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Research article

Down-flow fixed-structured bed reactor: An innovative reactor configuration applied to acid mine drainage treatment and metal recovery

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ABSTRACT

A down-flow fixed-structured bed reactor (DFSBR) was operated for 277 days treating a mixture of synthetic substrates simulating an iron-rich acid mine drainage (AMD) and the soluble fraction of a sugarcane vinasse. The synthetic sugarcane vinasse was used as electron donor for biological sulfate-reduction, resulting in influent chemical oxygen demand (COD) close to 4000 mg L^{-1} and volumetric organic loading rate of 4.8 g $L^{-1}d^{-1}$. The influent sulfate concentration was kept close to 2000 mg L^{-1} (volumetric sulfate loading rate of 2.5 g $L^{-1}d^{-1}$) while a gradual increase of iron concentration (2−400 mg L^{-1}) was applied. COD removal efficiencies were higher than 93% and the sulfate removal efficiencies were close to 100%. With the highest iron concentration (400 mg L^{-1}) applied, the DFSBR achieved 95% of iron removal efficiency. The precipitate collected at the reactor bottom showed increasing concentrations of fixed suspended solids (FSS), as well as an increasing proportion of iron, indicating the possibility of metal recovery from the system. The association between sulfidogenic and methanogenic processes also enables energy recovery from the methane-rich biogas produced.

1. Introduction

Mining activities are often associated with producing large volumes of acid mine drainage (AMD), which occurs when metal sulfides (usually pyrite – FeS_2) from rocks and mine tailings are exposed to oxygen and surface water (Johnson and Hallberg, 2005). The oxidation of these reduced minerals (Equation (1)) gives the AMD its low pH values and high concentrations of sulfate, dissolved metals and other toxic elements (Akcil and Koldas, 2006). When AMD is discharged into the environment it can severely affect the quality of water bodies, soils, aquatic life and human health (Chen et al., 2014).

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2H^+ \quad (1)$$

The most commonly used method for treating AMD is based on chemical neutralization (e.g., lime addition) resulting in the precipitation of metal hydroxides (Johnson and Hallberg, 2005). However, its application has been characterized by the following drawbacks: high operational costs, large solid generation and hard waste disposal (García et al., 2001).

On the other hand, the biological process carried out by sulfate reducing bacteria (SRB) under anaerobic conditions has become a suitable alternative for AMD treatment, since an external organic source is previously supplied (Kaksonen and Puhakka, 2007). Some of the advantages of this bioprocess pathway are alkalinity generation and metal sulfide precipitation (Ucar et al., 2011; Gallegos-Garcia et al., 2009). However, the insoluble metal sulfides produced can also be separated from the liquid phase by appropriate strategies (Johnson and Hallberg, 2005), making the sulfidogenic treatment of AMD an attractive alternative from an economic and environmental point of view.

Different reactor configurations have been tested for metal precipitation in the biological treatment of AMD (Kaksonen and Puhakka, 2007). Conventional single stage reactors (e.g., UASB and fixed-bed reactors) enable the precipitation of insoluble

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sulfides, but these cannot be effectively separated from the biomass or the carrier material (Villa-Gomez et al., 2011). In a long-term operation, the accumulation of metal sulfides on the biofilm surface could impair the bioprocess performance (Utgikar et al., 2002).

Reactors with two or more stages allow the segregation of sulfide production and metal precipitation in separate chambers. This configuration enables the selective recovery of metals by recirculating the effluent liquid or the sulfide-rich biogas (Jiménez-Rodríguez et al., 2009; Ucar et al., 2011; Xingyu et al., 2013). However, the gradients of sulfide in the bulk liquid, caused by its localized injection, may result in the formation of smaller particles with poor settling characteristics than those obtained in one-stage reactors, where a homogeneous sulfide concentration can be reached (Sánchez-Andrea et al., 2014; Esposito et al., 2006; Veeken et al., 2003a,b).

Another configuration for the precipitation and recovery of metals in the AMD treatment is the down-flow fluidized bed reactor, or inversed fluidized bed reactor (Celis-Garcia et al., 2007). In this configuration the support material floats to the top of the reactor and the bed fluidization is obtained by the recirculation of the effluent downward. During the process the insoluble sulfides are dragged to the bottom of the reactor, from which they can be removed (Sahinkaya and Gungor, 2010; Gallegos-Garcia et al., 2009). A drawback of this design is the high recirculation flow rates required for the continuous fluidization of the bed, which can reach up to about 600 times the influent flow rate (Gallegos-Garcia et al., 2009).

In this context, this study evaluates the down-flow fixed-structured bed reactor (DFSBR) for AMD treatment and metal recovery. This configuration was recently presented for continuous biohydrogen production (Anzola-Rojas and Zaiat, 2016). The maintenance of a free cross-sectional area in the bed structure prevents excessive biomass accumulation (Mockaitis et al., 2014). Moreover, the downward flow mode, the effluent recirculation ratio and the settling zone, without material support at the bottom of the reactor, are strategies that can also increase the potential of the system for the separation of metal sulfides.

