Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20163

64 (2017) 21–30
February

Performance of three bench-scale diffusive exchange systems during treatment of acid mine drainage with high copper concentration

Norma Pérez*, Alex Schwarz, Pamela Sanhueza, Gustavo Chaparro

Centro de Recursos Hídricos para la Agricultura y la Minería (CRHIAM), Universidad de Concepción Barrio Universitario s/n, Concepción, Chile, Tel. +56 41 2203258; emails: normaperez@udec.cl (N. Pérez), alexschwarz@udec.cl (A. Schwarz), pamsanhueza@udec.cl (P. Sanhueza), gchaparro@udec.cl (G. Chaparro)

Received 14 May 2016; Accepted 14 August 2016

ABSTRACT

An alternative passive biochemical treatment has been developed for acid mine drainage (AMD), called the Sulphidogenic Diffusive Exchange System (SDES). It differs from conventional designs in that, it includes vertical drainage tubes for preferential transport of the AMD through the reactor bed. Thus, the microorganisms in the reactor bed is never exposed directly to the AMD, but only indirectly in diffusive transport or exchange processes which allow generalised chemical gradients to be established which protect the communities. An additional advantage of the new configuration is the possibility of recovering valuable minerals from the bottom of the tubes if they form there and are then sedimented out. We assessed the performance of three prototype SDES at bench scale to treat first water with sulphate and then AMD with high copper concentration (528 mg/L), at two flow rates (Q1 = 3.75 L/d and Q2 = 7.5 L/d). The prototypes differed in the volume occupied by the drainage tubes and their diameter (SDES1: 10%, ϕ = 5.5 cm; SDES2: 20%, ϕ = 5.5 cm; SDES3: 10%, ϕ = 4 cm). When the AMD was fed at the lower flow rate the three prototypes were able to effectively eliminate all the metals (>99%), at a volumetric rate of 0.27 mol/m^3/d. The sulphate removal rates also presented no significant variation (between 0.30 mol/m^3/d (SDES1 and SDES2) and 0.33 mol/m^3/d (SDES3), indicating that diffusive transport does not limit reactor performance. When the flow rate was increased, differences were observed in metals removal. The reactors suffered overloading and only partial metals removal was achieved at rates which varied between 0.2 (SDES1) and 0.33 mol/m^3/d (SDES2 and SDES3). Precipitates with a high copper concentration were recovered at the base of the drainage tubes.

Keywords: Diffusive exchange reactor; Toxicity; Bioprotection; Copper; Sulphate reduction

1. Introduction

Acid mine drainage (AMD) is generated by the oxidation of sulphide ores [1–3]. It is typically highly acidic and contains high concentrations of metals and sulphate. When the AMD is generated in remote sites and abandoned mines, the low operating and maintenance costs, the use of small quantities of chemicals and the minimal energy consumption needed [4–6] make passive treatment options more attractive.

Passive biological treatment systems are composed of a reactive bed, commonly consisting of a mixture of organic waste particles, an inoculum and alkaline substrates such as limestone, sea shells, ash, etc., the function of which is to help neutralise the acidity [6–11]. Examples of passive biological systems are anaerobic organic substrate bioreactors (AOSB) [12] and compost bioreactors [13], which are grouped under the concept of biochemical reactors [6]. In these systems, a microbial consortium degrades the organic matter, allowing sulphate-reducing microorganisms to develop [5,14]. During sulphate-reduction, the sulphate in the acid drainage is used as an electron acceptor and is converted into sulphide, while alkalinity is generated at the same time [1,15]. The principal mechanism for metals removal in the biological processes is by precipitation with sulphide. At the same time the source of alkalinity commonly used is limestone [7,16]; when it

---

* Corresponding author.

dissolves it releases carbonate which neutralises acidity and promotes the precipitation of metals as carbonates and hydroxides [6,17]; thus, reducing the toxicity of the AMD for the microorganisms.

When construction of biochemical reactors is being considered, the materials/waste available *in situ* is evaluated for incorporation into a reactor as a homogeneous mixture with limestone [6,8,18,19]. However, the performance of biochemical reactors is limited by the long-term reactivity of the organic matter and the toxicity of the AMD. Furthermore, because the metals remain immobilised in the reactor bed, their recovery is not economically viable.

Schwarz and Rittmann [20] proposed an innovative biochemical reactor design, the Diffusive Exchange System (DES), which provides preferential routes to transport the AMD through the bed, thus, avoiding direct exposure of the microorganisms to the AMD and providing an important level of bioprotection. The scheme proposed initially was for a permeable reactive barrier consisting of horizontal reactive layers with low hydraulic conductivity, in which the microorganisms develop, alternating with layers of sand with high hydraulic conductivity through which water contaminated with AMD could flow [21]. Pérez et al. [22] compared the functioning of a traditional permeable barrier with a diffusive exchange barrier for treatment of AMD containing zinc (60 mg/L). Although, the zinc was completely removed by both reactors, greater bacterial diversity and high sulphides concentrations were found in the diffusive exchange reactor.

In this work we propose to change the design of the DES reactor layers to vertical flow, incorporating slotted drainage tubes (screens) to transport the AMD through the bed. It is expected that the tubes will also act as reactors for the formation, sedimentation and accumulation of precipitates, facilitating recovery and avoiding the reactor becoming blocked.

One of the important variables expected to affect the operation of the DES reactor is the percentage of the volume occupied by the drainage tubes. A larger drainage tube volume will reduce the reactor’s reactivity, but increase the hydraulic residence time of the AMD, which might be beneficial. Another variable which we propose to assess is the distribution of the drainage volume since the use of a larger number of smaller tubes might help to diminish the possible limitation of solute transport to and from the reactive zone.

We worked with three bench-scale DES reactors to assess the effects of these variables on their performance. During the first month they were fed solely with a sulphate solution to promote the development of sulphate-reducing microorganisms. Once the sulphate removal rate had stabilised, the functioning of the prototypes was assessed for two hydraulic residence times (HRT) using a synthetic AMD with metal concentrations representative of a copper mine in central Chile. At the end of the experiments the results were analysed to establish the metal contents in the reactive zone, in the precipitates accumulated at the bottom of the screens and in the external settlers.

2. Materials and methods

2.1. Bench-scale reactors

The reactors were constructed using 200 L drums. All the reactors had a base layer of sand (10 cm deep), followed by the reactive mixture (62 cm deep), covered by 5 cm of sand and a layer of water 10 cm deep (Fig. 1(a)). The particle size of sand was 0.5–5 mm. The reactive mixture contained cellulose fibres of forest origin (50%), cow manure (30%) and limestone at particle size 0.5–5 mm (20%). The reactors were saturated with sulphate solution (3,890 mg/L), leaving a layer of solution 10 cm deep on the top. Cow manure was used as the bacterial inoculum and in addition 750 mL of a culture of sulphate-reducing bacteria and 500 mL of a culture of cellulolytic bacteria were added during construction. The cellulolytic bacteria were isolated and enriched, with a culture medium in which cellulose is the only carbon source [23], from the sediment of a lagoon on the Universidad de Concepción campus. The sulphate-reducing bacteria were obtained from multiple transfers from the anaerobic sludge of the local sewage treatment plant into modified Postgate C culture medium [24].

