceeded the values given by TWPCR. In general, the sulfidogenic FBR was quite efficient in removing heavy metals from the real AMD.

Table 6
Average percent removal of soluble and total heavy metals throughout the FBR operation.

	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7
Removal effciencies for soluble metals						
Al	56.56	99.88	99.89	99.65	99.55	98.70
Co	97.59	99.87	100.00	99.95	99.74	99.78
Cu	97.30	99.96	100.00	100.00	99.92	99.93
Fe	74.73	99.89	99.92	99.81	99.92	99.73
Mn	55.93	55.28	94.26	90.57	61.59	85.01
Ni	98.45	99.92	100.00	99.88	98.08	99.04
Pb	98.18	99.74	99.92	ND	99.12	99.32
Zn	93.02	99.34	100.00	100.00	79.91	86.85
Removal effciencies for total metals						
Al		69.12	90.37	93.45	96.23	90.50
Co		91.51	99.18	99.64	99.33	99.04
Cu		99.90	100.00	100.00	99.92	99.77
Fe		98.35	99.05	96.51	98.05	97.57
Mn		54.74	94.74	93.77	72.65	84.63
Ni		86.24	98.23	99.17	96.51	97.74
Pb		99.60	99.90	ND	98.90	99.15
Zn		63.13	88.07	97.05	90.95	96.76

The maximum Fe, Cu and Al precipitation rates were observed in period 3 as 7.8, 0.8 and 2.0 mmol/L day, respectively. The maximum total metal removal rate was slightly higher than 11 mmol/L day. Nevatalo et al. (2010) reported Fe and Zn precipitation rates as 11 and 1 mmol/L day, respectively, in a sulfidogenic FBR. Similarly, Lakaniemi et al. (2010) reported the highest Fe and Zn precipitation rates as 15 and 0.22 mmol/L day, respectively. In another FBR study, Sahinkaya and Gungor (2010) reported the Cu and Zn precipitation rates as slightly higher than 3 mmol/L day.

4. Conclusions

This work demonstrates that ethanol-fed sulfidogenic FBR process efficiently removes sulfate, metals and acidity from real acid mine drainage water. Highest sulfate reduction rates (4.6 g/L day) were obtained with feed sulfate concentration of 2.5 g/L, COD/sulfate ratio of 0.85 and HRT of 12 h. The corresponding sulfate and COD removal efficiencies were about 90% and 80%, respectively. The electron flow from ethanol oxidation to sulfate reduction averaged 75 ± 14%. The alkalinity produced in sulfidogenic ethanol oxidation neutralized the acidic mine water. Highest metal precipitation efficiencies were observed at the longest tested HRT (24 h) and highest COD/sulfate ratio (0.85), the percent metal removal being over 99.9% for Al, Co, Cu, Fe, Pb and Zn, and 94% for Mn.

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