



Treatment of acid rock drainage using a sulfate-reducing bioreactor with zero-valent iron



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HIGHLIGHTS

- Electron donor from zero-valent iron (ZVI) drives sulfate reduction to sulfide.
- Sulfide converts soluble heavy metals into sulfide minerals.
- Excess sulfide is sequestered by iron preventing discharge.
- Corrosion of ZVI consumes acidity in acid rock drainage.
- ZVI as reactive material outlasted limestone in removing heavy metals.

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ABSTRACT

This study assessed the bioremediation of acid rock drainage (ARD) in flow-through columns testing zero-valent iron (ZVI) for the first time as the sole exogenous electron donor to drive sulfate-reducing bacteria in permeable reactive barriers. Columns containing ZVI, limestone or a mixture of both materials were inoculated with an anaerobic mixed culture and fed a synthetic ARD containing sulfuric acid and heavy metals (initially copper, and later also cadmium and lead). ZVI significantly enhanced sulfate reduction and the heavy metals were extensively removed (>99.7%). Solid-phase analyses showed that heavy metals were precipitated with biogenic sulfide in the columns packed with ZVI. Excess sulfide was sequestered by iron, preventing the discharge of dissolved sulfide. In the absence of ZVI, heavy metals were also significantly removed (>99.8%) due to precipitation with hydroxide and carbonate ions released from the limestone. Vertical-profiles of heavy metals in the columns packing, at the end of the experiment, demonstrated that the ZVI columns still had excess capacity to remove heavy metals, while the capacity of the limestone control column was approaching saturation. The ZVI provided conditions that enhanced sulfate reduction and generated alkalinity. Collectively, the results demonstrate an innovative passive ARD remediation process using ZVI as sole electron-donor.

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1. Introduction

Acid rock drainage (ARD) is the effluent generated from rock residues by oxidation of metal sulfides such as pyrite (FeS_2). ARD is often characterized by low pH values (2–6), and high sulfate and heavy metals content [1,2]. The high acidity and heavy metal concentrations typically found in ARD pose serious ecological risks, particularly for aquatic ecosystems [3,4]. High metal levels in drinking water resources or crops impacted by ARD can also have negative impacts on human health [5–7].

Remedial approaches for ARD tend to use low cost, low maintenance passive treatments, commonly limestone channels and constructed wetlands [2,8,9]. Another passive treatment option is to use permeable reactive barriers (PRB). PRB technology has been developed over the last two decades in order to provide passive, in-situ, treatment of groundwater. PRB is a subsurface emplacement of reactive materials through which a dissolved contaminant plume must move as it flows, typically under natural gradient [10–12]. Contaminants can be removed in PRBs by physico-chemical mechanisms (e.g., adsorption, precipitation) or microbial mechanisms. In permeable reactive biobarriers, biological activity is enhanced so that biotic processes can mediate the treatment of contaminants. PRB relying on sulfate-reducing bacteria (SRB) have been shown to be effective for the immobilization of heavy metals in ARD [13,14].

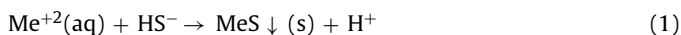
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Table 1
Solubility products (Ksp) at 25 °C of sulfides, carbonates and hydroxides of Cu²⁺, Cd²⁺, Pb²⁺ and Fe²⁺ [56].

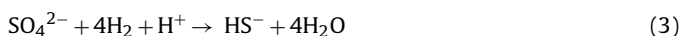
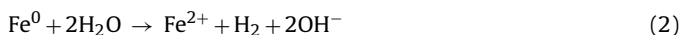
Metal ion	Metal sulfide	Metal hydroxide	Metal carbonate
Cu ²⁺	6.3 × 10 ⁻³⁶	2.5 × 10 ⁻¹⁹	3.1 × 10 ⁻¹²
Pb ²⁺	1.0 × 10 ⁻²⁷	7.9 × 10 ⁻¹⁷	7.9 × 10 ⁻¹⁴
Cd ²⁺	7.9 × 10 ⁻²⁷	2.5 × 10 ⁻¹⁴	1.0 × 10 ⁻¹²
Fe ²⁺	6.3 × 10 ⁻¹⁸	7.9 × 10 ⁻¹⁵	3.5 × 10 ⁻¹¹

SRB are anaerobic bacteria that utilize sulfate (SO₄²⁻) as an electron acceptor [15]. They reduce SO₄²⁻ to sulfide (S²⁻) utilizing H₂ and organic molecules such as lactate, pyruvate, and ethanol as electron donors (e-donor), resulting in an increase in alkalinity and pH. The biogenic sulfide produced is an excellent ligand for precipitating heavy metals. Eq. (1) illustrates how divalent metals can easily be removed in the presence of sulfide; Me stands for metal.



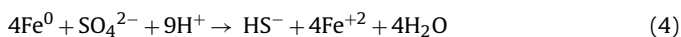
Sulfide minerals (MeS) are highly insoluble and can be dissolved only at highly acidic and/or strongly oxidizing conditions because their solubility constants (Ksp) are extremely low (Table 1). Under acidic conditions, metal sulfide precipitates are more stable than metal hydroxide and metal carbonate precipitates as indicated by their considerably higher Ksp constants (Table 1).