Three diffusive exchange systems were designed and constructed (Fig. 1(b)) and the conductive zones fitted with high density polyethylene screens (HDPE slotted drainage tubes). The diameter of the screens was varied (4 and 5.5 cm),

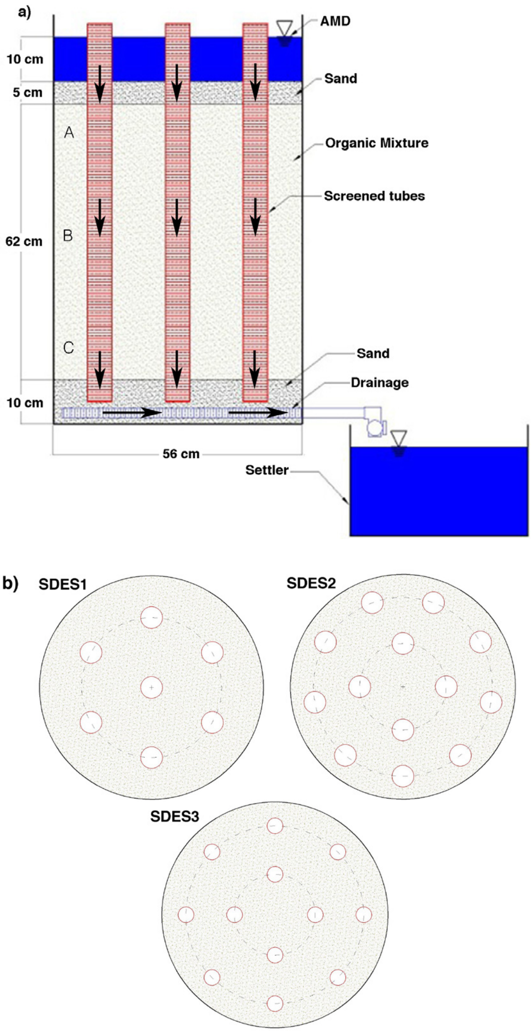

Fig. 1. (a) Side view of the diffusive exchange systems, (b) Representation of the characteristics of the diffusive systems (SDES). The vertical drainage tubes (conductive space) are represented as circles.

as was the percentage of the cross section, which they occupied (10% and 20%, Fig. 1(b)). The total opening area was respectively, 75 and 85 cm^2/m and the opening width 1 mm. The tubes were installed vertically, inserted in the lower sand layer and protruding to the top of the free water layer. SDES1 had screens of 5.5 cm internal diameter occupying 10% of the volume; SDES2 had screens of 5.5 cm internal diameter occupying 20% of the volume; while SDES3 had screens of 4 cm internal diameter occupying 10% of the volume.

Because of the reported small size of CuS precipitates [25], the effluent may carry away metals sedimented at the bottom of the screens; we therefore, included an external settler to capture them.

The object of these designs was to assess at bench scale the impact on the effectiveness of treatment of: (1) the distribution of reactive vs. conductive volume (10/90 vs. 20/80); and (2) screen diameter. If the relative volume of the conductive zone is increased, the amount of material available to react is reduced, although the hydraulic residence time of the fluid in the reactor increases. If however, the screen diameter is reduced with the same conductive zone volume, the number of screens increases, reducing the diffusion distance. In parallel the surface area for diffusive exchange increases, which could help to prevent the tubes from becoming blocked by scaling.

Two design variables were introduced in the reactors: the interface area and the diffusion distance. The area available for diffusive exchange in each reactor, called the specific interface area (SIA), was calculated for each reactor:

$$\text{SIA} = \frac{\text{tube surface area} \times \text{number of tubes}}{\text{reactor volume}} \tag{1}$$

The values were SDES1 = 6.3 m^{-1}, SDES2 = 12.6 m^{-1} and SDES3 = 8.1 m^{-1}.

The diffusion distance was calculated along a line passing through the axes of the tubes, from the mid-point of the reactive zone to a screen axis; this parameter was 17.8, 10.7 and 14.0 cm for SDES1, SDES2, and SDES3, respectively.

After the reactors had been constructed and the sulphate-reduction activity observed (by measuring the sulphate and sulphide inside the reactors), a solution of Na_2SO_4 (3,890 mg/L SO_4^{2-}) was added as the influent for 35 d at a flow rate of 7.5 L/d. Subsequently we began feeding the reactors with metals using a flow rate of 3.75 L/d (Q1), with a synthetic mine drainage containing metal concentrations representative of a copper mine in central Chile: SO_4^{2-} (3,890 mg/L), Cu^{2+} (528 mg/L), Al^{3+} (95 mg/L), Fe^{2+} (0.77 mg/L), Zn^{2+} (85 mg/L), K^+ (5.5 mg/L) and Cl^- (61 mg/L) at pH 4.2. The solution was prepared once or twice a week by dissolving appropriate amounts of Na_2SO_4, $CuSO_4$*$5H_2O$, $Al_2(SO_4)_3$*$18H_2O$, $FeSO_4$*$7H_2O$, $ZnSO_4$*$7H_2O$, K_2SO_4 and NaCl in potable water without chlorine. After 54 d the flow was doubled (Q2 = 7.5 L/d) to assess the behaviour of the reactors under overload. The HRT during Q1 were 4.1 d (SDES1 and SDES3) and 8.2 d (SDES2), based on the volume of the drainage tubes. When the flow rate was doubled (Q2), the HRTs were halved.

2.2. Chemical measurements

During feeding with sulphate, samples of both influent and effluent were taken weekly. The pH (HQ 40 d, HACH) and the oxide-reduction potential (ORP, Orion 370 Thermo) were measured immediately after sampling. The sample was filtered (pore size 0.45 μm) immediately after sampling to measure the concentrations of SO_4^{2-} (HACH, Sulfaver. Method 4500 E, [26]) and sulphide (HACH, Methylene blue. Method 4500-S2-D, [26]).

During the experiments with AMD we measured metals (copper, zinc, iron and aluminium) in samples of influent and effluent filtered using EAA (AAnalyst400 PerkinElmer). Every 2 weeks samples were taken from inside the screens (at 20 cm depth) to determine metals, pH, ORP, sulphate and sulphide. The total phosphorus (total P, TNT HACH), ammonium (Salicylate method, HACH) and total nitrogen (total N, TNT HACH) concentrations in the effluent were determined once per month.

The acidity and acidity load were calculated for the influent and effluent using the following formulas [17]:

$$\text{Calculated acidity}\left(\frac{\text{mgCaCO}_3}{\text{L}}\right) = 50 \times \left(2\frac{\text{Cu}^{2+}}{66.54} + 2\frac{\text{Zn}^{2+}}{65,4} + 3\frac{\text{Al}^{3+}}{27} + 1.000\left(10^{-\text{pH}}\right)\right) \tag{2}$$

where 50 = equivalent mass of $CaCO_3$ in mg/meq; and Cu^{2+}, Zn^{2+}, Al^{3+} = metal concentrations in mg/L units.

