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Authors Contribution

Vasquez Yaneth, Neculita Carmen and Roldan Fabio: conceptualization, methodology, supervision, validation, writing review and edition, Gerardo Caicedo, Jairo Cubillos, Jair Franco, Mario Vásquez, Angie Hernández performed field research, writing and review.

PASSIVE MULTI-UNIT FIELD-PILOT FOR ACID MINE DRAINAGE REMEDIATION: PERFORMANCE AND ENVIRONMENTAL ASSESSMENT OF POST-TREATMENT SOLID WASTE

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The authors declare no conflict of interest.

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Highlights

- Passive multi-unit systems are sustainable for remediation of acid mine drainage
- Pretreatment is necessary to maintain the effectiveness of the next treatment unit
- Passive systems configuration relates to changes in properties of the reactive mixture
- Pos-treatment solid waste should be assessed before disposal in a municipal landfill.

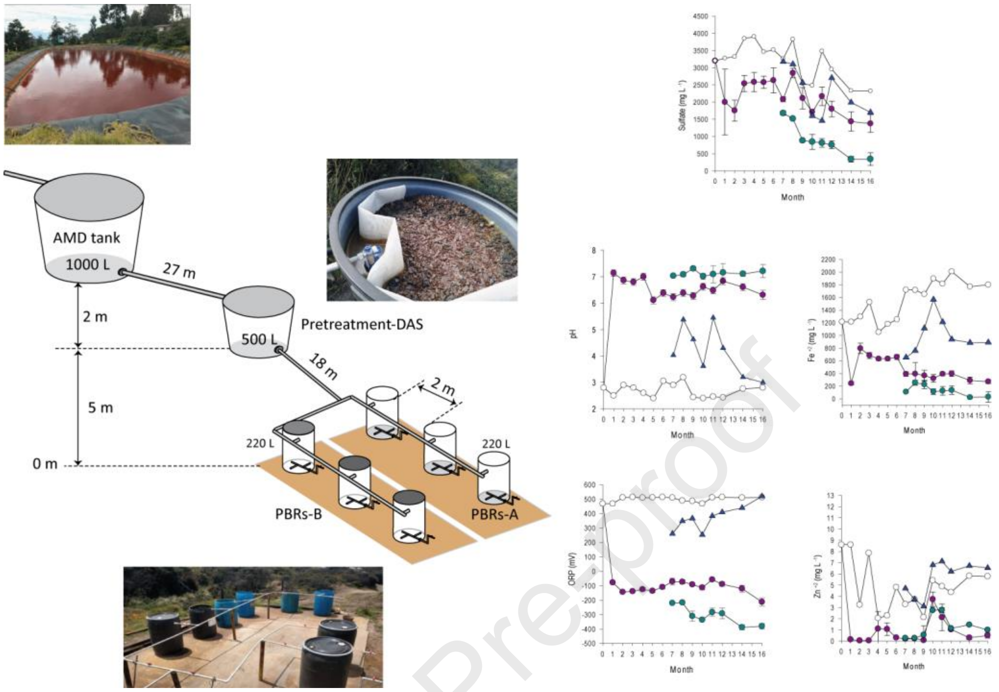
Abstract

This study evaluated the performance of a passive multi-unit field-pilot operating for 16 months to treat acid mine drainage (AMD) from a coal mine in Colombia Andean Paramo. The multi-unit field-pilot involved a combination of a pre-treatment unit (550 L) filled with dispersed alkaline substrate (DAS), and six passive biochemical reactors (PBRs; 220 L) under two configurations: open (PBRs-A) and closed (PBRs-B) to the atmosphere. The AMD quality was 1,200 ± 91 mg L^{-1} Fe, 38.0 ± 1.3 mg L^{-1} Mn, 8.5 ± 1.6 mg L^{-1} Zn, and 3,200 ± 183.8 mg L^{-1} SO_4^{2-}, at pH 2.8. The input and output effluents were monitored to establish AMD remediation. Physicochemical stability of the post-treatment solids, including metals (Fe^{2+}, Zn^{2+}, and Mn^{2+}) and sulfates for environmental contamination from reactive mixture post-treatment, was also assessed.

The passive multi-unit field-pilot achieved a total removal of 74% SO_4^{2-}, 63% Fe^{2+}, and 48% Mn^{2+} with the line of PBRs-A, and 91% SO_4^{2-}, 80% Fe^{2+}, and 66% Mn^{2+} with the line of PBRs-B, as well as 99% removal for Zn^{2+} without significant differences ($p < 0.05$) between the two lines. The study of the physicochemical stability of the post-treatment solids showed they can produce acidic leachates that could release large quantities of Fe and Mn, if they are disposed in oxidizing conditions; contact with water or any other leaching solutions must be avoided. Therefore, these post-treatment solids cannot be disposed of in a municipal landfill. The differences in configuration between PBRs, open or closed to the atmosphere, induced changes in the performance of the passive multi-unit field-pilot during AMD remediation.

Keywords: Acid mine drainage (AMD); Dispersed alkaline substrate (DAS); Passive biochemical reactors (PBRs); Colombia Andean Paramo; Post-treatment solid waste

Graphical Abstract



1 Introduction

Coal mining operations have left a trail of environmental problems, including acid mine drainage (AMD), which is responsible for physical, chemical, and biological degradation of aquatic habitats and surrounding soil quality (Adams et al., 2014). AMD is characterized by strong acidity, high concentrations of metals and sulfate (Sharma et al., 2020). AMD entails damage on aquatic ecosystems lead to the change of pH, incorporation of toxic metals, and the formation of ochreous precipitates (Carneiro Brandão Pereira et al., 2020). In Colombia, AMD generation is a significant and costly problem, especially in remote areas like the Colombia Andean Paramo, where more than 500 coal mine licenses have been issued since 2010 (McIntyre et al., 2018). The are very sensitive ecosystems, considered strategic not only for their high capacity to regulate water resources but also for their endemic biodiversity (Vargas et al., 2016). To avoid detrimental impacts, AMD must be collected and treated before being discharged into the environment. Due to the complex chemistry of AMD, which is dominated by Fe (with thermodinamicaly favored precipitation at pH higher than 3 to 3.5, with respect to its total concentration, and accumulation of large volumes of sluggish precipitates), passive multi-unit field-pilots are one of the best available options for AMD remediation (Ayora et al., 2013; Neculita et al., 2021).

Passive multi-unit field-pilot treatment as train-type systems is based on biological, geochemical, and physical processes to improve water quality (Skousen et al., 2017). These systems consist of a combination of physicochemical or biochemical units and both aerobic and anaerobic, which aim to increase pH and alkalinity and remove metal and sulfate from AMD (Adams et al., 2014). Physicochemical passive systems include limestone/dolomite drains, sorbent materials, dispersed alkaline substrates (DAS), anoxic limestone drains, and alkaline leach beds. Biochemical passive systems include constructed wetlands, passive biochemical reactors (PBRs), and permeable reactive barriers (Ben Ali et al., 2019; Habe et al., 2020; Skousen et al., 2017). The train-type systems are suitable because they do not require the continuous addition of chemicals, electrical power, and systematic maintenance, and they are particularly adapted to remote locations (Fernandez-Rojo et al., 2018).

The DAS-based systems are usually filled with a reactive mixture composed of alkaline materials (e.g., calcite, dolomite, wood ash, magnesia), which provides high reactivity and neutralizing capacity, and a coarse inert matrix (e.g., woodchips) to supply a high porosity substrate (Macías et al., 2012a). The PBRs are reservoirs or trenches filled with reactive mixtures composed of organic residual materials (e.g., manure, compost, straw, wood, biosolids) as a substrate for the microbes (including sulfate-reducing bacteria, SRB), and inorganic materials (inert, e.g., sand and gravel, and neutralizing, e.g., calcite, dolomite, and wood ash), which improve hydraulic parameters of the reactor (permeability and conductivity) and contribute to AMD neutralization (Habe et al., 2020).

