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Performance of two differently designed permeable reactive barriers with sulfate and zinc solutions

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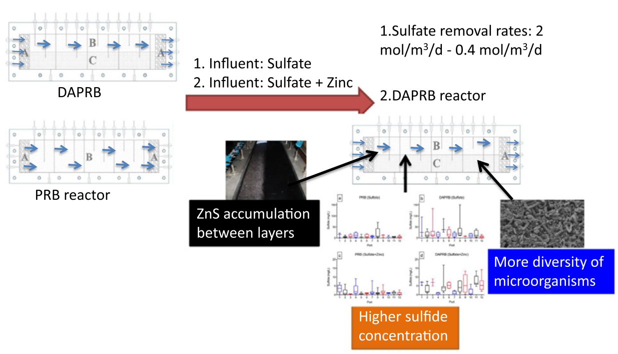
HIGHLIGHTS

- The diffusion active PRB (DAPRB) holds promise for groundwater bioremediation.
- The DAPRB is a layered permeable reactive barrier design that bioprotects bacteria.
- In the DAPRB layer interface, the sulfide reacts by forming complexes with zinc.
- Chemical gradients confirm that the DAPRB provides bioprotection to microorganisms.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, this laboratory-scale study evaluates the feasibility of incorporating diffusive exchange in permeable reactive barriers. In order to do this, the performance of two permeable reactive barriers (PRB) with different internal substrate arrangements were compared during the administration of a sulfate solution without metals (for 163 days) and with metals (for 60 days), simulating groundwater contaminated with acid mine drainage (AMD). In order to simulate a traditional PRB, a homogeneous distribution was implemented in the first reactor and the other PRB reactor utilized diffusion-active technology (DAPRB). In the DAPRB, the distribution of the reactive material was interspersed with the conductive material. The measurements in the internal ports showed that transverse gradients of sulfide formed in the DAPRB, causing the diffusion of sulfide from the substrate toward the layer interface, which is where the sulfide reacts by forming complexes with the metal. The DAPRB prevents the microorganisms from direct contact with AMD. This protection caused greater activity (sulfide production).

1. Introduction

Acid mine drainage (AMD) is a global problem that occurs in areas of mining activity, mainly associated with residual rock deposits (Nordstrom et al., 2000; Blowes et al., 2003). The intrusion of oxygen and water in these deposits causes the oxidation of sulfur containing

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minerals, which triggers the release of sulfates, metals and protons that contaminate surface water and aquifers (Benner et al., 1999; Nordstrom et al., 2000; Akcil and Koldas, 2006).

In order to prevent environmental impacts of AMD, it is necessary to treat the drainage through either passive or active technologies; the latter being characterized by a high consumption of energy and chemical reagents. When AMD volumes are high, which generally occurs during the operating phase of projects, active neutralizing solutions such as lime slurry are used (e.g., the High-Density Sludge process), or membrane filtration. Passive solutions, which are characterized by promoting AMD contact with reactive material (organic residues and mainly limestone) in porous beds with low gravitational flow, are generally considered in the closure phase of projects, low flux environments, or remote places that are difficult to access. Compared with active systems, there are benefits such as low operating and maintenance costs, reduced use of chemicals and minimal energy consumption (Sheoran et al., 2010; Kaksonen and Puhakka, 2007; Fitch, 2015).

When AMD comes into contact with the bed particles in passive treatment systems, chemical and/or biochemical reactions take place that remove sulfates, immobilize metals and neutralize acidity. Particularly, in biological passive systems, the reactive bed is mainly constituted of organic material (generally residues) that promotes the biological reduction of sulfate and its transformation to sulfide, which forms complexes that are scarcely soluble with most toxic metals (Kijjanapanich et al., 2012; Zhang and Wang, 2014; Yim et al., 2015; Waybrant et al., 1998). Organic matter, which provides nutrients to the sulfate-reducing microbial consortium, is classified into short and long-term sources according to its bioavailability (ITRC, 2013). The reactive bed contains a bacterial inoculum as well as alkaline substrates, such as limestone, sea shells and ash, among others, whose function is to help neutralize acidity (Klein et al., 2014; McCauley et al., 2010; Uster et al., 2014). The microbial consortium degrades organic matter which promotes the development of sulfate-reducing microorganisms. In this metabolism, the sulfates coming from acid drainage are used as electron acceptors, thus transforming them into sulfides while also generating alkalinity (Klein et al., 2014; Sheoran et al., 2010). (Oxy)hydroxide, carbonate and sulfide precipitation are fundamental metal removal mechanisms in bioreactors (Neculita et al., 2008; Weisener et al., 2015). Sulfate bioreduction has been successfully implemented in technologies such as permeable reactive barriers, reducing and alkalinity producing systems, anaerobic wetlands and biochemical reactors (Sheoran et al., 2010; Klein et al., 2014; Fitch, 2015).