The acidity load was calculated by:

$$\text{Acidity load}\left(\frac{\text{mgCaCO}_3}{\text{d}}\right) = \text{F} \times \text{Calculated acidity} \tag{3}$$

where F = flow rate (L/d).

2.3. Determination of solid phase metal contents

On completion of the experiments, the drums were pierced and three samples were taken of the reactive material (A: top; B: middle; C: bottom, Fig. 1(a)). Peristaltic pumps were used to extract sedimented precipitates from the bottom of the drainage tubes and from the base of the external settler for each reactor.

The samples of reactive material and sediments were dried at 80°C (Binder) to constant mass. To digest the precipitates, 1 g of ground, dry sample was digested for 24 h at 60°C (Binder) with nitric acid at 65% (Suprapur, Merck). The temperature was increased to 120°C for 1 h and then kept at 180°C until a concentrate of approximately 5 mL was obtained. This was allowed to cool to ± 60°C and digestions were carried out with perchloric acid at 70% (Suprapur, Merck) for 30 min at 220°C. The residuum was cooled to ambient temperature and diluted to 100 mL with deionised water to determine the copper and aluminium concentrations with EAA (AAnalyst400, PerkinElmer).

3. Results and discussion

3.1. Feeding with sulphate solution

The reduction in the ORP (Fig. 2(a)) from day 5 of feeding with sulphate solution indicated biological activity. The lowest ORP values (–364 and –302 mV) were recorded in the effluent from reactor SDES3. The inoculum used showed

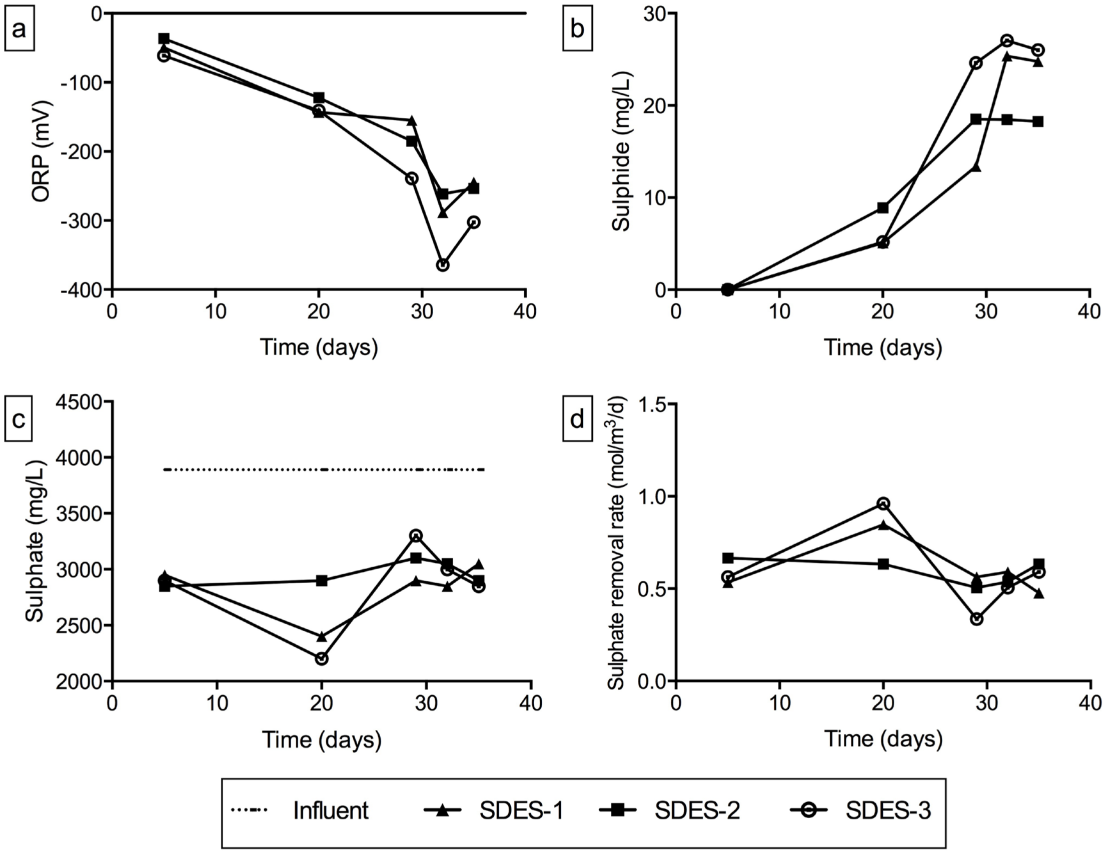

Fig. 2. Variations in (a) the ORP (mV); (b) the sulphide and (c) sulphate concentrations; and (d) the sulphate removal rate of three diffusive systems during feeding with sulphate solution (flow rate = 7.5 L/d).

biological activity from the start of the experiments; sulphate reduction (production of sulphide and consumption of sulphate) was evident from day 20, while 20 to 30 mg/L of sulphide were obtained from day 29 (Fig. 2(b)). After day 29 all the reactors showed removal rates of between 0.4 and 0.7 moles/m^3/d (Fig. 2(d)), converging on values of around 0.5 mole/m^3/d, regardless of the diffusion distance or the diffusive exchange area. The reactors therefore, appear not to present any limitation due to sulphate transport by diffusion. This may be explained by the high sulphate concentration in the influent and the fact that sulphate removal rates in biochemical reactors range only around 30%. This means that the pore space of the reactive material is always saturated with sulphate regardless of the diffusion distance calculated.

Although, no major differences were observed in the performances of the reactors during the test, the larger reactive volumes of SDES1 and SDES3 appear to have produced a higher sulphide concentration in the effluent from day 32. The reactors were fed with sulphate solution to promote the establishment of sulphate reducing communities and determine the sulphate removing potential of the reactors before they were fed with metals.

It should be noted that both the reduction in ORP and the increase in sulphide concentration reflect an increase in biological activity. Nevertheless, despite this gradual increase in biological activity, the sulphate was removed at a constant rate from the first time it was measured. Furthermore, only 10% of the sulphate removed resulted in sulphide in the effluent. This appears to indicate a significant chemical sulphate removal mechanism, for example by precipitation as $CaSO_4$ [27] considering that the reactive mixture contained limestone, a possible source of Ca^{2+}. Sulphate assimilation [28], adsorption of sulphate and sulphide by the organic substrate [29,30] and volatilisation of H_2S [28] are other possible causes of sulphate removal and the lower quantities of sulphide measured. Wu et al. explained the difficulty of calculating a S balance in wetlands formed by the coexistence of sulphate reduction with the presence of sulphites and other intermediaries of sulphate reduction, absorption of sulphides by the organic matter and the occurrence of "disproportionation" [30,31], a metabolic process described for sulphate-reducing bacteria like *Desulfotomaculum, Desulfovibrio* and *Desulfocapsa* [32]. None of the above processes can be discounted for SDES.

3.2. Feeding with a synthetic AMD solution

During experiments with a synthetic AMD solution at the lower flow rate of 3.75 L/d (Q1), the effluent pH of all the reactors was higher than the influent pH (Fig. 3(a)), tending to stabilise around values above 5.

