

# Iron and Sulfate Removal in Highly Contaminated Acid Mine Drainage Using Passive Multi-Step Systems

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**Abstract** Remediation of high Fe and SO<sub>4</sub><sup>2-</sup> acid mine drainage (AMD) with passive multi-step systems is less prone to clogging, but could show variable efficiency. Hence, four scenarios (MS1 to MS4) of passive multi-step treatment systems were tested. The system (MS3) composed of two pretreatment units of dispersed alkaline substrate reactors and one unit of passive biochemical reactor was found the most efficient (Fe and SO<sub>4</sub><sup>2-</sup> removal of 99% and 77%, respectively). Clogging issues were not encountered in all reactors. Nonetheless, further studies on the treatment of highly contaminated Fe and SO<sub>4</sub><sup>2-</sup> AMD with other dissolved metals should be undertaken.

**Key words** acid mine drainage, passive biochemical reactor, multi-step systems, dispersed alkaline substrate, wood ash

## Introduction

Treatment of highly contaminated acid mine drainage (AMD) often involve passive multi-step systems because they are less subjected to clogging and/or passivation. Their design includes pretreatment, principal and polishing units, which can be aerobic and anaerobic, chemical, and biological. Some types may involve the combination in series of dispersed alkaline substrate (DAS – mixture of coarse (wood chips) and neutralizing materials (calcite or magnesite)) units with cascade aeration (Rötting et al. 2008) or decantation ponds (Caraballo et al. 2011; Macías et al. 2012). Passive biochemical reactors (PBRs) were combined with anoxic limestone drains (ALD) (Figuerola et al. 2007; Prasad and Henry 2009) or with peat biofilters (Clyde et al. 2016). However, a multi-step treatment has variable efficiency (in terms of Fe and SO<sub>4</sub><sup>2-</sup> removal) depending on the water quality, and on the type and number of units composing the system. The DAS-based multi-step systems could remove up to 99.9% of Fe in AMD, at initial Fe concentrations <0.5 g/L, whereas at higher concentrations (0.5–1 g/L), the efficiency decreased to as low as 20% (Rötting et al. 2008; Caraballo et al. 2009, 2011). In addition, the SO<sub>4</sub><sup>2-</sup> was marginally removed (Rötting et al. 2008; Caraballo et al. 2011; Macías et al. 2012). PBRs-based multi-step treatment could remove up to 99.7% of Fe and 53% of SO<sub>4</sub><sup>2-</sup>, at initial concentrations <0.5 g/L and 0.3–3 g/L, respectively (Figuerola et al. 2007; Prasad and Henry 2009). Oppositely, Fe and SO<sub>4</sub><sup>2-</sup> removal was found around 78% and 55%, at initial Fe and SO<sub>4</sub><sup>2-</sup> concentrations of 1.8 g/L and 4.7 g/L, respectively (Genty et al. 2016). However, AMD originating from abandoned mines and tailings can be characterized by extremely high concentrations of dissolved Fe (up to 141 g/L) and SO<sub>4</sub><sup>2-</sup> (up to 760 g/L) (Nordstrom et al. 2000). Hence, an optimization of the performance of multi-step systems to allow treating an AMD of such quality is still

necessary.

In this context, the present study aims to evaluate the efficiency of four scenarios of laboratory PBRs-based and PBR–DAS-based multi-step systems for the treatment of AMD with initial Fe and  $\text{SO}_4^{2-}$  up to 4 g/L and 9 g/L, respectively.

## Methods

Six 10.7 L columns (14 cm in diameter and 70 cm height), filled with six different mixtures were set-up (tab. 1).