To date, most studies of PBRs focus on closed systems, but full-scale PBRs in remote areas are sometimes exposed to the atmosphere (ITRC, 2013). Furthermore, while laboratory tests are necessary to select the design parameters for satisfactory performance, pilot-field tests provide realistic conditions that influence AMD treatment (Neculita et al., 2021). The pilot tests allow the validation of design parameters during the treatment of real AMD under on-site dynamic conditions, such as maximum exposure to light, weather changes, and variations in flow and concentration of AMD (Skousen et al., 2017). Field-pilot experiments also provide information about operating costs and requirements for pre- and post-treatment. When these data are required, the treatment system’s performance must be determined, including its efficiency in contaminant removal, compliance with prescribed discharging limits of the treated waters, and biogeochemical stability of metal-rich solid waste (Neculita et al., 2021).

At the end of their operation period (>10 years), passive systems generate solid waste with variable chemical composition and physical properties, depending on treated water quality (Jouini et al., 2019a; Macías et al., 2012b). Solid waste from a passive multi-unit field-pilot could subsequently regenerate a contaminated mine drainage, once exposed to water and oxygen (Jouini et al., 2019a). Therefore, the potential mobility of metal and sulfates from post-treatment solid waste from AMD treatment using passive treatment must be evaluated for the most appropriate management. To this end, various tests have been used to evaluate the environmental behavior of solid waste (Caraballo et al., 2018; Jouini et al., 2019b; Macías et al., 2012a).

Among these tests, the most common are toxicity characteristic leaching procedure (TCLP), sequential extraction procedures (SEP), and acid volatile sulfide (AVS) as simultaneously extracted metals (SEM) ratio. The TCLP classify the wastes as hazardous or non-hazardous to the environment based on the concentration of several metals in the leachates (USEPA, 1992). The SEP assess the potential mobilization of contaminants under variable environmental conditions and provide useful information regarding the chemical reactivity and forms of associations of metals and, indirectly, of their bioavailability (Caraballo et al., 2018). Finally, the AVS is comprised mainly of free sulfides and metal sulfides in solid, and SEM are released during the AVS extraction. Thus, solids in which SEM exceeds AVS (SEM/AVS ratio > 1) could be potentially toxic (Jong and Parry, 2004).

Passive treatment provides satisfactory efficiency for slightly contaminated AMD, but the treatment of iron-rich AMD (> 500 mg L^{-1}) is more challenging (Genty et al., 2017). This is the case of Milpa-2 mine site in Colombia Andean Paramo, where AMD is characterized by up to 1,200 mg L^{-1} Fe and 3,200 mg L^{-1} SO_4^{2-} as well as low concentrations of other metals. To date, bioremediation processes for this site with PBRs have been well studied under controlled lab-scale conditions; however, performance of these systems with real AMD in field-pilot experiments has not yet been evaluated.

Previous studies for this site, using batch tests and synthetic AMD, allowed the selection of the most efficient reactive mixture (15% cow manure, 10% mushroom compost, 25% sawdust, 15% gravel, 20% limestone, and 15% sediment) to increase pH and alkalinity as well as to remove sulfates and metals from AMD (Vasquez et al., 2016a). Later, column tests were also carried out with the aim of evaluating the effect of hydraulic retention time (HRT) on the treatment efficiency of AMD. These column experiments allowed to fix HRTs at 2 days for the treatment of AMD (Vasquez et al., 2016b). Additional changes were established in column tests' solid waste including the composition of the reactive mixture, enzymatic activity, and microbial community (Vasquez et al., 2018). Finally, in the present study the evaluation of passive multi-unit field-pilot treatments in the field allows the use of real AMD under high altitude mountains conditions and determines the number of units necessaries to achieve the optimal efficiency of the system.

In this context, the main objective of the present study was to evaluate the performance of a passive multi-unit field-pilot during a 16-month operation period. A secondary objective was to assess the chemical stability and mobility of metals (Fe, Zn, and Mn) from post-treatment solid waste.

2 Material and methods

2.1 Site description and AMD composition

The Milpa-2 is an active coal-mining site (5°27'59" N; 73°33'23" O) located in the Zipaquirá mining district (Samacá, Colombia). The mine is located at 3,200 m.a.s.l. in the foothills of the Colombia Andean Paramo. This place is a sensitive and important region for its high capacity to regulate water resources and its endemic biodiversity. The underground mine exploits a coal deposit with minor amounts of pyritic sulfur (2.5%). The AMD generated (~800 m^3 d^{-1}) emerges from the mineshaft, is pumped to the surface, and is then stored in an impoundment (~6,000 m^3). The AMD composition from Milpa-2 mine was evaluated for major elements (Al, Ca, Cu, Fe, Mn, S, Si, Cd, Pb and Zn) and trace elements (Cr, Co, Ni, As), but only the elements presented in table 1 have concentrations greater that Colombia's guideline criteria for wastewater (Ministerio de Ambiente y Desarrollo Sostenible, Regulation 0631, 2015). The AMD is strongly acidic; it is an oxidizer with a high concentration of iron and sulfate and low concentration of other metals.

Table 1. Water quality sampled on Milpa-2 mine

Parameters	**AMD**	Regulation 0631
pH	2.8 – 3.2	6.0 – 9.0
Redox potential (ORP; mV)	450.5 ± 2.4	Not Available
Acidity mg L^{-1} $CaCO_3$	1,880 ± 184	Not Available
Fe_{tot} mg L^{-1}	1,200 ± 91	2
Mn mg L^{-1}	23.5 ± 7.9	Not Available
Zn mg L^{-1}	8.5 ± 1.6	3
SO_4^{2-} (mg/L)	3,200 ± 184	1,200

Results are expressed as mean ± standard deviation from *n* = 48 (16 sites ×3 sample)

2.2 Pilot multi-unit treatment system: Design, setup, and operating conditions

Based on the results obtained from previous studies in laboratory, in batch (Vasquez et al., 2016a) and column reactors (Vasquez et al., 2016b), a pilot multi-unit treatment system was designed to treat the AMD generated in the Milpa-2 mine (Fig. 1a). A polyethylene (PE) barrel (1,000 L) was used as an AMD receiver downstream from the impoundment. This barrel was used to increase the hydrologic head of the system and allowed for the continuous feed of drainage by gravity into each separate reactor during the study. Initially (during the first 6 months), three independent reactors (PBRs-A) of 220 L (PE barrels; 80 cm height x 60 cm diameter) with downward flow were built. The top of each reactor was open, simulating a future full-scale AMD remediation system planned to be installed *on-site*. The affluent inlet port contained a plastic hydraulic float valve that prevented the AMD from overflowing, while effluent exit ports were connected to hollowed perforated pipe in a cross shape that was installed at the bottom of each reactor to allow a spatially equivalent collection of fluid to exit the reactor.

The exit port was fitted with a valve that allowed the maintainence of a continuous downward vertical flow during the 2-day HRT. To minimize clogging at the exit ports, the lower part of the reactors (10 cm) was filled with gravel (1 cm Ø). Then, a nylon mesh filtering screen (70 micron; Sefar America, Switzerland) disc was placed on the gravel layer to prevent loss of organic particles to the effluent port. The reactors were then packed with 155 L of the reactive mixture, which consisted of 15% cow manure, 10% mushroom compost, 25% sawdust, 15% gravel, 20% limestone, and 15% sediment from a nearby stream as inoculum (dry weight in % w/w) (Vasquez et al., 2016a). Finally, above the reactive mixture was placed another nylon disc, another 10 cm layer of gravel, and 10 cm layer of compacted woodchips as a cover to consume and minimize the entrance of oxygen. The reactors were then saturated slowly with AMD and were left for two weeks at rest for bacterial acclimation. Afterwards, continuous downward flow (27.4 L d^{-1}) of mine-site AMD through of PBRs was started.

After 6 months of operation, low efficiency of PBRs-A to remove metals and sulfate from AMD justified the decision to install a DAS unit and three new independent bioreactors closed to the atmosphere (PBRs-B). The DAS was installed after the AMD barrels collector; it consisted of a PE barrel of 500 L (85 cm height x 76 cm diameter in bottom x 93 cm in top) equipped with a perforated pipe and a 15 cm layer of gravel (1 cm Ø) at the bottom (Fig. 1b). The barrel was filled with 100 L of the reactive mixture, composed of wood ash and woodchips (1:1) (Rakotonimaro et al., 2016). Three months after the installation of the DAS unit, the reactive mixture packed in the unit was covered with a red precipitate, which caused coating and passivation of the wood ash and clogging of the pore space. Therefore, it was necessary to change the reactive mixture to keep the pre-treatment test running (Fig. 1c). The PBRs-B were constructed using the same process as the PBRs-A; however, these reactors were covered with a plastic lid and hermetic seal to maintain anaerobic conditions.