This flow rate was chosen so that the metals load would be lower than the sulphate removal capacity of the reactor based on the previous experiment with sulphate solution.

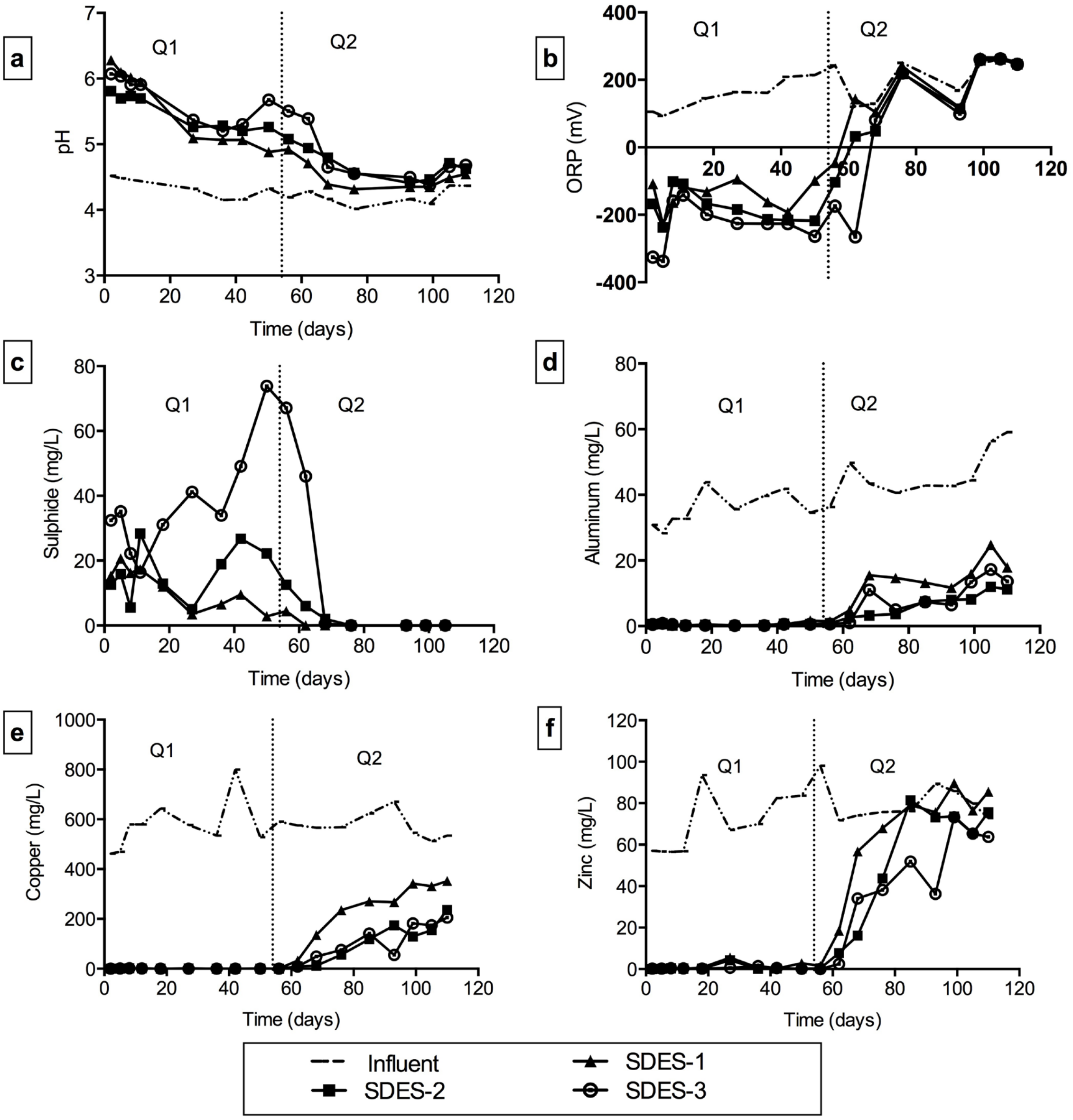

Fig. 3. Results of (a) pH; (b) ORP; (c) sulphide, (d) aluminium, (e) copper and (f) zinc concentrations in the effluent of three diffusive systems during operation with a synthetic AMD solution at two flow rates.

When the influent flow rate was doubled to 7.5 L/d (Q2), the reactors were expected to suffer overload and their effluent pH values did indeed stabilise at values around 4.6 and 4.7, close to that of the influent. Despite this diminution in the effluent pH for Q2, the sulphate removal capacity was maintained (Fig. 4(a)). The alkalinity generated by microorganisms and limestone dissolution was not enough to buffer the proton and metal acidity of the AMD [Eq. (2)]. The effect was more notorious for Q2.

During the first phase (Q1), the ORP of the effluent (Fig. 3(b)) maintained negative values, coinciding with sulphide generation in the reactors (Fig. 3(c)). On day 50, reactor SDES3 presented the highest sulphide concentrations recorded (73 mg/L). Similar sulphide concentrations in the effluent were reported by Gallagher et al. [33] and Yim et al. [34]. When the flow rate was doubled, the sulphide practically disappeared from the effluent and the ORP rose immediately to values very similar to those of the influent (from 140 to 200 mV). The metals load was also doubled at the same time as the flow rate, eliminating the free sulphide (reducing agent) and causing the ORP to rise.

In homogeneous passive reactors, the ORP correlates with the sulphate reduction rate. For example, in column experiments by Zhang and Wang [35], the lack of electron donors (lactate) caused the ORP to rise. In diffusive exchange reactors on the other hand the sulphate reduction rate did not fall (Fig. 4(a)) when the ORP rose. In this case the ORP was an indicator of the metals overload, since the sulphide in the effluent and the ORP changed drastically with the increase in the metals load.