**Table 1** Six columns and the filling mixtures used to compose each unit of the multi-step systems

| Mixture  | WA50 | C50 | PBR#1 | PBR#2 | PBR#3 | WA  | DOL |
|--|------|-----|-------|-------|-------|-----|-----|
|  | %v/v |     |       | % w/w |       |     |     |
| <b>Structural agent</b> (sand)                               | -    | -   | 10    | 10    | 20    | -   | -   |
| <b>Cellulosic wastes</b><br>(wood chips and/or sawdust)      | 50   | 50  | 40    | 15    | 30    | -   | -   |
| <b>Organic wastes</b><br>(chicken manure and/<br>or compost) | -    | -   | 30    | 15    | 30    | -   | -   |
| <b>Inoculum</b> (sediments)                                  | -    | -   | -     | 8     | 15    | -   | -   |
| <b>Nutrients</b> (urea)                                      | -    | -   | -     | 2     | 3     | -   | -   |
| <b>Neutralizing agents</b>                                   |      |     |       |       |       |     |     |
| Wood ash   | 50   | -   | -     | -     | -     | 100 | -   |
| Calcite  | -    | 50  | 20    | 50    | 2     | -   | -   |
| Dolomite   | -    | -   | -     | -     | -     | -   | 100 |
| <b>Total</b>   | 100  | 100 | 100   | 100   | 100   | 100 | 100 |

WA: wood ash; DOL: dolomite

All the mixtures filling the columns (tab. 1) were fully characterized prior and/or after use, and showed effective Fe removal (>91%) for the (pre)treatment of Fe-rich AMD during previous batch testing (Genty 2012; Rakotonimaro et al. 2016). In addition, the WA mixture showed Fe and  $\text{SO}_4^{2-}$  removal >99% and 44%, respectively (Genty et al. 2012a). At the same time, the anoxic dolomitic drain (DOL) was found to have efficiency similar to calcite when used to treat moderately contaminated AMD (Genty et al. 2012b). In each column, the mixture was placed between two layers of gravel ( $\approx 5$  cm) and fine-mesh geotextiles, at the top and bottom, prior to their covering. Thereafter, four multi-step scenarios (MS1 to MS4) were tested using the set-up reactors (tab. 2).

The first three scenarios involved diverse combinations of DAS units, DOL, and PBRs. One type among these three included 1 DAS-based pretreatment unit (WA50), whereas the two

| Multi-step system | Composing units                   | HRT (d)                | Duration (d) |
|-------------------|-----------------------------------|------------------------|--------------|
| MS1               | WA50 + PBR#1 + DOL                | 3 + 5 + 3 = 11         | 70           |
| MS2               | WA50 + C50 + PBR#1                | 3 + 3 + 5 = 11         | 70           |
| MS3               | WA50 (1) + WA50 (2) + PBR#1 + C50 | 3 + 3 + 5 + 3 = 14     | 217          |
| MS4               | PBR#2 + WA + PBR#3                | 5.1 + 8.9 + 5.6 = 19.6 | 365          |

**Table 2** Components of the multi-step systems, tested HRTs, and duration of the experiments

others were comprised of two pretreatment units (WA50/C50 or 2 WA50) (tab. 2). The fourth scenario was composed of two PBRs (PBR#2 and PBR#3) separated by a wood ash (WA) unit, where PBR#2 and WA were considered as the pretreatment units. All four scenarios were run for 70 to 365 d. The reactors were started at 3 d of HRT, except the PBRs and WA, which were operated at HRT  $\geq$  5 d for total HRTs of 11 d (MS1, MS2), 14 d (MS3), and 19.6 d (MS4) (tab. 2).

Prior to starting the continuous feed of the columns with AMD, the PBRs were saturated with a Postgate B medium, which composition was prepared in distilled water with 3.5 g/L sodium lactate (or 4,67 mL lactate liquid 56.8%); 2.0 g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; 1.0 g/L  $\text{NH}_4\text{Cl}$ ; 1.27 g/L  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; 1.0 g/L yeast extract; 0.5 g/L  $\text{KH}_2\text{PO}_4$ ; 0.5 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; 0.1 g/L thio-glycolic acid, and 0.1 g/L ascorbic acid (Postgate 1984). Then, the columns were incubated with the medium at room temperature (four weeks for PBR#2 and #3 and 2 weeks before being acclimated for another week with diluted AMD (3:1 of DI water: AMD) for PBR#1). Finally, calibrated peristaltic pumps (Masterflex) were used to feed upward all the columns with synthetic AMD (pH 2–5, 1.8–5 g/L Fe, <0.007 g/L Al, <0.33 g/L Mn, 4–9 g/L  $\text{SO}_4^{2-}$  and <0.033 g/L of Pb, Ni, Zn), which quality is typical of effluents from hard rock mines in Canada (Zinck and Griffith 2013).