For this reason, the PBRs-B were packed with a higher (10 cm) reactive mixture layer for a final volume of 180 L to reduce headspace; then, they were left in bacterial acclimatization for two weeks. To finish the set-up, the PBRs (A and B) and DAS unit operated for 10 months with downward vertical flow (41 L day^{-1}) at 3-day HRT. In order to keep the flow constant during the study, the inlet and outlet valves of the reactors were cleaned weekly to remove accumulated minerals. Besides, once a week the outflow of the reactors was monitored by measuring the volume using a graduated cylinder and recording the time.

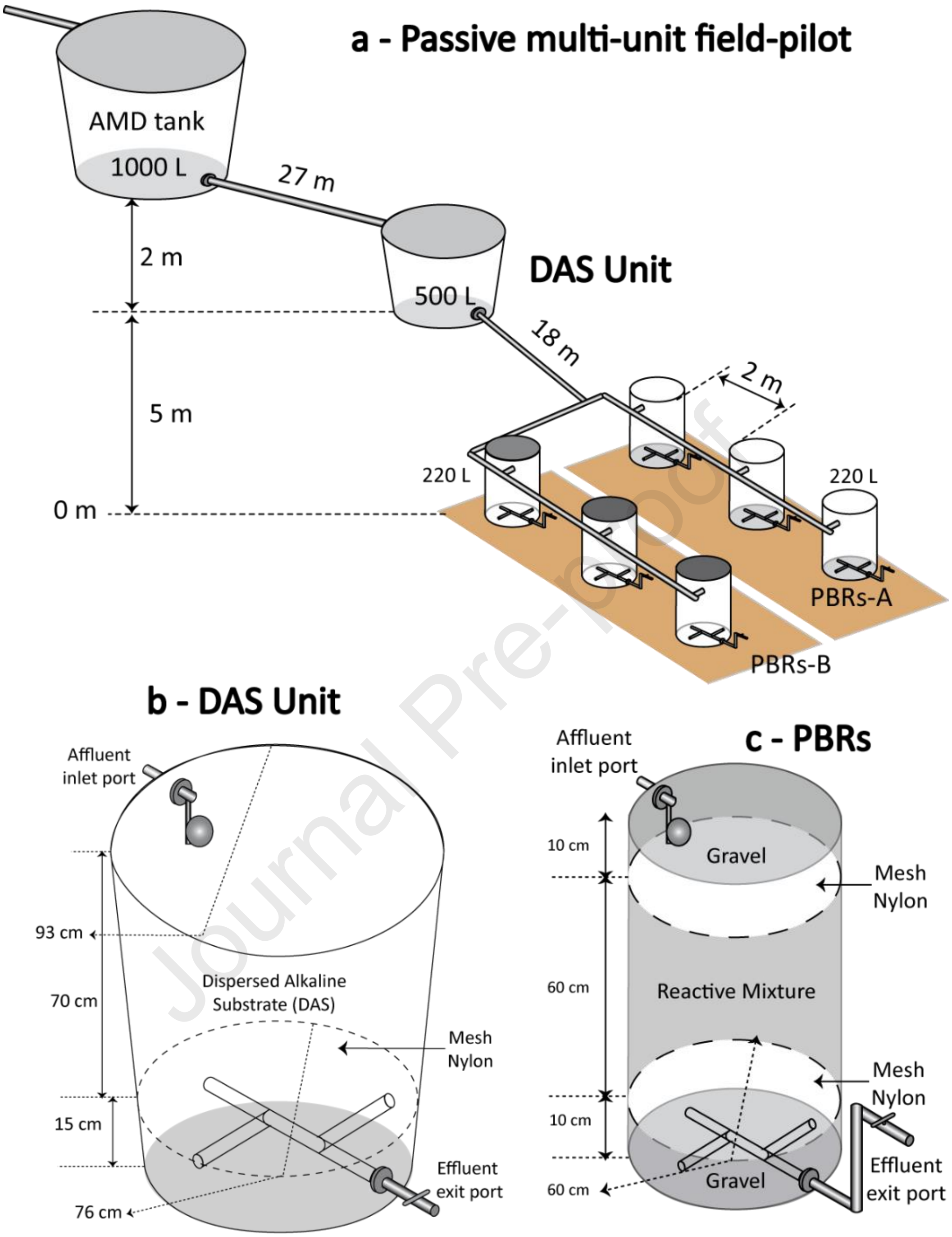


Fig. 1 a. Passive multi-unit field-pilot for AMD treatment, PBRs-A and PBRs-B were both composed of three independent reactors **b**. Dispersed alkaline substrates (DAS); **c**. Passive biochemical reactors (PBRs).

2.2.1 Efficiency of pilot passive multi-unit field-pilot

The efficiency of the pilot system was defined as pH and alkalinity increase, as well as sulfates and metals removal during AMD treatment. Liquid samples were collected once a month at the exit of the different units of the treatment system. Effluent flows were quantified using a 50 mL volumetric flask and timed on a stopwatch, and field parameters were analyzed on unfiltered samples immediately following sample collection. Temperature, pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) were measured with a multiparameter probe (HI 9828, Hanna Instruments; Woonsocket, RI), alkalinity was determined using standard method 2320B (APHA, 2005) and Fe^{2+} concentrations were determined on filtered samples (0.45 µm, Minisart®; Sartorius Germany) with a DR/890 HACH colorimeter (Method 8146: 1,10-Phenanthroline).

Samples for physicochemical laboratory analyses were collected in 150 mL amber glass bottles with lined caps and stored at 4°C. Samples to determine metals were filtered (0.45 µm,) and acidified to pH 2.0 with analytical concentrated HNO_3. Total sulfides samples were preserved with 4 drops of 2 N zinc acetate solution, without headspace and preventing exposure to air. In the laboratory, dissolved metals (Fe^{2+}, Mn^{2+} and Zn^{2+}) were quantified by atomic absorption spectrometry (Varian 240 FS, Agilent Technologies; Santa Clara, CA), using standard method 7000B (USEPA, 2007). Calibration curves for specific metals were evaluated by external standards (NIST traceable quality control standards, Perkin–Elmer Corporation, Merck, Germany) and were monitored by independently prepared check standard. One spike duplicate sample for every 50 samples was also prepared, with mean recoveries in the range 95.5–98.2 %. The blanks were run all the time and replicate analyses and the detection limits for Fe, Mn, and Zn were of 0.05, 0.03, and 0.03 mg L^{-1}, respectively.

Sulfate and sulfide were quantified by UV-VIS spectrophotometry (Genesys 10, Thermo Scientific; Waltham, MA) using standard methods 4500-SO_4 and methylene blue 4500 D, respectively (APHA, 2005). Net acidity (mg L^{-1} as $CaCO_3$ equivalents) was calculated according to the standard method 2310 (APHA, 2005). SRB counts were performed with an unfiltered sample using the most probable number (MPN) technique as per method D4412 (ASTM, 2012).

2.3 Physicochemical stability of the solid waste post-treatment

Two PBRs (A and B) were sacrificed at the end of the study to evaluate physicochemical stability of the solid waste post-treatment. The effluent exit port was opened to drain the treated liquid. Once emptied, the gravel layer and nylon disc were removed, and the solid waste was recovered from three levels: the bottom (0–20 cm), middle (20–40 cm), and top (40–60 cm). Twenty samples were collected from each level and mixed to form a composite sample that was divided into three subsamples. Samples were collected immediately to minimize the oxidation of the minerals generated during the AMD treatment. The representative samples of the solid waste post-treatment were stored at 4°C until physicochemical analysis were performed in triplicate.