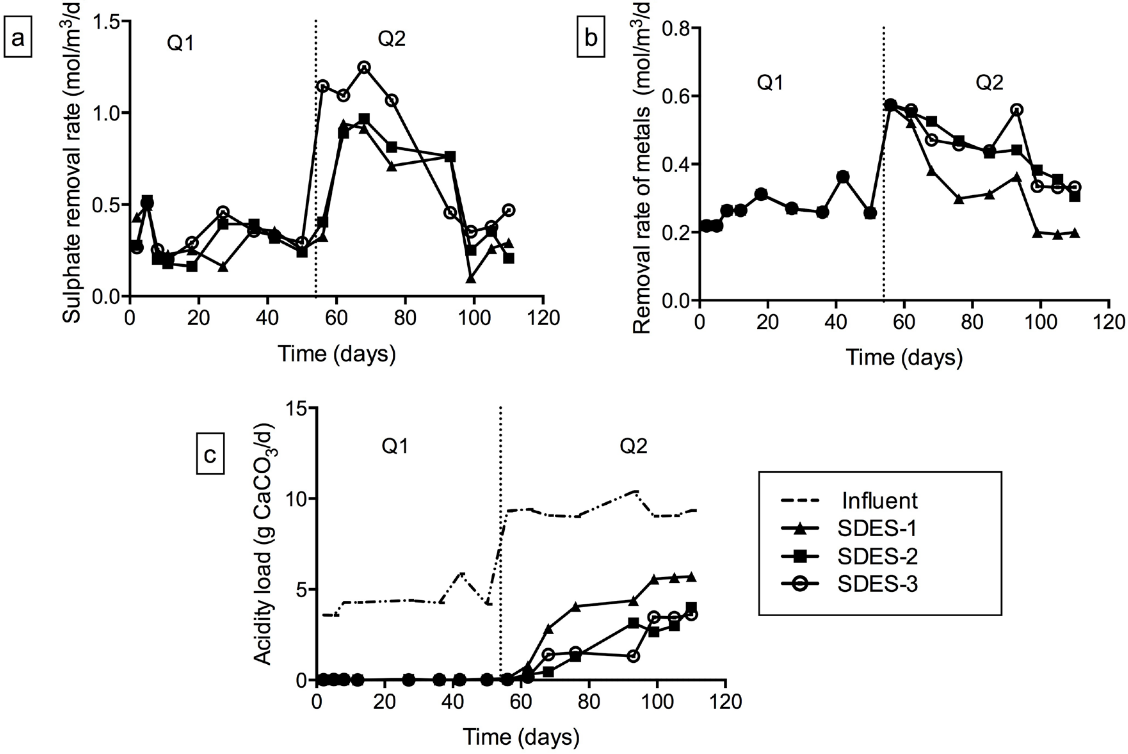

Fig. 4. Removal rates of (a) sulphate, (b) metals, and (c) specific acidity.

In the initial phase of the experiments, metals removal was immediate in all the reactors, with removal rates in excess of 99% for aluminium (Fig. 3(d)), copper (Fig. 3(e)) and zinc (Fig. 3(f)). When the flow rate was doubled, the metals removal diminished. Aluminium presented the highest removal rate with Q2. From day 68 we observed a trend for the aluminium concentration in the effluent to stabilise; the mean aluminium removal values during this period were 66% for SDES1, 84% for SDES2 and 78% for SDES3. Aluminium is removed in biochemical reactors as hydroxide and by reaction with sulphate, calcium and/or potassium, precipitating as $Al(SO_4)(OH)$, $Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$ (ettringite) and $KAl_3(OH)_6(SO_4)_2$ (alunite) [6].

When the flow rate was increased, the zinc content in the effluent increased drastically to equal the concentrations in the influent in reactors SDES1 and SDES2 from day 99. Over this period reactor SDES3 removed only between 12% and 18% of zinc. The copper concentration in the effluent also increased, and from day 99 reactor SDES1 removed only 36% while SDES3 removed 64%. During the second phase, when the metals load was doubled, it exceeded the sulphate reduction rate and metals removal was only partial. The higher copper removal is explained by the lower solubility product of CuS ($K_{sp} = 4 \times 10^{-38}$) compared to ZnS ($K_{sp} = 4.5 \times 10^{-24}$) [28].

During the first 53 d all the reactors presented mean sulphate removal rates between 0.30 mol/m³/d (SDES1 and SDES2) and 0.33 mol/m³/d (SDES3) (Fig. 4(a)). Again, no significant difference was observed in the sulphate removal rates, indicating that transport to the reactive zone is not a limiting factor, considering the different diffusion distances of the reactors. Likewise the reactors removed over 99% of the influent metals (metals load 0.27 mol/m³/d).

When the flow rate was increased, the removal rates of sulphate and metals rose temporarily, however this reflects the speed of response of the reactor, not the removal processes. It was only after 40 d that the generalised gradients of the metals and sulphate concentrations in systems SDES1 and SDES3 reached equilibrium. The sulphate removal rates stabilised at 0.27 in SDES1 and 0.39 mol/m³/d in SDES3, indicating that under overload conditions there may be some differences between reactors. Reactors SDES1 and SDES3 presented metals removal of 0.20 and 0.33 mol/m³/d, respectively (Fig. 4(b)), again showing a difference under overload. However, to determine the differences between reactors would require operation under overload conditions for a longer period, observing whether the removal rates obtained are stable over time. The metals removal rates obtained for SDES3 are higher than those reported by Behum et al. [36] for biological reactors (0.21 mol/m³/d) and by Jung et al. [37] for successive alkalinity-producing systems (SAPS, 0.02 and 0.113 mol/m³/d).

The mean acidity loads in the influent were 4.3 and 9.3 g of $CaCO_3$/d for flow rates Q1 and Q2, respectively (Fig. 4(c)). Acidity is associated mainly with metals, which explains the removal rate of 99% for flow Q1. As the metals removal with flow Q2 was partial, the acidity removal was also partial, of 38% and 61% for reactors SDES1 and SDES3, respectively. The high acidity of the influent (1.2 ± 0.1 g $CaCO_3$/L) did not affect sulphate removal.

Reactor SDES3 presented higher sulphide concentrations in the effluent and higher metals removal; this may be due to the greater relative volume of reactive material and the ratio between the diffusion distance and the SIA, which would facilitate diffusive exchange of solutes between zones.

3.3. Nutrients content

Because the principal reactive material of biochemical reactors is organic, the effluent may contain high concentrations of nutrients. Knowing the nutrients content in the effluent will allow post-treatment measures to be taken to improve the quality of the effluent. The total nitrogen content in the effluent (Fig. 5(a)) was variable over time, presenting a falling trend with each flow rate until it reached levels below the detection limit (<10 mg/L) from day 68. Ammonium (Fig. 5(b)) and total P (Fig. 5(c)) diminished constantly to reach concentrations below the detection limits (0.01 and 0.02 mg/L, respectively). The change in flow rate did not affect the concentrations of ammonium and total P. The results obtained for total N and total P agree with the low concentrations reported by Yepez and Nairn [38]; these authors found that the total N and total P concentrations did not exceed 0.6 and 0.5 mg/L, respectively. The highest concentration of nutrients is detected during the first years of operation of biochemical reactors; furthermore, nutrient discharge is affected by seasonal variations [39].

Both nutrients and excessive sulphides (Fig. 3(c)) can be eliminated by implementing aeration lagoons with a hydraulic residence time >2 d [39].

3.4. Metals content inside the reactor

During the second phase of the experiment (flow rate Q2), the reactor worked under metals and acidity overload. The sulphide and alkalinity generated were insufficient to precipitate the metals and neutralise the acidity. For this reason metals diffusion must have occurred into the reactive zone.

The quantification of copper in the reactive zone of the reactors is detailed in Table 1. No trend was detected towards higher concentrations in any specific part of the reactor since the metals gradients were established horizontally from the screens. Although, no effect of the metals load was detected in the sulphate removal rates, the presence of metals in the reactive zone can affect sulphate removal in the long term. It has been described that amorphous metal sulphides encapsulate cells [25], affecting their viability. Chaparro found that after a diffusive exchange reactor is subjected to metals overload, a metals gradient forms in the reactive zone (higher concentration closer to the screen) allowing the interior of the reactive zone to remain biologically active [40].

