



Biochemical passive reactors for treatment of acid mine drainage: Effect of hydraulic retention time on changes in efficiency, composition of reactive mixture, and microbial activity



Yaneth Vasquez ^{a, b}, Maria C. Escobar ^b, Carmen M. Neculita ^c, Ziv Arbeli ^b, Fabio Roldan ^{b, *}

^a Departamento de Ciencias Naturales, Universidad Central, Cra. 5 No. 21-38, Bogotá, Colombia

^b Unidad de Saneamiento y Biotecnología Ambiental (USBA), Departamento de Biología, Pontificia Universidad Javeriana, Cra. 7 No. 40-62, Bogotá, Colombia

^c Canada Research Chair on Passive Treatment of Contaminated Mine Water, Research Institute on Mines and Environment (RIME), University of Quebec in Abitibi-Temiscamingue (UQAT), 445 Boulevard de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

HIGHLIGHTS

- Biochemical passive treatment represents a sustainable approach for treating acid mine drainage.
- Hydraulic retention times had a strong influence in the sulfate-reducing bacteria and dehydrogenase activity.
- Long hydraulic retention time (4 d) generated higher alkalinity and excess residual sulfides in the effluent.
- The hydraulic retention time strongly influenced performance of biochemical passive reactors.

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ABSTRACT

Biochemical passive treatment represents a promising option for the remediation of acid mine drainage. This study determined the effect of three hydraulic retention times (1, 2, and 4 days) on changes in system efficiency, reactive mixture, and microbial activity in bioreactors under upward flow conditions. Bioreactors were sacrificed in the weeks 8, 17 and 36, and the reactive mixture was sampled at the bottom, middle, and top layers. Physicochemical analyses were performed on reactive mixture post-treatment and correlated with sulfate-reducing bacteria and cellulolytic and dehydrogenase activity. All hydraulic retention times were efficient at increasing pH and alkalinity and removing sulfate (>60%) and metals (85–99% for Fe²⁺ and 70–100% for Zn²⁺), except for Mn²⁺. The longest hydraulic retention time (4 days) increased residual sulfides, deteriorated the quality of treated effluent and negatively impacted sulfate-reducing bacteria. Shortest hydraulic retention time (1 day) washed out biomass and increased input of dissolved oxygen in the reactors, leading to higher redox potential and decreasing metal removal efficiency. Concentrations of iron, zinc and metal sulfides were high in the bottom layer, especially with 2 day of hydraulic retention time. Sulfate-reducing bacteria, cellulolytic and dehydrogenase activity were higher in the middle layer at 4 days of hydraulic retention time. Hydraulic retention time had a strong influence on overall performance of passive reactors.

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1. Introduction

The major type of contaminated effluent generated by the mining industry is acid mine drainage (AMD), which originates

from prolonged exposure of sulfide ores to air and water (Nordstrom et al., 2015). First, there is formation of sulfuric acid and progressive acidification of water, which then dissolves metals in the rock, resulting in low pH and high metal and sulfate loading. These characteristics make AMD responsible for physical, chemical, and biological degradation of aquatic habitats and surrounding soil quality (Adams et al., 2014).

* Corresponding author.

E-mail address: fabio.roldan@javeriana.edu.co (F. Roldan).

A sustainable approach to remediate AMD-impacted water is to use biochemical passive reactors (BPRs), which are columns filled with mixtures of organic and inorganic substrates, referred to as “reactive mixture”. BPRs have potential advantages, such as low costs, ability to work in remote areas, use of recycled or waste organic materials, and natural appearance (Adams et al., 2014). Because diverse contaminants, specific environments, and locally available substrates require appropriate design of BPRs, laboratory testing is still necessary (Gusek, 2008). This is usually performed through testing in columns to determine the effectiveness of the treatment and select essential design parameters, including hydraulic retention time (HRT) and the composition of reactive mixtures (Adams et al., 2014). The HRT has a direct influence on the performance of BPRs (Younger et al., 2002; Neculita et al., 2008a). Flow velocity, which determines the HRT, plays an important role in the overall activity of microorganisms in the reactors. Very short HRT may not allow adequate time for bacteria activity to neutralize acidity and precipitate metals or may result in biomass being washed out of the reactor (Neculita et al., 2007). Very long HRT may deplete the substrate or build up bacterial growth and mineral precipitates that eventually lead to low hydraulic conductivity and short-circuiting of the treatment system (Younger et al., 2002).

To date, the effect of the HRT on the efficiency of BPRs has been studied with a focus on metal-removing efficiencies, mainly in iron-rich AMD (Chang et al., 2000; Neculita et al., 2008a). Performance of these systems in the treatment of AMD, characterized by high sulfate concentrations with low metal loading, has not yet been addressed.

The key parameter in an efficient BPR is the activity of sulfate-reducing bacteria (SRB), because they reduce sulfates to sulfides, which then react with dissolved heavy metals to form solid metal sulfides that are immobilized in the reactor. Although SRB metabolism conducts the sulfate reduction reaction, these bacteria rely on activity of anaerobic cellulolytic and fermentative bacteria to break down complex organic materials, such as cellulose, to provide them with available carbon and energy sources (Pruden et al., 2007). Therefore, the cellulose and dehydrogenase enzymes can be used as indicators of general microbial activity in anaerobic systems (Serra-Wittling et al., 1995). However, there are limited data available related to the changes in microbial activity under different HRTs in the long-term operation of BPR, under laboratory conditions.