Moisture was determined by difference in weight between wet and dry samples at 105°C for 20 h by standard method D 2216-98 (ASTM, 1999). The pH was measured (Lab 870, Schott; Mainz, Germany) using standard method 4972-01 (ASTM, 1995) and a ratio of solid to deionized water of 1:1. Total organic carbon (TOC) was measured on air-dried and sieved (0.210 mm) samples using the Walkley-Black method (Schumacher, 2002). Metal content (Fe^{2+}, Mn^{2+}, and Zn^{2+}) was determined by atomic absorption spectrometry after a total acidic digestion (0.5 g of solid and 20 mL of HNO_3 to 5 mL $HClO_4$ to 10 mL HCl to 1 mL HF) (Neculita et al., 2008). To evaluate chemical stability and mobility of metals (Fe^{2+}, Zn^{2+}, and

Mn^{2+}) as well as their potential for environmental contamination, sequential extraction procedures (SEP) were also performed (Jong and Parry, 2004). The SEP assesses the potential of metals leaching out from solid waste post-treatment. The SEP consisted of successive, 5-phase extracting: soluble compounds; exchangeable compounds; acid-soluble compounds, such as carbonates; reducible compounds, such as oxides and hydroxides of Fe and Mn; oxidizable compounds, such as organic matter and sulfides; and, finally residual mineral compounds. The SEP accuracy was determined with a comparison of the weighted sums of the five fractions obtained during the sequential extractions with the total metal concentrations obtained in one step by the digestion acid method. This comparison provides an estimation of the overall accuracy for the procedure when the variation of ±10 % (Tessier et al., 1979).

Notably, potentially bioavailable of metal concentrations and toxicity of solid waste post-treatment was previously assessed with the ratio SEM/AVS procedure modified (Neculita et al., 2008). Finally, the toxicity characteristic leaching procedure (TCLP), using standard method 1311, (USEPA, 1992) was employed to evaluate whether leachates from the post-treatment solid waste from the DAS unit and PBRs (A and B) were hazardous and whether they conformed to criteria for organic and inorganic waste solid pollutants in Colombia (Ministerio de Ambiente y Desarrollo Sostenible, Decree 4741 of 2005).

The extraction fluid of TCLP depends on the pH os waste material. Very basic wastes are leached with extraction fluid #2, while acid o neutral wastes are leached with extraction fluid #1, as it happened in this study (USEPA, 1992). The solid waste and extraction fluid #1 (0.087 M CH_3COOH: 0.0064 M NaOH, pH = 4.93 ± 0.05). at a solid:liquid ratio of 1:20, were placed in agitation (150 rpm) for 18 h. The samples were centrifuged (5,000 rpm); the supernatant was filtered and acidified (analytical HNO_3, pH 2.0); and then the metals (Fe^{2+}, Mn^{2+} and Zn^{2+}) and sulfate were quantified.

3 Results and Discussion

3.1 *Performance of pilot multi-unit treatment system*

The field-pilot was divided into two different sections: pre-treatment by the DAS unit, and main treatment by PBRs, under two configurations; open (PBRs-A) and closed (PBRs-B) to the atmosphere. The evolution of the physicochemical parameters as well as removal of metals (Fe^{2+}, Mn^{2+}, and Zn^{2+}) and sulfates within the different units are presented below.

3.1.1 pH, Alkalinity, ORP, and DO

During operation of DAS unit, a rise of pH values (from 2.8 to 5.2) was observed in the effluent for the first 3 months. However, in the fourth month the pH value droped to 3.2, affecting effluent quality (Fig. 2). At the same time, a by-passing layer of red precipitate was observed on reactive mixture of the DAS unit, which caused coating and passivation of the wood ash and clogging of the pore space. The high iron concentration in AMD resulted in a high acidity (Genty et al., 2012), which decreased the pH from 5.2 to below 3.2 after of contact with air. Thus, the replacement of reactive mixture of the DAS unit was necessary, and favored a new increase in pH up to 5.6, which was maintained until the end of the study. These results imply that the neutralizing capacity of substrate composed of 50% wood ash and 50% woodchips could be exhausted in only few months of operation. These problems have been overcome by using wood ash dispersed in woodchips in the DAS unit (Genty et al., 2012). Notably, layers of red precipitate as Fe oxide-hydroxides, which are the major issue during the passive treatment of Fe-rich AMD, were previously documented (Rakotonimaro et al., 2018).

In the DAS unit, a rise in ORP (from 280 to 590 mV) was observed simultaneously with a decrease in Fe concentrations (from 1,200 to 420 mg L^{-1}) due to the oxidation (Fe^{2+} to Fe^{3+}), hydrolysis and subsequent precipitation of iron oxyhydroxides. The ORP increase was observed caused by the layer formed by iron oxy-hydroxide minerals of a yellow-brown color. The yellow-brown precipitates also correspond to the schwertmannite ($Fe_8O_8(OH)_6 \cdot nH_2O$ or $Fe^{3+}_{16}O_{16}(OH, SO_4)_{12-13} \cdot 10\text{-}12H_2O$) precipitation that usually occurs when SO_4^{2-} and Fe^{2+} are present in high concentrations in the AMD (Orden et al., 2021), as in the current study (3,200 ± 183 mg L^{-1} and 1,200 ± 91 mg L^{-1}, respectively). Pre-treatment is the key for a performant multi-step treatment system; therefore, it is crucial to continue studying other mixtures of alkaline substrates that encourage an increase in pH and alkalinity as well as the removal of iron from AMD.

The PBRs acted as the main treatment for increasing the pH throughout the study (Fig. 2). The pH of AMD significantly increased at the outlet of both configurations of PBRs: the effluent of PBRs-A had a pH of 7.5 ± 0.8 during the first 4 months but then decreased to 6.2 ± 0.8, while the effluents of PBRs-B reached a pH of 7.5 ± 0.9, which was maintained for the rest of the study. The pH was correlated with an increased alkalinity (404 ± 114 mg L^{-1} $CaCO_3$, for PBRs-A, and 1588 ± 92 mg L^{-1} $CaCO_3$, for PBRs-B) and decreased net acidity (505.6 ± 13.3 mg L^{-1} of $CaCO_3$ equivalent by PBRs-A and 1157.6 ± 18.6 mg L^{-1} of $CaCO_3$ equivalent by PBRs-B) in the effluents. However, PBRs-A effluents acquired acidic conditions again, only a few hours after being discharged from the reactor, which had negative effects on the quality of water and entail further increases in acidity (540.7 ± 58.2 mg L^{-1} $CaCO_3$) and a decrease in pH (< 3.5).