During Q1 and Q2 a total of 355.1 g Cu^{2+} were fed into each reactor (Q1 = 108.7 g; Q2 = 246.4 g). Table 2 shows in detail the amount of copper removed and the percentage of metal retained in the reactive zone.

A very small fraction of copper (between 4% and 6%) was contained in the reactive zone. The precipitation reactions occurred mainly in the conductive zone, and as a result the highest copper concentrations were found in the external settler and screens (Fig. 6). Zinc and iron behaved similarly to copper with regard to metal accumulation (data not shown).

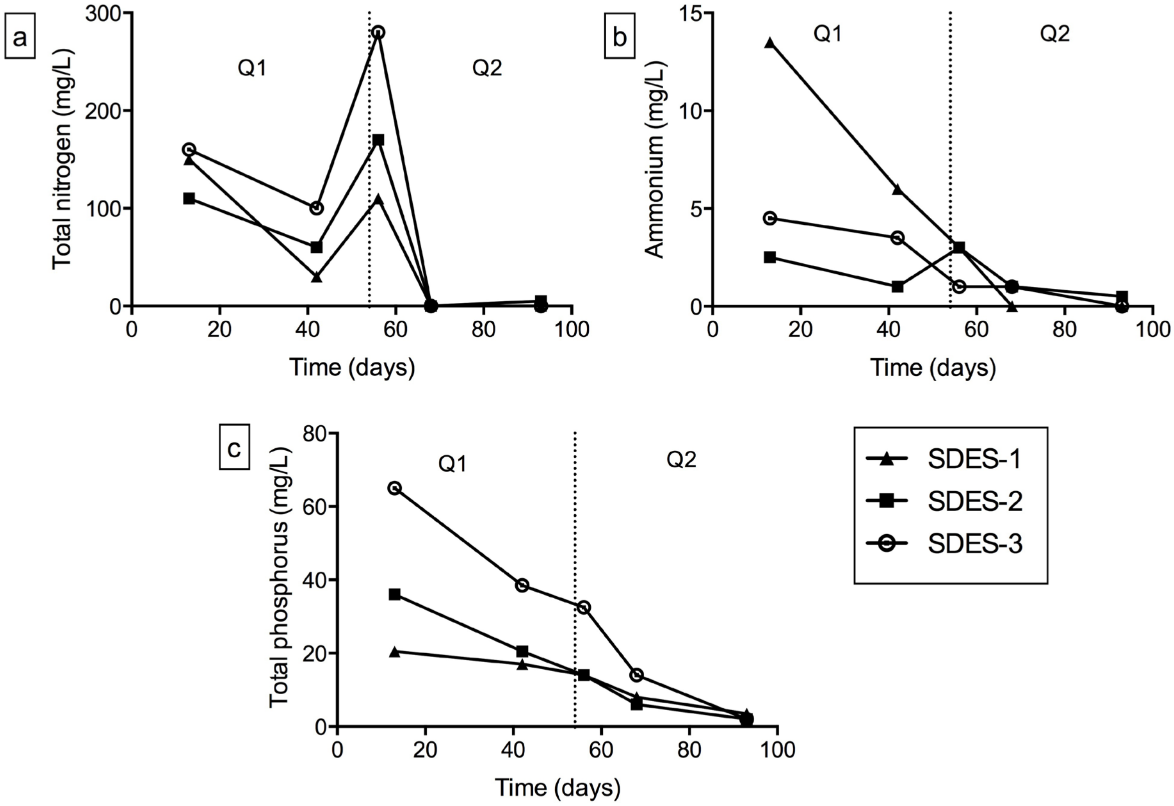

Fig. 5. Contents of (a) total N, (b) ammonium and (c) total P in the effluents of the diffusive systems.

Table 1
Copper content (g/Kg) in the reactive zone of the reactors

Reactor	Sample		
	A	B	C
SDES1	0.07	0.06	0.22
SDES2	0.35	0.06	0.16
SDES3	0.20	0.21	0.19

Samples A, B and C taken from the reactive beds at different heights (Fig. 1(a)).

Table 2
Copper removal and amount retained (%) within the reactive zone of the reactors

Reactor	Copper removal (*g*)	Copper retained in the reactive material	
		(*g*)	(%)
SDES1	259.7 (Q1 = 108.5; Q2 = 151.25)	10.6	4.1
SDES2	311.9 (Q1 = 108.5; Q2 = 203.5)	15.4	4.9
SDES3	311.1 (Q1 = 108.5; Q2 = 202.6)	18.2	5.8

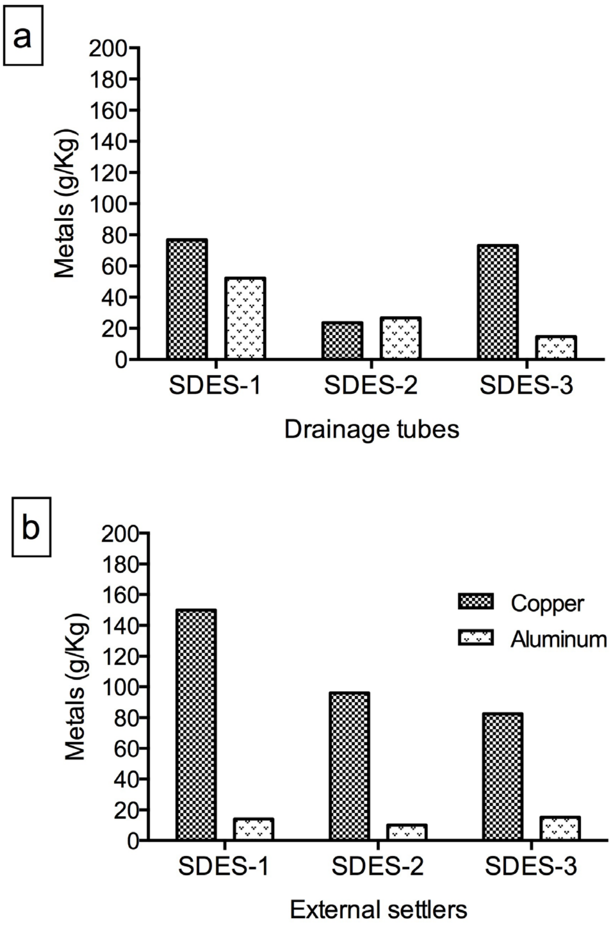

Fig. 6. Content of metals accumulated at the bottom of (a) the drainage tubes and in (b) the external settlers of SDES.

The vertical configuration of the SDES allows valuable minerals to be recovered from the bottom of the screened tubes. The challenge is to design and study over the long term an optimised reactor with an internal settler which will capture a higher percentage of the precipitates at the bottom of the screened tubes, so that they are not carried out of the reactor. For example, at pH 7 CuS particles show a tendency to agglomerate because of reduced electrical repulsion [41], improving their solid-liquid separation characteristics, and a higher pH can be achieved by increasing the alkaline material content of the reactive media. Particle retention could be also enhanced passively by adding "seeding material" such as sand into screened tubes [41]. Finally, reducing supersaturation has been shown to favor crystal growth over nucleation resulting in larger precipitates [41,42], and thus, extremely overloaded (metal excess) and underloaded (sulphide excess) conditions should be avoided.