A potential biological treatment problem, however, is the toxicity of acid drainage and sulfides. Particularly, the toxic conditions can affect the microbial activity inside of permeable barriers, reducing the restoration rates. In order to mitigate toxicity during AMD treatment, Schwarz and Rittmann (2010) proposed a new barrier design in which the distribution of reactive material is interspersed among layers of conductive material (known as diffusion-active permeable reactive barrier, DAPRB). This arrangement provides protection for microorganisms because the AMD is transported through the conductive layers of the barrier, which avoids direct contact with the microorganisms via advective mechanisms. Additionally, metals cannot reach the microorganisms by diffusion because the diffusive flux of the sulfides is coming from the reactive layer which opposes the flux of metals by precipitating them in the interface area (Schwarz and Rittmann, 2007a; Schwarz and Rittmann, 2007b).

A DAPRB reactor prototype has been successfully tested for the treatment of AMD with high copper concentrations (Perez et al., 2017a); however, the diffusion-active concept being applied to permeable reactive barriers needs to be studied further as well as gathering evidence that supports the protection mechanism based on chemical gradients. Therefore, a prototype of a diffusion-active permeable reactive barrier (DAPRB) was developed in this study and its operation was compared to a traditional permeable reactive barrier (PRB). The sulfate reduction capacity was assessed in a spring water influent modified with sulfate and different concentrations of zinc. In order to evaluate the presence of chemical sulfide gradients in the pore water of the DAPRB reactor, inner sampling points were included in the design. In addition, by using molecular and microscopic techniques, descriptions of the microorganisms present in the two reactors were made in order to determine the effect of reactor type on the diversity of microorganisms.

2. Methodology

2.1. Design of reactors

Two stainless steel reactors were built (Fig.1) with an internal volume of 2.1 L (not including the material) and with an approximate pore volume of 1.3 L, one based on a homogeneous substrate and another based on diffusive exchange. The diffusion reactor simulates the space of a diffusion-active permeable reactive barrier (DAPRB) spanned between two planes of symmetry, one bisecting a conductive layer and the other a contiguous reactive layer. Therefore, this reactor includes a conductive half layer, a reactive half layer and the interface between both. Particularly, the thickness of the half layers is 7.5 cm, so the reactor represents the processes that occur in a barrier with 15 cm thick layers (Schwarz and Rittmann, 2007b; Schwarz and Rittmann, 2010).

A design with a steel back cover and stainless steel frames, central cell, fittings and sampler tubes (ports, 316 L) was made (Fig. 2a); it also included a polycarbonate front hatch that allowed for the observation of the reactor's interior. At the top, 12 ports were located (Fig.2b) from where the samples were extracted at different depths (50, 100, 150 mm). The exterior portions of the ports were connected to hoses and syringes, and lateral perforations were located at the bottom to suction the samples (Φ: 1 mm).

Peristaltic pumps were used in the reactors (Masterflex L/S 0.02–100 rpm). The influent flow rate value varied within the range of 0.72 to 1.44 L/d, giving estimated pore water flow velocities in the range of 0.5–1.0 m/day. The homogeneous and diffusion-active reactors contained the same quantity and type of materials, but with a different arrangement (Fig. 1). The homogeneous reactor contained a mixture of all the materials, while the DAPRB reactor contained two half layers; one reactive half layer and one conductive half layer, made of only sand. In both reactors, we used a mixture modified from Perez et al. (2017b) with *Pinus radiata* compost (439.8 g), anaerobic digester sludge

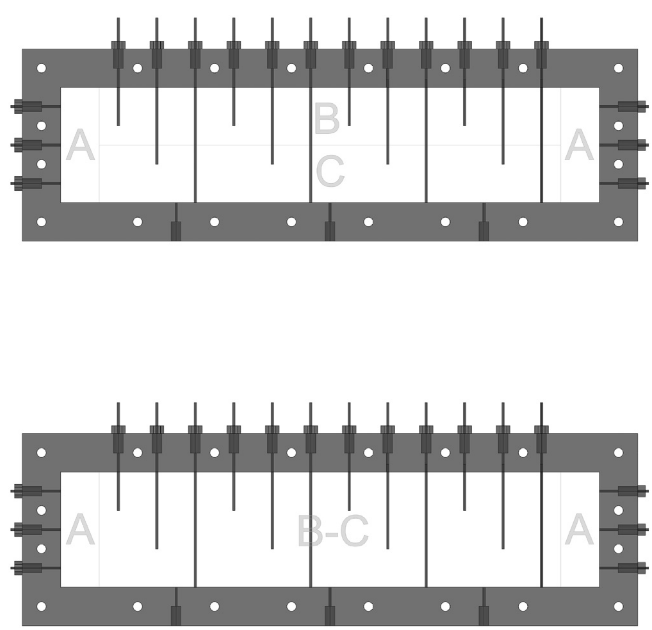

Fig. 1. Transverse section of the DAPRB and homogeneous reactors. A: Loading zones for the homogenization of the influent and effluent; B: conductive zone; C: reactive zone.