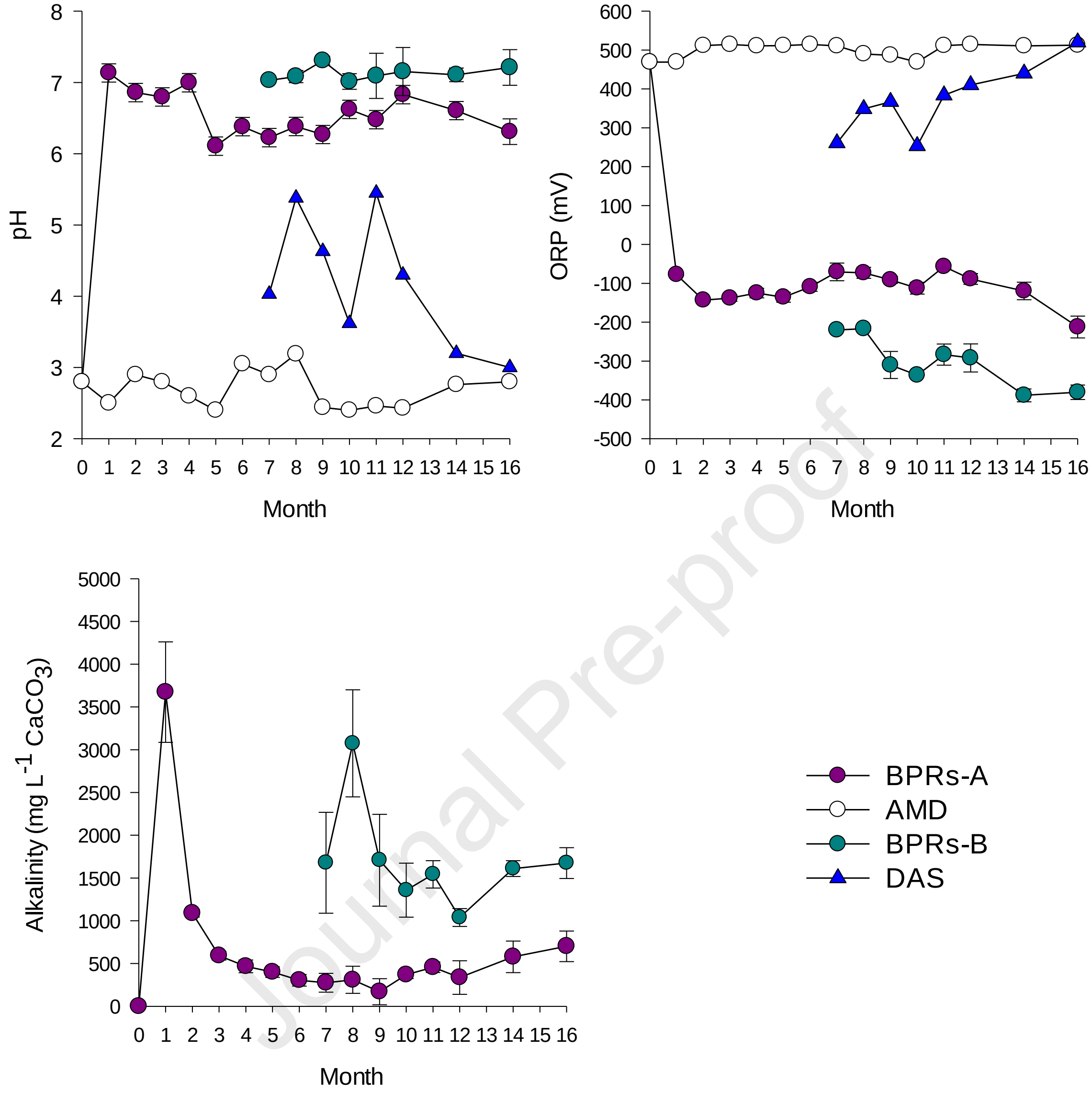


Fig. 2 Evolution of pH, alkalinity, and ORP, the passive multi-unit field-pilot during AMD treatment.

The difference in alkalinity, net acidity, and pH between reactors is due to their configuration open (A) or closed (B) to the atmosphere. The PBRs-B had an airtight lid that limited the entry of DO (0.6 ± 0.1 mg L^{-1}) and entailed lower ORP (-287 ± 58 mV), which favored anaerobic environmental conditions within the pore water suitable for SRB, while PBRs-A had a layer of woodchips that served as a lid but nonetheless allowed the passage of DO (4.5 ± 1.6 mg L^{-1}) in the reactor, which led to higher ORP (-105 ± 39 mV).

The increase in pH and alkalinity in PBRs is associated with dissolution of limestone from reactive mixtures of PBR or oxidation of readily available organic substrates by SRB, as well as from the dissolution of surface-bound hydroxyl ions in the substrate materials under acidic conditions (Genty et al., 2018). For optimal performance, the PBRs require anaerobic conditions and an anoxic and reduced microenvironment because these conditions favor SRB activity that improves mine water quality by increasing the pH (via the bicarbonate produced by organic material mineralization) and reducing sulfate to soluble sulfides, which precipitate metals as low soluble metal sulfides (Habe et al., 2020).

3.1.2 Sulfate and sulfide

Sulfate concentrations in the effluent of the pilot treatment system were consistently less than in the influent (3,200 ± 183 mg L^{-1}), with significant differences ($p < 0.05$) between the two configurations of PBR (Fig. 3). The pre-treatment by the DAS unit showed a total sulfate removal efficiency of 29% with a final concentration of 2,271 ± 573 mg L^{-1}. Comparatively, the PBRs-A showed lower sulfate removal efficiency (~ 40 %), with a final concentration of 1,920 ± 280 mg L^{-1}, than PBRs-B, which had the highest total sulfate removal (~ 62%) and a final concentration of 1216 ± 124 mg L^{-1}. In a previous study, a DAS unit composed of wood ash and woodchips (1:1) removed 46% to 80% of sulfate, but a rapid decrease in alkalinity was noted, thus leading to a decline of efficiency (Rakotonimaro et al., 2018). The literature shows that sulfate can be removed by formation of gypsum ($CaSO_4{\cdot}2H_20$) in wood ash materials but also by sorption onto iron hydroxide and oxi-hydroxi-sulphate (Genty et al., 2012). In the DAS unit, the precipitation of schwertmannite led to the removal of sulfate

(Caraballo et al., 2011). However, Wang et al. (2021) reported that sulfate and Fe are mainly removed by the formation of jarosite with an increase in pH, as shown below (Eq 1)

$$8FeOOH_{(S)} + xSO4_{(aq)} \longrightarrow Fe_8O_8(OH)_{8-2x}(SO_4)_{x(s)} + 2xOH \text{ (Eq. 1)}$$

It was also reported that in PBRs open to the atmosphere, sulfate removal efficiency can vary from 36% to 55% due to the difficulty of maintaining anaerobic conditions and weather influences (Lefticariu et al., 2015). Sulfate removal in PBRs was ORP and pH dependent, and it was achieved through a combination of biotic and abiotic processes. In the DAS unit, sulfate removal was due to abiotic processes only. In PBRs, sulfate reduction can be achieved biotically by SRB activity, which reduces sulfate to sulfide (Eq 2.), and abiotically by precipitation of insoluble sulfides or gypsum (Eq 3.), and adsorption of sulfate on mineral and organic substrate surfaces (Ben Ali et al., 2020; Lefticariu et al., 2017).

$$2CH2O + SO_4{}^{2-} \xrightarrow{SRB} 2HCO_3{}^{-} + H_2S \qquad \text{(Eq 2)}$$

$$Ca^{2+} + SO_4{}^{2-} + 2H_2O \longrightarrow CaSO_4.2H_2O \qquad \text{(Eq 3)}$$

At the end of the study, when PBRs were sacrificed (16 months), sulfate removal was confirmed as a function of distance above the inlet PBRs and of operation time. The solid waste post-treatment analysis revealed that sulfate was more concentrated in the bottom layer than in the top layer. Thus, PBR-A had a sulfate concentration of 54.7 ± 10.3 mg kg^{-1} in the bottom layer and 21.6 ± 6.5 mg kg^{-1} in the top layer, while in PBR-B sulfate was 32.6 ± 14.3 mg kg^{-1} in the bottom layer and 12.8 ± 9.5 mg kg^{-1} in the top layer. However, the AVS concentration was higher in the bottom layer of PBR-B (15.6 ± 4.8 mg kg^{-1}) than in the bottom layer of PBR-A (10.3 ± 3.2 mg kg^{-1}), which indicates that, in PBR-B, the main mechanism for sulfates removal was probably dominated by biotic processes, while, in PBR-A, those processes were abiotic. The presence of sulfides in PBRs is indicative of active sulfate reduction. Sulfides were found in the PBRs-A effluent samples at concentrations above the detection limit (0.5 mg L^{-1}) only during the first three months of operation (Fig. 3), possibly as a remnant of the biological acclimatization stage. Later, sulfides concentrations decreased in effluents as a consequence the reduction of the number of SRB (Fig. 3). Furthermore, the few sulfides produced could be trapped inside the reactor or escape as gas. In an open system under acidic conditions, as is the case of PBRs-A (pH 6.2 ± 0.8), the sulfides might escape as gas, at acidic pH ($H_2S_{(g)}$; pka1 = 7.02). In neutral conditions, the sulfides would have been in the monoprotic (HS^-) form and stayed inside the reactor.

In PBRs-B effluent sulfide concentrations ranged from 16.8 ± 2.9 to 45.7 ± 3.5 mg L^{-1} during the first 5 months of operation, but after the low-flow episode of AMD input due to a damage in the mine pipe, dissolved sulfide significantly increased in the output water (180.5 ± 28.7 mg L^{-1}). Although this concentration deteriorated the effluent quality, no impact on the number of SRB or their activity was noted, even as it was above the concentration reported as inhibitory (100 mg L^{-1}) (Caraballo et al., 2011). Closed configuration of the PBRs-B favored a lower ORP, which maintained anaerobic conditions that allowed degradation of the reactive mixture's organic by active microbial communities and simultaneously provided conditions in which SRB can reduce sulfate to sulfide.