The AMD and treated water quality were monitored by a weekly sampling and analysis of the physicochemical parameters, including the pH, redox potential (ORP), alkalinity, acidity, and concentrations of total iron ( $\text{Fe}_t$ ),  $\text{SO}_4^{2-}$  and total metal. Measured hydraulic parameters included the  $k_{\text{sat}}$  and porosity ( $n$ ). Water pH was measured with an electrode Orion 3 Star Thermo (GENEQ Inc.). The ORP was determined with a potentiometer (Sension1 POR HACH 51939-00) coupled with an internal Pt/Ag/AgCl electrode. Alkalinity and acidity were determined by titration with a Metrohm Binkmann, 716 DMS Trinitro titrator (APHA 2012). Concentrations of  $\text{Fe}_t$  and  $\text{SO}_4^{2-}$  were analyzed on filtered samples (0.45  $\mu\text{m}$ ), within 1–2 h after collection, with a DR/890 HACH colorimeter (Method 8008 – 1, 10 phenanthroline, Method 8146 – 1, 10 phenanthroline, and Method 8051– barium chloride powder pillows for  $\text{Fe}_t$  and  $\text{SO}_4^{2-}$ , respectively). Total metal concentrations of filtered (0.45  $\mu\text{m}$ ) and acidified (with 2% (v/v) of nitric acid) samples were analyzed by ICP-AES. Removal of metals  $r$  (%) was calculated with the following equation:  $r = [(C_{\text{in}} - C_{\text{out}})/C_{\text{in}}] \cdot 100$ ; where  $C_{\text{in}}$  and  $C_{\text{out}}$  are input and output concentrations (mg/L).

Sulfate reducing bacteria (SRB) counting in effluents from PBRs was performed by using

the most probable number (MPN) method (Cochran 1950; ASTM 1990). After 21 d of incubation at 30°C and under anaerobic conditions, the SRB growth was either indicated by the presence of black FeS precipitate. When this last was not obvious, a test with FeCl<sub>3</sub>/HCl and p-aminodimethylaniline dihydrochloride/HCl was performed (Postgate 1984; ASTM 1990). The  $k_{\text{sat}}$  was evaluated by using the falling head method (ASTM 1995). Porosity was calculated as the ratio between void volumes, which considers the specific gravity ( $G_s$ ), and total volume of the reactive mixture.

## Results and discussion

In general, multi-step treatment with two pretreatment units gave better performance compared to one unit. Nonetheless, all systems allowed pH increase from 2–4.1 to 4.4–8.1 (fig. 1). The low ORP values showed that reducing conditions were maintained in all reactors (fig. 1). Better acidity removal was observed in MS3 (89%) and entailed a higher removal of Fe (99%) and SO<sub>4</sub><sup>2-</sup> (61%) all along the testing (217 d), at input Fe and SO<sub>4</sub><sup>2-</sup> concentrations <2.5 g/L and <5 g/L, respectively (fig. 2). On the contrary, MS1 showed the lowest efficiency