The composition of reactive mixture changes during the life of BPRs by precipitation of oxy-hydroxide, carbonate, and sulfide minerals (Neculita et al., 2007). Metals extracted during the acid-volatile sulfide (AVS) process are known as simultaneously extracted metals (SEM) and the molar ratios of both (i.e. SEM/AVS) indicate which are the predominant metal removal mechanisms. When this ratio is ≤ 1.0 , it indicates that metals are mainly present as solids in the form of sulfide minerals, whereas at ratio > 1.0 , the oxy-hydroxide and carbonate minerals are predominant (Di Toro et al., 2005). Although the SEM/AVS molar ratio can provide valuable information on reactor efficiency and metal removal mechanisms in AMD, limited data is available about the influence of HRT on the potential mobility of metals in the reactive mixture evaluated after sacrificing the reactor (post-treatment) (Neculita et al., 2008b).

The main objective of this study was to measure the effect (temporal and spatial) of HRT (1, 2 and 4 days) on the efficiency of BPRs for the treatment of sulfate-rich AMD. In addition, the correlation between microbial activity (cellulolytic and dehydrogenase) and physicochemical characteristics of the reactive mixture after treatments was determined.

2. Materials and methods

2.1. Passive reactors: set-up, operation, and sampling

Seven 5 L laboratory reactors were constructed using acrylic columns (73 × 10 cm) and acrylic caps at both ends. The bottom cap contained a valve used as an influent port for AMD, and the top cap contained a double valve: one for collecting treated AMD and another for instantaneous sampling of effluent. The columns were packed, using the procedure described by Neculita et al. (2008a) and Song et al. (2012). Briefly, each column was filled with the same reactive mixture, consisting of 15% cow manure, 10% mushroom compost, 25% sajo sawdust, 15% gravel, 20% limestone, and 15% wetland sediment as inoculum (dry weight in % w/w); this was slightly compacted in layers of 10 cm. This reactive mixture (components and proportions) was selected because was found highly efficient for treating synthetic AMD in batch testing (Vasquez et al., 2016). The reactive mixture was sandwiched in the reactor between two porous plates coated with a fine geotextile (25 mesh), with a 7 cm layer of gravel (0.6–1.0 cm) at the bottom influent port and a 3 cm layer of gravel at the top effluent port to prevent loss of organic matter and clogging. Finally, the columns were sealed and saturated with synthetic AMD prepared according to the maximum concentrations for metals and sulfate found in real effluent quality data found at five active mine sites in the Zipaquirá Mining District, Colombia (Vasquez et al., 2016). The synthetic AMD, which was prepared weekly (Zagury et al., 2006), had the following composition (in mg L⁻¹): 201 ± 44 Fe²⁺; 30 ± 2 Mn²⁺; 19 ± 2 Zn²⁺; 215 ± 11 Ca²⁺; 128 ± 13 Mg²⁺ and 2500 ± 105 SO₄²⁻, at pH 3.0–3.7.

After the packing procedure, the columns were wrapped in aluminum foil to exclude light and prevent growth of phototrophic bacteria (Waybrant et al., 2002; Neculita et al., 2008a). The columns remained at room temperature in the dark for two weeks. During this acclimation period, 20 mL samples were collected twice weekly, from the top port and tested until favorable conditions for SRB (pH 5–8, ORP < -100 mV) prevailed (Postgate, 1984). Following acclimation, continuous upward flow of synthetic AMD was started, with three columns at a flow rate of 0.74 mL min⁻¹ (for 2-day HRT), and four columns at a flow rate of 0.37 mL min⁻¹ (for 4-day HRT). Continuous flow was maintained for 36 weeks, using precision peristaltic pumps (Masterflex L/S, Cole-Parmer, Vernon Hills, IL), which were calibrated prior to starting the tests. After 17 weeks, a strong increase of soluble sulfide concentrations in treated effluents from the columns with 4-day HRT was recorded. These results justified the decision to change one of the reactors from 4-day HRT to 1-day HRT, at a flow rate of 1.48 mL min⁻¹. Columns were sacrificed throughout the study to monitor the changes in the post-treatment reactive mixture and microbial activity. Four columns, two of 2-day HRT and two of 4-day HRT, were sacrificed at weeks 8 and 17. The other three columns (one each of 1, 2, and 4-day HRT) were analyzed at the end of the study (36 weeks). The reactive mixture from the sacrificed columns was removed in three cores (20 × 10 cm), one from the bottom (at 0–20 cm), one from the middle (at 20–40 cm), and one from the top (at 40–60 cm). Each sample was homogenized and refrigerated at 4 °C until analyzed.

2.2. Effect of the hydraulic retention time on efficiency of biochemical passive reactors

To determine the effects of HRT on the efficiency of reactors for increasing pH and alkalinity, as well as promoting reduction of sulfates and metals during treatment of AMD, 50 mL effluent was collected with a syringe each week from the valve located at the top cap of each column. The pH and redox potential (ORP) were immediately measured with a multi-parameter probe (HI 9828,

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