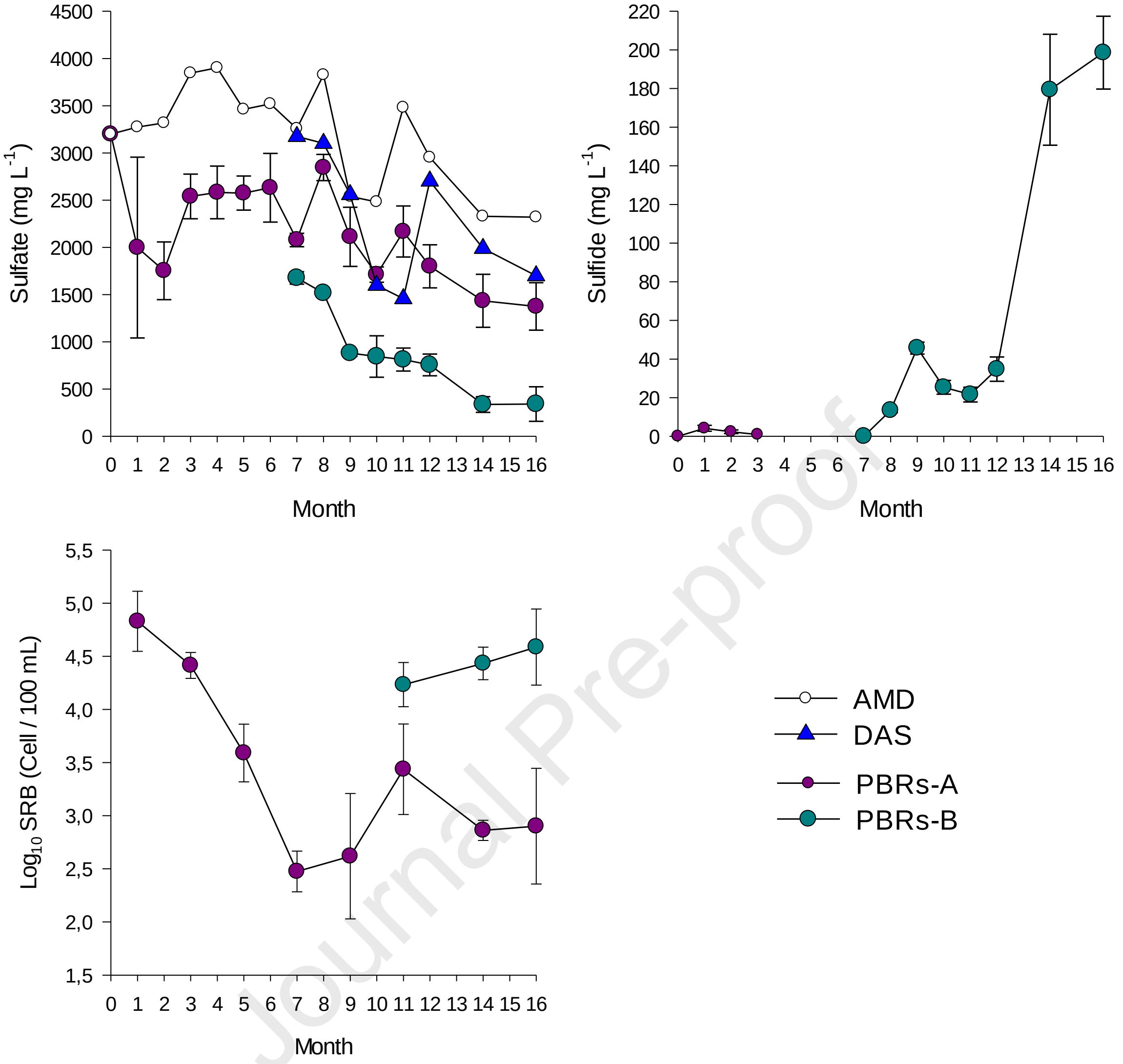


Fig. 3 Evolution of sulfate and sulfide concentrations, and SRB counts the passive multi-unit field-pilot during AMD treatment.

The pilot treatment system removed sulfate at 84% with the line of PBRs-A and 91% by PBRs-B. The difference between PBRs-A and PBRs-B efficiencies is probably due to the ability to create and maintain an anaerobic environment that facilitates the establishment of SRB and the consequent production of sulfides. PBR design not only ensures sulfate reduction and metal sulfides precipitation; it also strongly influences the overall treatment performance and affects investment and operating costs.

3.1.3 Metal removal

The Fe^{2+} concentrations in AMD govern the performance of the pilot treatment system when other metal concentrations are significantly lower or absent (Rakotonimaro et al., 2018), as in the case of the present study; the high concentration of iron (1,200 ± 91 mg L^{-1}) was the major issue during the treatment of AMD (Fig. 4). Besides, Fe^{2+} increased in AMD during the study because the damage in the mine pipe that conducted AMD from mineshaft to impoundment. This damage was repaired after two weeks but during this time the volume of AMD in the impoundment was reduced (~ 30%) by evaporation due to dry season. The low volume of AMD in the impoundment was maintaining until the end of the study.

The first 6 months of the study when only PBRs-A were operating, iron removal was ~ 30 % with a final concentration of 840 ± 188 mg L^{-1}. This removal is very low, even in uncovered PBRs, as has been reported by studies of pilot field trials, where they achieved an iron removal between 40% and 62% under 3 days of HRT (Lefticariu et al., 2015).

The DAS removed ~ 20% of iron with a final concentration of 960 ± 88 mg L^{-1}, but its surface had become covered by reddish-brown precipitates (~20 cm depth), likely creating a passivation of the substrate. The fast reactivity of the wood ash favored a pH increase and the precipitation of ferric oxide-hydroxides, visible as yellow-brown armoring. However, in month 10, removal of the brownish precipitates significantly increased iron removal up to 30%, but it dropped rapidly to 20%, remaining constant until the end of the study. Previous studies reported precipitation, sorption, and co-precipitation as the main iron-removal mechanisms in DAS (Schwarz et al., 2020). Besides, pretreatment unit are efficient for precipitate Fe and neutralize acidity reducing the impact of AMD on the microorganisms present in the PBRs (Chen et al., 2020).

The installation of the DAS unit allowed for an increase in iron removal in PBRs-A to 46% with a final concentration of 440 ± 51 mg L^{-1}, which also remained stable until the end of the study. At the same time, PBRs-B achieved a removal of ~ 75 % with a final concentration of 240 ± 10 mg L^{-1}. During the start-up and acclimation, metals could be removed by precipitation in the form of hydroxides and carbonates, as well as by sorption on fresh organic substrate. Then, during the continuous flow operation, metal removal (as MeS) might be explained by the formation of sulfides during microbial metabolism (Eq. 4) (Fan et al., 2019).

$$Me^{2+} + H_2S \longrightarrow MeS_{(solid)} + 2H^+ \quad (Eq. 4)$$

The removal of Zn^{2+} (99 %) from the AMD was observed during the pilot treatment, without significant differences ($p < 0.05$) between PBRs-A and -B (Fig. 4). From month 10, an increase of Zn^{2+} (6 mg L^{-1}) was observed in the effluents of the DAS unit, which yielded higher concentrations of metal than the AMD source. However, after the initial leaching out of Zn^{2+} from the reactive mixture (50% woodchips, 50% wood ash), the PBRs were able to reduce Zn^{2+}. In the literature, both low releases (1.3 – 4.0 mg kg^{-1}) as well as higher releases (42 – 110 mg kg^{-1}) (Fan et al., 2019; Freire et al., 2015) of Zn from wood ash can be found. Maresca et al., (2017), performed essays on columns using acidified distilled water (pH < 2) as leaching media. They showed that Zn^{2+} is generally leached in the exchangeable and reducible fractions of the ash wood, indicating the presence of Zn in more mobile form. These results coincide with leaching of Zn^{2+} from the reactive mixture from the DAS unit, showing a direct relationship between the metal dissolution and low pH of AMD. Therefore, leaching of metals from wood combustion ash is an issue to be considered when these materials are used in bioremediation processes.