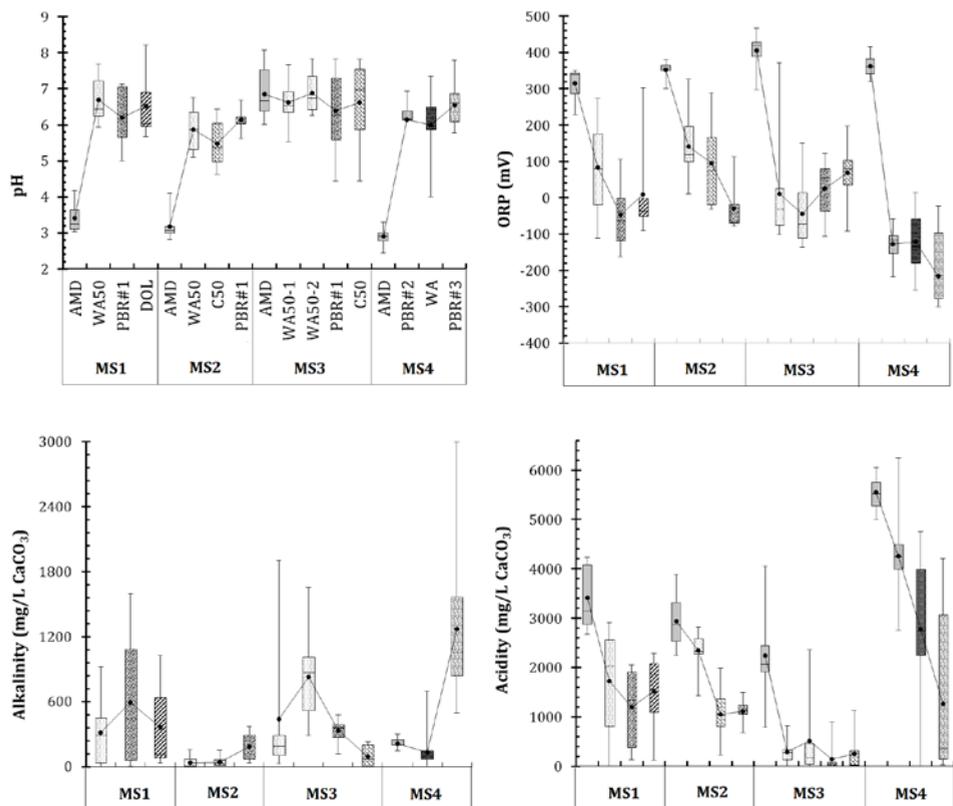
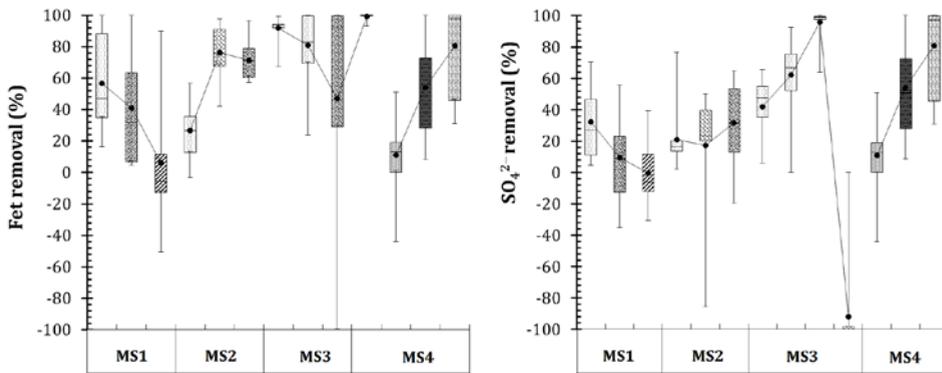


Figure 1 Physicochemical evolution of effluents in the columns during laboratory multi-step treatment of AMD (minimum, 25% percentile, median, 75% percentile, mean, maximum) AMD, WA50, PBR#1, PBR#2, PBR#3, DOL, C50, WA

(acid, Fe and  $\text{SO}_4^{2-}$  removal of 51, 53 and 29%, respectively) (tab. 3). Over time (after 139 d), the effectiveness of MS4 decreased to half fold, probably due to WA unit saturation as well as a decrease of alkalinity (down to 73%). Hence, Fe and  $\text{SO}_4^{2-}$  removal dropped, respectively from 99% to 45% and from 49% to 13%. Moreover, only half of the acidity was neutralized (45%).

The performance of a multi-step treatment appears to be dependent on the effectiveness of the pretreatment units as well as on the initial Fe and  $\text{SO}_4^{2-}$  concentrations. Higher efficiency was found with two WA50 pretreatment units in MS3 (removal of up to 96% of Fe; load of 427 g Fe/m<sup>3</sup>/d and 58% of  $\text{SO}_4^{2-}$ ). Subsequently, the following PBR#1 could treat 4–73 g Fe/m<sup>3</sup>/d. At the same time, a possible oxidation of sulfur/sulfide from the PBR#1 could have



**Figure 2** Relative removal of Fe and  $\text{SO}_4^{2-}$  (minimum, 25% percentile, median, 75% percentile, maximum, mean) during multi-step treatment of AMD