Sulfate-reducing PRBs often utilize insoluble, slow release organic substrates such as sewage, manure, compost, lignocellulosic residues, and food waste as source of carbon and an e-donor [16–18]. This work determines for the first time whether zero-valent iron (ZVI or Fe⁰) can be used as a sole e-donor to generate sulfide and stimulate heavy metal removal in a flow-through bioreactor simulating a PRB system. ZVI has been shown to serve as e-donor for SRB in batch bioassays [19,20]. However, the application of ZVI as the sole e-donating substrate in sulfate-reducing systems for heavy metal remediation has not been described to date. ZVI is readily oxidized in water under anaerobic conditions to produce H₂. As iron is oxidized, Fe⁰ produces Fe²⁺ + 2e⁻ and H⁺ is reduced to H₂. Concomitant with the formation of H₂ is the release of OH⁻ (Eq. (2)). SRB use the electrons via hydrogen formation to reduce sulfate (Eq. (3)).



Sulfate reduction driven by abiotically formed H₂ has been demonstrated in a special culture flasks system where the abiotic corrosion of mild steel was separated from an H₂-consuming sulfate-reducing culture except for a shared headspace [21]. However there is also evidence for direct e-transfer from ZVI to microorganisms based on SRB accelerating the rate of ZVI corrosion beyond the abiotic rate [19,22], evidence for involvement of c-type cytochromes in the electron transfer [23,24], and evidence that enzymes in the cell-free-extract of a methanogen could catalyze the formation of H₂ and formate from ZVI [25].

Eq. (4), which is obtained combining Eqs. (2) and (3), shows that a molar ratio of 4 moles of iron is required to reduce 1 mol of sulfate. Fe²⁺ and biogenic sulfide are produced and H⁺ is consumed, leading to an increasing the pH.



The utilization of ZVI as substrate in sulfate-reducing PRBs designed to treat ARD has the potential to provide important benefits compared to conventional organic substrates. First, ZVI is a promising strong reductant and widely available material that can drive sulfate reduction and promote the precipitation of highly stable metal sulfides. Secondly, corrosion of ZVI leads to formation of Fe²⁺ ions that can sequester excess sulfide, minimizing discharge

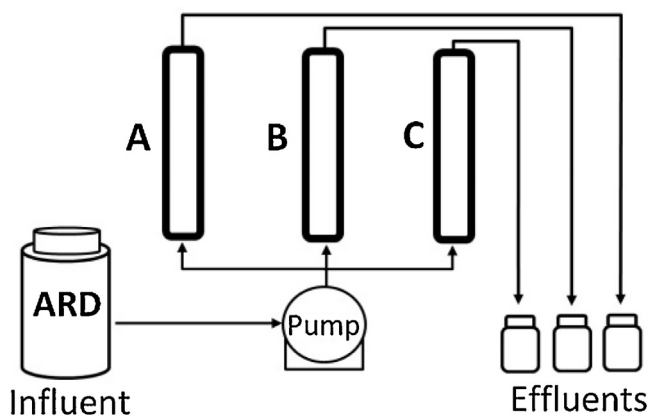


Fig. 1. Diagram of the packed-bed columns used in this study. A: Column packed with limestone (LS), B: column packed with ZVI and limestone (ZVI-LS) column, and C: column packed with ZVI (ZVI).

of this toxic and malodorous contaminant into the PRB effluent. Thirdly, corrosion of ZVI consumes acidity, thereby contributing to neutralize the high acidic levels often found in ARD.

This study assessed the bioremediation of ARD in a laboratory-scale sulfate-reducing reactor using ZVI as the sole exogenous electron donor. Continuous-flow bioreactors packed with either limestone or limestone and ZVI were run in parallel to investigate the benefits of supplying limestone. The nature of the minerals deposited in the packing material of the reactors was elucidated to gain insights on the mechanisms of metal immobilization.

2. Materials and methods

2.1. Microorganisms

Anaerobic granular sludge was obtained from an upward-flow sludge bed reactor treating brewery effluent (Mahou, Guadalajara, Spain). The sulfate-reducing activity of this sludge was demonstrated in batch experiments [26]. The sludge contained 7.13% volatile suspended solids (VSS) in wet-weight.

2.2. Chemicals

ZVI (325 mesh; 97%) was obtained from Sigma (St., Louis, MO), limestone (CaCO₃, 2–4 mm) from Oglebay Norton Industrial Sands (Buchanan, VA) and silica (2 mm) from Premier Silica (Colorado Springs, CO).

2.3. Basal medium

The basal mineral medium used to prepare the synthetic ARD contained (in mg L⁻¹): NH₄Cl (80); NaHCO₃ (50); K₂HPO₄ (171); CaCl₂·2H₂O (20), MgCl₂·6H₂O (29), yeast extract (20), and 1 mL L⁻¹ of trace element solution [20]. Copper (added as CuSO₄ 5H₂O) was gradually increased from 10 to 50 mg L⁻¹. Additional sulfate (250 mg SO₄²⁻ L⁻¹) was added as H₂SO₄. The pH was adjusted to the desired value (see Section 2.5) by addition of NaOH or HCl.

2.4. Continuous-flow bioreactors

Three up-flow packed-bed columns (0.385 L) were inoculated with anaerobic sludge (10 g VSS L⁻¹) and operated in parallel to evaluate the removal of heavy metals using ZVI as the only exogenous source of e-donor in the presence and absence of limestone (Fig. 1). Limestone served as a pH buffer and as supplemental source of inorganic carbon for lithoautotrophic SRB that can grow using

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