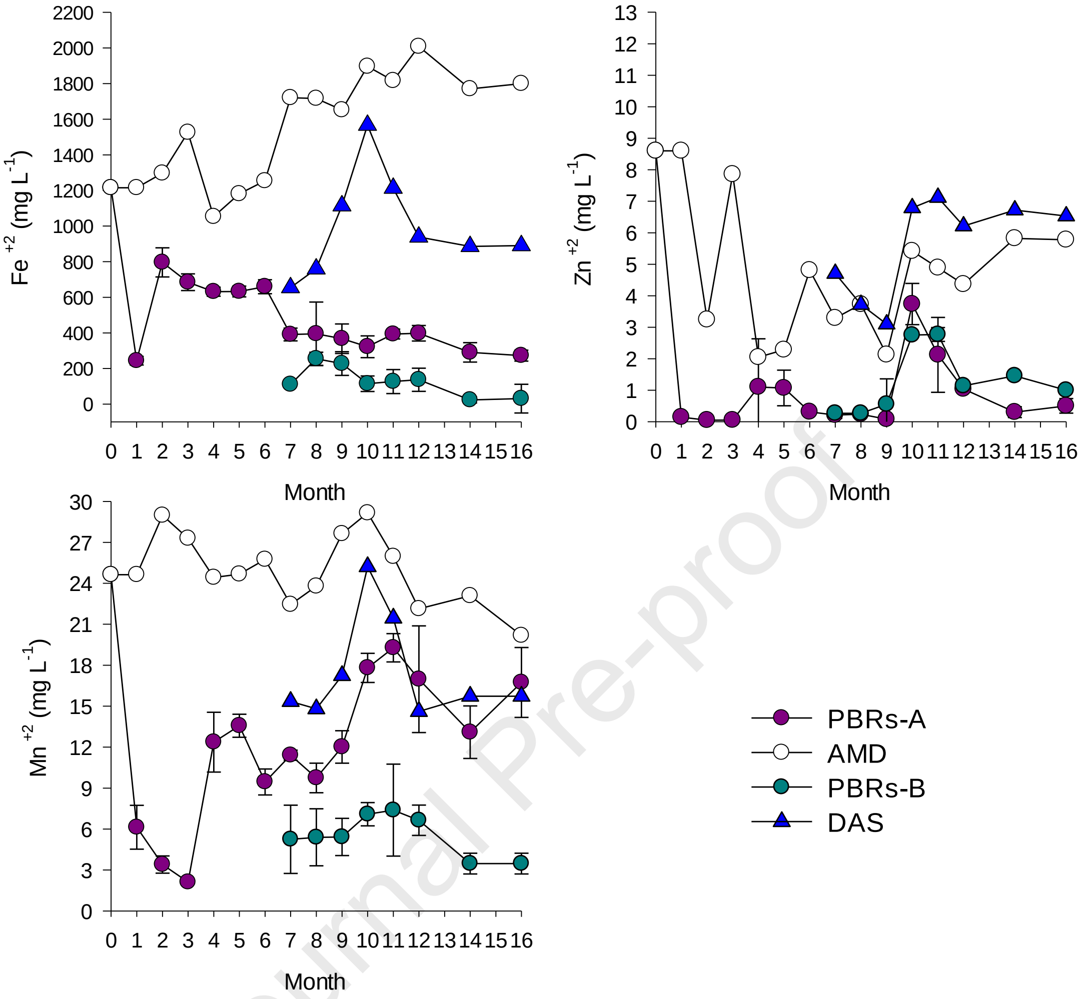


Fig. 4 Evolution of metals concentrations during the treatment of AMD in passive multi-unit field-pilot.

Mn^{2+} has been acknowledged as the most challenging metal to remove in PBRs, especially under reducing conditions (Neculita and Rosa, 2019). This was observed in PBRs-A, where Mn^{2+} was removed around 20% after the start of continuous flow operations, and it was constant until month 10, when Mn^{2+} concentrations increased again in the effluent and the efficiency decreased by 10%. However, multi-unit systems are more efficient because the oxidation of Mn^{2+} occurs more slowly than that of Fe^{2+} (Le Bourre et al., 2020).

Therefore, when the field-pilot system started, Mn^{2+} removal increased up to 76% with a final concentration of 5.5 ± 1.5 mg L^{-1}. The DAS unit removed Mn^{2+} by 28%, while PBRs-B removed it by 48%. Mn^{2+} removal required an optimal pH of between 8 to 10, which is difficult to achieve in PBRs by limestone dissolution because its equilibrium is reached at a pH 6 to 7 (Gibert et al., 2013). Furthermore, Mn^{2+} removal mechanisms are not completely documented because its removal processes are highly dependent on Eh-pH conditions and other dissolved metals and metalloids (Neculita and Rosa, 2019).

Therefore, at the end of the study in month 16, the pilot passive multi-unit field-pilot achieved a total removal of 63% for Fe^{2+} and 48% for Mn^{2+} with the line of PBRs-A, and 80% for Fe^{2+} and 66% for Mn^{2+} with line of PBRs-B, as well as 99% removal for Zn^{2+} without significant differences between the two lines ($p < 0.05$).

3.2 Stability of the solid waste post-treatment

Results showed that solid waste post-treatment of PBRs presented an acid to neutral paste pH (Table 2). Solid waste from the PBRs-A showed lower pH (4.3 ± 0.5) relative to PBRs-B with neutral pH (6.5 ± 0.8), while the initial reactive mixture had alkaline pH (8.2 ± 2.0). The decline in pH in the reactive mixture of the reactors is probably due to depletion of neutralizing agents caused by constant AMD input and downward flow in the reactors during continuous operation. Moreover, paste pH in PBRs-A was lower than in PBRs-B because the former operated for 16 months while the latter operated only 10 months. In addition, PBRs-B operation started at the same time as the DAS unit and received the AMD at a less acidic pH (from 4.5 to 5.2).

Table 2. Physicochemical parameters of the solid waste from passive multi-unit field-pilot passive treatment.

Parameters	**Unit**	**Reactive mixture**	**Solid waste post-treatment**	
			PBRs-A	**PBRs-B**
Paste pH		8.2 ± 2.0	4.3 ± 0.5	6.5 ± 0.8
Humidity	%	18.5 ± 3.2	19.2 ± 1.5	18.0 ± 6.3
TOC	%	28.3 ± 1.7	3.82 ± 0.3	10.43 ± 0.9
Fe	$g\ kg^{-1}$	23.0 ± 3.1	104.7 ± 4.1	78.0 ± 0.5
Mn		1.4 ± 0.1	33.8 ± 0.1	29.3 ± 0.1
Zn		2.3 ± 0.0	12.4 ± 0.2	10.2 ± 0.4
Sulfate		2.6 ± 0.6	34.7 ± 0.0	21.6 ± 0.5
AVS	$\mu mol\ kg^{-1}$	---	4.3 ± 0.3	9.7 ± 0.5
SEM		---	$7.6\times10^{4} \pm 2.0\times10^{-2}$	$3.8\times10^{2} \pm 2.0\times10^{-3}$
SEM/AVS		---	1.8×10^{3}	3.9×10^{1}

The high TOC content in the initial reactive mixture of PBRs was mainly due to the presence of cow manure, mushroom compost, and sawdust. However, TOC in bioreactors during the operation time drastically decreased (Table 2). The major reason for TOC loss in PBRs is the leach out in the form of dissolved organic carbon (DOC) at low pH conditions (Song et al., 2012). Loss of TOC in reactors could be a problem for long-term use because it limits the growth of microorganisms (Mirjafari and Baldwin, 2016).

Metals (Fe, Mn, and Zn) in solid waste were concentrated in the all reactors, mainly in PBRs-A because of its longer operation time than PBRs-B. High concentrations of Fe and Zn in solid waste after treatment indicated that the reactors were efficient in removing these metals from the influent AMD and confirmed the importance of the DAS unit because the final concentration of metals was lower in the effluents, after the installation of the pre-treatment.

Results of AVS/SEM analysis showed that PBRs a higher concentration of SEM and AVS, presenting ratios greater than 1 (Table 2). The ratio AVS/SEM of PBRs-A (1.8×10^{3}) was 400 times greater than that of ratio PBRs-B (3.9×10^{1}). Therefore, the precipitation as oxy-hydroxide and carbonate minerals were the predominant mechanism of removing metals in

PBRs-A, while the formation of metals sulfide was predominant in PBRs-B. These findings indicate that, in PBRs-A, metals (Fe^{2+}, Mn^{2+}, and Zn^{2+}) persisted in the interstitial water, were not immobilized in the reactive mixture, and leached to the environment. Consequently, these results (SEM/AVS/ > 1) suggest high metal toxicity with regards to bioavailable heavy metals in pore water of solid waste post-treatment. Consistent findings were reported by Jouini et al., (2019b) and Jong and Parry, (2004) who observed that solids generated from PBRs with SEM /AVS/ > 1 can be toxic if not properly disposed.