Furthermore, a synthetic wastewater composed of different organic compounds found in the sugarcane vinasse (carbohydrate, alcohol, organic acids and phenol) (Bustamante et al., 2008; Parnaudeau et al., 2008) was chosen as electron donor for the SRB metabolism. In fact, a mixture of different carbon sources has been considered as a more favourable approach for the different groups of microorganisms involved in the sulfate reduction (Neculita et al., 2007; Liamleam and Annachhatre, 2007; Zagury et al., 2006; Waybrant et al., 1998).

2. Materials and methods

2.1. Reactor configuration

A down-flow fixed-structured bed reactor (Fig. 1) with total volume of 1.9 L and effective volume of 1.7 L (including the water level equalizer) was operated at hydraulic retention time (HRT) of 20 ± 1 h and an influent flow rate (Qi) close to 87 mL h^{-1}. The reactor was kept at controlled temperature (30 °C) throughout the entire experimental period (277 days). An effluent recirculation ratio (Qr/Qi) equal to 100 was used to increase the superficial flow velocity ($\upsilon_S = 3.5$ m h^{-1}), promoting mixed conditions and the drag forces of the metal sulfides to the reactor's conical-shaped bottom. The fixed-structured bed consisted of four vertical columns containing 13 low-density polyethylene rings (25 mm diameter and 30 mm length) (Fig. 2).

2.2. Synthetic wastewater

The reactor was fed with a synthetic effluent simulating the mixture of an AMD and the soluble fraction of a diluted (1:5) sugarcane vinasse, which was based on real vinasses characterized by Alves (2015), Longo (2015) and Fuess (2017). The synthetic vinasse was used as carbon source and electron donor for the SRB metabolism (Gonçalves et al., 2007). The pH of the synthetic medium was adjusted to 6.0 with a concentrated (12 mol L^{-1}) NaOH solution. To simulate the sulfate concentration resulted from the addition of an AMD, the organic medium was complemented with Na_2SO_4 (3 g L^{-1}). To avoid iron oxidation and precipitation in the feed tank, a concentrated solution of $FeCl_2 \cdot 4H_2O$ (42 g L^{-1}) was dosed in the influent line to achieve the gradual increase in iron concentration (2–400 mg Fe L^{-1}). Table 1 presents the final composition of the synthetic medium utilized. Table S1 (Supplementary Material) provides complete information about the stock solutions and its dosage utilized in the preparation of the synthetic vinasse. The substrate was supplemented with additional micronutrients (Adapted from Torres, 1992) and vitamin solution (Touzel and Albagnac, 1983) (Table S2, Supplementary Material).

2.3. Experimental design

Inoculation of the support material was performed with biomass from an up-flow anaerobic sludge blanket reactor (UASB) treating poultry slaughterhouse effluent. The procedure applied consisted of an adapted method based on Zaiat et al. (1994). The granules from the UASB reactor were crushed in a blender and mixed with the synthetic medium (proportion of 1:5 in volume). The reactor was filled with the liquid obtained and allowed to stand for 24 h. Next, the system was loaded with 5 L of diluted medium (COD influent = 2000 mg L^{-1} and COD/sulfate ratio = 1.0) and kept in a batch recycling mode for 7 days. After this time, the COD influent was raised to 4000 mg L^{-1} and the continuous operation was started.

The COD/sulfate ratio was kept close to 2.0 throughout the experimental period. The reactor was subjected to COD and sulfate volumetric loading rates of 4.8 g $L^{-1}d^{-1}$ and 2.5 g $L^{-1}d^{-1}$, respectively. The iron (Fe^{2+}) concentration was gradually increased from 2 mg L^{-1} (phase I) to 50 mg L^{-1} (phase II), 100 mg L^{-1} (phase III), 200 mg L^{-1} (phase IV) and 400 mg L^{-1} (phase V). Therefore, in the phases II, III, IV and V, the applied Fe/S ratios were 0.075, 0.15, 0.30 and 0.60, respectively. During the phase I, the iron was introduced (2 mg Fe^{2+} L^{-1}) only to provide the nutritional requirements for anaerobic biomass.

To remove the precipitated metal sulfides from the settling zone, the conical bottom of the reactor was purged monthly during phases I to IV. In the last step (phase V) the purge frequency was increased to weekly, in order to prevent the saturation of the reactor's settling zone and the significant losses of suspended metal sulfides in the effluent. 500 mL of the reactor's internal liquid was discharged in each purge. To avoid the contact of biomass support material with air for long periods, the volume lost in the purge was quickly replaced by 500 mL of a neutralized (pH = 7.0) synthetic medium.

2.4. Analytical procedures

COD, pH, alkalinity, solids and sulfate were determined according to Standard Methods (APHA, 2005). The samples for iron measurement were extracted in a 1 mol L^{-1} HCl solution and analysed by the Ferrozine method (Viollier et al., 2000). Volatile fatty acids were determined by gas chromatography (Adorno et al., 2014). The biogas production was measured by a Ritter