**Table 3** Efficiency of the different multi-step systems

|   | MS1     | MS2       | MS3       | MS4       |
|---|---------|-----------|-----------|-----------|
| pH  | 5–8.21  | 4.73–6.68 | 4.44–8.09 | 5.78–7.79 |
| ORP (mV)                                    | -18     | -29       | 81        | -65–101   |
| Fe <sub>t</sub> removal (%)*                | 53      | 76        | 99        | 31–100    |
| SO <sub>4</sub> <sup>2-</sup> removal (%)** | 29      | 61        | 65        | -16–83    |
| Acid removal (%)                            | 51      | 78        | 89        | -27–100   |
| Alkalinity (mg CaCO <sub>3</sub> /L)        | 26–1597 | 3–630     | 7–1905    | 500–3000  |

\*Input concentrations in MS1, MS2, and MS3: 2.5±0.4 g/L and 4±0.4 g/L in MS4

\*\* Input concentrations in MS1, MS2, and MS3: 5±0.6 g/L and 9±1.2 g/L in MS4

increased  $\text{SO}_4^{2-}$  concentration in the last unit (i.e. C50) of the system (fig. 2). Even when exposed to higher acidity as well as Fe and  $\text{SO}_4^{2-}$  concentrations, the first pre-treatment unit in MS4 (i.e. PBR#2) showed a steady acidity and Fe removal (23% and 12% or equivalent to 13 g Fe/m<sup>3</sup> substrate/d, respectively) all along the testing. In addition, the produced alkalinity was also maintained (around 214 mg/L as  $\text{CaCO}_3$ ; fig. 1). However, this alkalinity was not sufficient enough to allow SRB to thrive. Accordingly, the SRB counts did not exceed 200 cells/100 mL, which may explain the negligible  $\text{SO}_4^{2-}$  removal. Nevertheless, the following WA unit presented a better efficiency (Fe removal of 40%, and 32% of  $\text{SO}_4^{2-}$ ) during the first 125 d and subsequently the last unit (PBR#3) could remove 98% of Fe and 33% of  $\text{SO}_4^{2-}$  (fig. 2).

Additionally, all the tested multi-step systems could decrease up to 98% of Al, Ni, Pb and Zn concentrations. These metals were removed early in the pre-treatment units (>72%). The most significant Zn removal (94%) in PBR#1 during MS2 was possibly promoted by its adsorption onto Fe and Al (oxy) hydroxides. Up to 99.4% of Mn was also removed during the first phase of the pretreatment unit(s) in MS1 to MS3 because of the high pH value (>8). On the contrary, higher Mn removal (83%) was found in the last unit of MS4 before day 132, when Fe concentration was lowered before WA saturation (Fe/Mn ratio <1).

Little change of the overall  $k_{\text{sat}}$  in all reactors (from the initial value  $7.7 \times 10^{-3}$ –  $1.4 \times 10^{-2}$  cm/s to an order of  $10^{-4}$ – $10^{-3}$  cm/s) suggested that clogging issues and short circuiting did not occur during the experiments. Hence, mixtures with  $k_{\text{sat}} > 10^{-3}$  cm/s are recommended for an efficient multi-step treatment composed of DAS and PBR units.

## Conclusions

Amongst the four tested multi-step treatment systems, MS3, composed of two pretreatment units (WA50) and one PBR, was the most efficient in Fe and  $\text{SO}_4^{2-}$  removal from highly contaminated AMD. MS4 (consisting of two PBRs separated by a WA unit) showed a higher efficiency (Fe and  $\text{SO}_4^{2-}$  removal of 99% and 50%, respectively) before WA saturation (i.e. during the first 132 d). A PBR-based pretreatment unit could be an efficient Fe-pretreatment (even at a low load; around 13 g/m<sup>3</sup>/d) at initial Fe concentrations up to 2.5 g/L, providing that enough alkalinity can ensure acid neutralization and microbial activity. Even though clogging was not observed during testing and the  $k_{\text{sat}}$  was relatively stable ( $10^{-3}$ – $10^{-4}$  cm/s) in all multi-step systems, the use of mixture with  $k_{\text{sat}} > 10^{-3}$  cm/s is recommended when using DAS and PBR units. Further studies on passive multi-step treatment of AMD with high Fe,  $\text{SO}_4^{2-}$  and other dissolved metals need to be carried out.

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