The SEP has previously been applied to solid waste from PBRs to obtain information on the chemical stability and mobility potential of metals in the environment (Jouini et al., 2020a, 2019a, 2019b). In the present study, the SEP was performed to evaluate metal leaching potential of the solid waste from PBRs and therefore predict their potential fate and stability for disposal.

The results showed that Fe from initial and PBRs-A solid waste were mainly associated with soluble compounds (50%). This fraction released the exchangeable cations and weak acid soluble phases; therefore, the elements recovered in this step are considered the most labile fraction of the pollutants in the residues (Macías et al., 2012a). Moreover, Zn was associated with exchangeable and carbonate compounds, and these fractions in solids residues correspond to pollutants with a moderate lability and are subordinated to the existence of an oxidizing or reducing environment (Jouini et al., 2019a). The Mn concentrations in the water soluble, exchangeable, and carbonate fractions in solid waste of PBRs-A were higher than 70%. Lower Mn concentrations were found bound to organic matter and sulfides (15%), while about 14% were associated with Fe–Mn oxides.

At the same time, in PBRs-B, metals (Fe, Mn, and Zn) were associated with to phases such as oxides and hydroxides of Fe and Mn and oxidizable phases such as organic matter and sulfides. This was not surprising since metals sulfides were expected to be generated in PBRs-B due to the high concentration of soluble sulfides in the effluents. This fraction comprises both labile and more refractory organic substances in combination with sulfidic metal associations (Jong and Parry, 2004).

The sum of the principal pollutant concentrations in the most labile fractions (soluble and carbonate compounds) was the residues of PBRs-A, which can be classified according to their environmental hazard as follows: Fe> Mn> Zn. Moreover, solid waste from PBRs-B present association of the metals with relatively stable phases (sulfides and residual mineral compounds) that can be released if conditions of pH-Eh change, as previously was reported by Lounate et al., (2020).

The leaching solution used to perform the TCLP tests was the leaching medium #1 (pH 4.93 ± 0.05), which was selected taking into account the pH of solid waste post-treatment of the PBR A and B (4.3 ± 0.5, 6.5 ± 0.8, respectively). Results of TCLP test (Table 3) showed that pH of leachates varied from near neutral from the solid waste of PBRs-A and PBRs- B (7.2 ± 0.3 and 6.3 ± 1.5, respectively) to acid from the DAS waste (4.8 ± 1.2). The pH in PBRs is attributed to the buffer capacity of the reactive mixture due to the presence of carbonate, while, in the DAS waste, the substrate with wood ash and woodchips has little capacity to neutralize the leachate. A previous study showed that the dissolution of the residual carbonates present in solid waste of PBRs neutralized the acidity of leachates in the TCLP test (Jouini et al., 2020b).

The TCLP test results meet the criteria to designate it (this residue/waste) as hazardous material that cannot be conventionally landfilled. For TCLP leachates from solid waste of the PBRs, higher concentrations of Fe and Mn were found while relative low concentration of Zn and sulfate (Table 3) were present. However, TCLP has the disadvantage not to take into account contaminants such as Fe, Zn, and Mn. Therefore in Colombian legislation these residues, are classified as low risk (Ministerio de Ambiente y Desarrollo Sostenible,Decree 4741 of 2005). Nevertheless, reactive mixtures of passive treatment should not be disposed of in landfills due to large quantities of organic mater that could generate organic acids inducing metal dissolution (Lounate et al., 2020) or by dissolution mediated by microorganisms under natural weathering (Jouini et al., 2019a). This statement is confirmed by the results from AVS/SEM (> 1) and SEP that suggest high potential mobility of metals, specially for PBRs-A and SEP when Fe and Mn areoxidizable phases such as organic matter are present. In such situations, Fe dissolution could become environmentally problematic if your destination is a water source because Fe concentrations were 50 times higher than criteria set by waterwaste Colombia's 2015 Regulation 0631 (2 mg L^{-1}) (Ministerio de Ambiente y Desarrollo sostenible, 2015) and hundreds of times higher for inorganic pollutants according to the US National Recommended Water Quality Criteria of continuous concentration (1 mg L^{-1}) (USEPA, 2000). Further contaminated leaching can be produced from this reactive mixtures and research with other leaching tests are required to ensure appropiate long-term management and to control the potential contaminants release.

Table 3. Physicochemical parameters of the leached effluents after TCLP tests of solid waste from the passive multi-unit field-pilot treatment.

Solid waste	**Total Extractable TCLP (mg L^{-1})**				
	pH	**Metals**			**Sulfate**
		Fe	**Mn**	**Zn**	
PBRs-B	7.2 ± 0.3	105.1±0.4	8.8±0.1	1.8±0.6	4.5±1.0
PBRs-A	6.3 ± 1.5	258.7±4.1	12.8±0.0	1.1±0.0	17.3±1.5
DAS	4.8 ± 1.2	352.4±9.4	15.5±1.8	10.6±2.3	520±6.5

4 Conclusions

This study evaluated the performance of passive multi-unit field-pilot treatment during a 16-month operation at a coal mine in Colombia Andean Paramo. Chemical stability and mobility of metals (Fe^{2+}, Zn^{2+}, and Mn^{2+}) from post-treatment solid waste were also assessed. The passive multi-unit field-pilot achieved a total removal of 74 % SO_4^{2-}, 63% Fe^{2+}, and 48% Mn^{2+} with the line of PBRs-A (open to the atmosphere), and 91% SO_4^{2-}, 80% Fe^{2+}, and 66% Mn^{2+} with line of PBRs-B (close to the atmosphere), as well as 99% removal for Zn^{2+} without significant differences between the two PBrs ($p < 0.05$). Moreover, the results of SEM/AVS, SEP, and TLCP tests indicated that solid waste from the pilot passive multi-unit field-pilot can produce acidic leachates that could release large amounts of Fe and Mn if they were disposed in oxidizing conditions; contact with water or any other leaching solutions must be avoided.

The results show that a passive multi-unit field-pilot treatment can efficiently increase pH and alkalinity, and remove sulfates and metals from AMD. However, anaerobic conditions in reactors must be ensured for stimulating SRB. The differences in performance between PBRs open or closed to the atmosphere induced changes in the chemical environment, metal removal mechanisms, and physicochemical properties of the solid waste post-treatment. Therefore, to enhance the remediation capacity of PBRs, future design must optimize coverage but also include a DAS unit to allow the removal of high concentrations of iron. The present study also evaluated the chemical stability and mobility potential of metals (Fe^{2+}, Zn^{2+}, and Mn^{2+}) and the potential for environmental contamination of solid waste; we conclude that these wastes cannot be disposed of in a municipal landfill. Although passive multi-unit field-pilot treatment exhibited good performance, additional efforts need to be undertaken to improve the efficiency of the DAS unit. Further research is required to ensure adequate long-term management and thus prevent toxicity of biological organisms. It is advisable disposing of solid waste from passive treatment in a dry environment to prevent the generation of new metal pollution sources.

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Statement of novelty

The present manuscript is part of a larger study with the aim of find a sustainable solution for the significant environmental degradation occasioned by acid mine drainage (AMD) in Zipaquirá Mining District of Colombia. Previous studies for this site, using batch tests and synthetic AMD, allowed the selection of the most efficient reactive mixture (15% cow manure, 10% mushroom compost, 25% sawdust, 15% gravel, 20% limestone, and 15% sediment) to increase pH and alkalinity as well as to remove sulfates and metals from AMD (Vasquez et al., 2016a). Later, column tests were also carried out with the aim of evaluating the effect of hydraulic retention time (HRT) on the treatment efficiency of AMD. These column experiments allowed to fix HRTs at 2 days for the treatment of AMD (Vasquez et al., 2016b). Additional changes were established in column tests' solid waste including the composition of the reactive mixture, enzymatic activity, and microbial community (Vasquez et al., 2018). Finally, in the present study the evaluation of passive multi-unit field-pilot treatments in the field allows the use of real AMD under high altitude mountains conditions and determines the number of units necessaries to achieve the optimal efficiency of the system. In this context, the main objective of the present study was to evaluate the performance of a passive multi-unit field-pilot during a 16-month operation period. A secondary objective was to assess the chemical stability and mobility of metals (Fe^{2+}, Zn^{2+}, and Mn^{2+}) from post-treatment solid waste.

Conflict of interest

The authors declare that they have no conflict of interest