3.5. Evidence of growth

At the end of the experiment the cellulose fibres were observed by scanning electron microscope (SEM). Physical degradation was detected in the form of a loss of layers (Fig. 7(a)) and the growth of bacteria on the fibres (Fig. 7(b)).

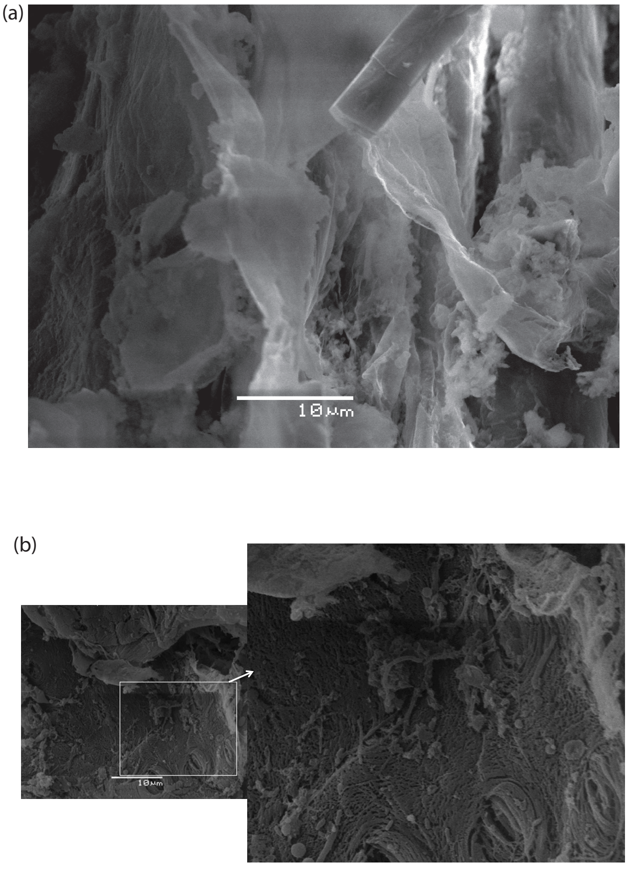

Fig. 7. SEM image of (a) degraded cellulose fibres and (b) microorganisms adhering to cellulose fibres.

4. Conclusions

During operation with sulphate, all the reactors presented mean removal rates of 0.60 mol SO_4^{2-}/m^3/d. The reactors were then used to treat an AMD with a high copper concentration (529 mg/L) and acidity (1.2 ± 0.1 g $CaCO_3$/L). During the first phase, when the flow rate was 3.5 L/d (acidity load ≈ 4.3 g $CaCO_3$/d), the three reactors removed over 99% of the metals (metals removal rate 0.27 mol/m^3/d) and presented sulphate removal rates of between 0.30 (SDES1 and SDES2) and 0.33 mol/m^3/d (SDES3). In this phase sulphide was detected in the effluent, meaning that metals were removed predominantly as sulphides. No differences were found in the performances of the reactors.

When the flow rate was doubled, the reactors operated under overload conditions. After 40 d, the metal removal rates stabilised in reactors SDES1 and SDES3. Reactor SDES3 presented a metals removal rate of 0.30 mol/m^3/d, removing principally aluminium (78%) and copper (64%). No significant difference was observed in the sulphate removal rates, indicating that sulphate transport to the reactive zone is not a limiting factor, considering the different diffusion distances of the reactors.

The concentration of the copper accumulated in the sludge at the bottom of the screens (20–80 g/Kg) and in the external settler (80–150 g/Kg) was higher than the copper measured in the reactive zone (0.12–0.2 g/Kg). Therefore, the precipitation reactions occurred principally in the conductive zone. By improving reactor design it would be possible to accumulate the precipitates inside the reactor and recover economically important minerals.

Acknowledgements

This work was financed by Conicyt Doctorate Grant 63100133 and projects VIU 120015, FONDAP/CRHIAM/15130015 and FONDECYT 1140451.

References

[1] J.J. Stumm, W. Morgan, Aquatic Chemistry, 2nd ed., New York: John Wiley & Sons, 1981.

[2] B. Dold, Basic concepts in environmental geochemistry of sulfidic mine-waste management, Waste Manage., 24 (2010) 173–198.

[3] D.W. Blowes, C.J. Ptacek, J.L. Jambor, C.J. Weisener, The Geochemistry of Acid Mine Drainage, H.D. Holland, K. Karl, Eds., Treatise on Geochemistry, Elsevier, Oxford, 2003, pp. 149–204.

[4] C.M. Neculita, G.J. Zagury, B. Bussiere, Passive treatment of acid mine drainage in bioreactors using sulphate-reducing bacteria: critical review and research needs, J. Environ. Qual., 36 (2007) 1–16.

[5] A.S. Sheoran, V. Sheoran, R.P. Choudhary, Bioremediation of acid-rock drainage by sulphate-reducing prokaryotes: a review, Minerals Eng., 23 (2010) 1073–1100.

[6] ITRC (Interstate Technology & Regulatory Council), Biochemical Reactors for Treating Mining- Influenced Water. BCR-1. Washington, DC. Interstate Technology & Regulatory Council, Biochemical Reactors for Mining-Influenced Waste Team, 2013, Available online at: http://www.itrcweb.org/bcr-1/

[7] K.R. Waybrant, D.W. Blowes, C.J. Ptacek, Selection of reactive mixtures for use in permebale reactive walls for treatment of mine drainage, Environ. Sci. Technol., 32 (1998) 1972–1979.

[8] O. Gibert, J. de Pablo, J.L. Cortina, C. Ayora, Chemical characterisation of natural organic substrates for biological mitigation of acid mine drainage, Water Res., 38 (2004) 4186–4196.

[9] C.A. McCauley, A.D. O'Sullivan, M.W. Milke, P.A. Weber, D.A. Trumm, Sulfate and metal removal in bioreactors treating acid mine drainage dominated with iron and aluminum, Water Res., 43 (2009) 961–970.

[10] M. Lindsay, C.J. Ptacek, D.W. Blowes, W.D. Gould, Zero-valent iron and organic carbon mixtures for remediation of acid mine drainage: batch experiments, Appl. Geochem., 23 (2008) 2214–2225.

[11] B. Uster, A.D. O'Sullivan, S.Y. Ko, A. Evans, J. Pope, D. Trumm, B. Caruso, The use of mussel shells in upward-flow sulfate-reducing bioreactors treating acid mine drainage, Mine Water Environ., 34 (2014) 442–454.

[12] L. Lefticariu, E.R. Walters, C.W. Pugh, K.S. Bender, Sulfate reducing bioreactor dependence on organic substrates for remediation of coal-generated acid mine drainage: field experiments, Appl. Geochem., 63 (2015) 70–82.

[13] V. Biermann, A.M. Lillicrap, C. Magana, B. Price, R.W. Bell, C.E. Oldham, Applicability of passive compost bioreactors for treatment of extremely acidic and saline waters in semi-arid climates, Water Res., 55 (2014) 83–94.

[14] M.V. Logan, K.F. Reardon, L.A. Figueroa, J.E.T. McLain, D.M. Ahmann, Microbial community activities during establishment, performance, and decline of bench-scale passive treatment systems for mine drainage, Water Res., 39 (2005) 4537–4551.

[15] R. Klein, J.S. Tischler, M. Mühling, M. Schlömann, Bioremediation of Mine Water, A. Schippers, F. Glombitza, W. Sand, Eds., Geobiotechnology I: Metal-related Issues, Springer Berlin Heidelberg, Berlin, 2014, pp. 109–172.

[16] J. Schmidtova, S.A. Baldwin, Correlation of bacterial communities supported by different organic materials with sulfate reduction in metal-rich landfill leachate, Water Res., 45 (2010) 1115–1128.

[17] R.S. Hedin, R.W. Nairn, R.L. Kleinmann, Passive Treatment of Coal Mine Drainage (Vol. 9389), US Department of the Interior, Bureau of Mines, Pittsburgh, PA, 1994, pp. 1–44.

[18] J.J. Gusek, L.A. Figueroa, Mitigation of Metal Mining Influenced Water, Littleton, CO, Vol. 2, SME, 2009.

[19] C.M. Neculita, J. Zagury, Biological treatment of highly contaminated acid mine drainage in batch reactors: long-term treatment and reactive mixture characterization, J. Hazard. Mater., 157 (2008) 358–366.

[20] A.O. Schwarz, B.E. Rittmann, Modeling bio-protection and the gradient-resistance mechanism, Biodegradation, 18 (2007) 693–701.

[21] A.O. Schwarz, B.E. Rittmann, The diffusion-active permeable reactive barrier, J. Contam. Hydrol., 112 (2010) 155–162.

[22] N.R. Pérez, I.C. Diaz, E. Barahona, A.O. Schwarz, H. Urrutia, Effect of Reactive Material Distribution in the Biological Treatment of Acid Mine Drainage, Proc. Enviromine 2011, Santiago de Chile, GECAMIN, Santiago.

[23] R.M. Atlas, Handbook of Media for Environmental Microbiology, CRC Press, Boca Raton, FL, 2005.

[24] S.G. Benner, W.D. Gould, D.W. Blowes, Microbial populations associated with the generation and treatment of acid mine drainage, Chem. Geol., 169 (2000) 435–448.

[25] A.E. Lewis, Review of metal sulphide precipitation, Hydrometallurgy, 104 (2010) 222–234.

[26] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Water Works Association, Water Environment Federation, Washington, DC, USA, 2005, pp. 174, 175, 188, 189.

[27] C. Ayora, M.A. Caraballo, F. Macias, T.S. Rötting, J. Carrera, J.M. Nieto, Acid mine drainage in the Iberian Pyrite Belt: 2. Lessons learned from recent passive remediation experiences, Environ. Sci. Pollut. Res., 20 (2013) 7837–7853.

[28] T.R. Machemer, S.D. Reynolds, J.S. Laudon, L.S. Wildeman, Balance of S in a constructed wetland built to treat acid mine drainage, Idaho Springs, Colorado, USA, Appl. Geochem., 8 (1993) 587–603.

[29] J.W. Rudd, C.A. Kelly, A. Furutani, The role of sulfate reduction in longterm accumulation of organic and inorganic sulfur in lake sediments, Limnol. Oceanogr., 31 (1986) 1281–1291.

[30] S. Wu, P. Kuschk, A. Wiessner, J. Müller, R.A.B. Saad, R. Dong, Sulphur transformations in constructed wetlands for wastewater treatment: a review, Ecol. Eng., 52 (2013) 278–289.

[31] S. Wu, C. Jeschke, R. Dong, H. Paschke, P. Kuschk, K. Knöller, Sulfur transformations in pilot-scale constructed wetland treating high sulfate-containing contaminated groundwater: a stable isotope assessment, Water Res., 45 (2011) 6688–6698.

[32] H.L. Ehrlich, D.K. Newman, Geomicrobiology of Sulfur, Geomicrobiology, 5th ed., CRC Press, Boca Raton, FL, 2008, pp. 508–559.

[33] N. Gallagher, E. Blumenstein, T. Rutkowski, J. De Angelis, D. Reisman, C. Progess, R.J. Schipper, J.J. Gusek, Passive Treatment of Mining Influenced Wastewater with Biochemical Reactor Treatment at the Standard Mine Superfund Site, Crested Butte, Colorado, ASMR, Lexington, KY, 2012, pp. 137–153.

[34] G. Yim, S. Ji, Y. Cheong, C.M. Neculita, H. Song, The influences of the amount of organic substrate on the performance of pilot-scale passive bioreactors for acid mine drainage treatment, Environ. Earth Sci., 73 (2015) 4717–4727.

[35] M. Zhang, H. Wang, Organic wastes as carbon sources to promote sulfate reducing bacterial activity for biological remediation of acid mine drainage, Minerals Eng., 69 (2014) 81–90.

[36] P.T. Behum, L. Lefticariu, E. Walter, R. Kiser, Passive Treatment of Coal-mine Drainage by a Sulfate-reducing Bioreactor in the Illinois Coal Basin, Proceedings, West Virginia Mine Drainage Task Force Symposium, Morgantown, WV, 2013.

[37] S.P. Jung, Y. Cheong, G. Yim, S. Ji, H. Kang, Performance and bacterial communities of successive alkalinity-producing systems (SAPSs) in passive treatment processes treating mine drainages differing in acidity and metal levels, Environ. Sci. Pollut. Res., 21 (2014) 3722–3732.

[38] S.A. Yepez, R.W. Nairn, Nutrient and Sulfide Export from a Mine Drainage Passive treament System, Proc. National Meeting of the American Society of Mining and Reclamation, Tupelo, MS Sustainable Reclamation, 2012, pp. 539–556.

[39] E.P. Blumenstein, J.J. Gusek, Nuisance Constituents in Passive Water Treatment Systems – a Specific Case Study 1, Proc. Am. Soc. Mining Reclamation 27th Annual National Conference, Pittsburgh, PA, 2010, pp. 31–53.

[40] G. Chaparro, Sistema de Intercambio Difusivo Para el Tratamiento de Drenajes Ácidos con Elevadas Concentraciones de Cobre, Universidad de Concepción, 2015.

[41] D.K. Villa-Gomez, E.D. Van Hullebusch, R. Maestro, F. Farges, S. Nikitenko, H. Kramer, G. Gonzalez-Gil, P.N.L. Lens, Morphology, mineralogy, and solid-liquid phase separation characteristics of Cu and Zn precipitates produced with biogenic sulfide, Environ. Sci. Technol., 48 (2014) 664–673.

[42] D. Villa-Gomez, H. Ababneh, S. Papirio, D.P.L. Rousseau, P.N.L. Lens, Effect of sulfide concentration on the location of the metal precipitates in inversed fluidized bed reactors, J. Hazard. Mater., 192 (2011) 200–207.