

Performance of passive systems for mine drainage treatment at high salinity and low temperature ©

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Abstract

Low temperatures and high salinities can deteriorate the performance of passive biochemical reactors (PBRs) for mine drainage (MD) treatment. A 8-month parametric study was performed in eight 11 L PBRs using two mine drainage (MD) qualities (acidic and neutral), two salinities (0 and 20 g/L) and two temperatures (22 and 5°C) to select the optimal hydraulic retention times (HRTs) based on the PBRs' performance. HRTs of 1 and 5 days were required to efficiently treat acidic and neutral MD, respectively. The simultaneous effect of low temperature and high salinity decreased PBR efficiency by 30%-70%, especially for acidic MD.

Keywords: Saline mine drainage, passive treatment, cold climate, passive biochemical reactor.

Introduction

Passive treatment systems are considered as an essential complementary approach for successful mine site reclamation (USEPA, 2014). Their addition to conventional reclamation techniques prevents or improves the control of acid mine drainage (AMD) and contaminated neutral drainage (CND).

A passive biochemical reactor (PBR) is an efficient technology for the treatment of slightly contaminated MD in temperate or semi-arid climates (Neculita et al., 2011; Vasquez et al., 2016). However, PBR performance is less documented in northern climates, characterized by low temperatures (<4°C) and often high salinities (up to 40 g/L). In general, low temperatures reduce the efficiency of MD treatment by decreasing the kinetics of biogeochemical processes. The rate of sulfate reduction by sulfate reducing bacteria (SRB) decreased by over 50% when the temperature dropped from 16°C to 4°C (Benner et al., 2002). To improve PBR efficiency at low temperature, the addition of easily degradable substrate such as methanol, ethanol, lactate, acetate or glucose into PBR

mixtures has been attempted (Gould et al., 2012; Nielsen et al., 2017). However, in these cases, the treatment system became semi-active rather than passive due to the occasional addition of substrate and, thus, operation costs increased.

High salinity represents another challenge, in addition to low temperature. Some of the main sources of salinity, which is an integrative measure of the major ions concentrations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl-, SO₄²- and HCO₂) (Van Dam et al., 2014) are: (1) drainage water on mine sites (2) seawater intrusion at mines near the coasts, and (3) anthropogenic activities such as addition of de-icing agents (e.g. CaCl₂) (Feng et al., 2014; Kaushal et al., 2005; Nordstrom et al., 2015). Depending on the nature and concentration of the major ion components of salinity, PBRs have shown a good efficiency for sulfate reduction under high salinity (>40 g/L) at ambient and high temperature (70°C) (Vallero et al., 2005). At the same time, PBR effectiveness can decrease at high salinity due to the toxicity and osmotic stress on microorganisms, increases in metal solubility, as well as the competition



of major ions with metals on sorption sites (Warrender and Pearce, 2007). Depending on the reactive mixture used in PBRs, a successful treatment of saline groundwater in semi-arid conditions (at 15-30°C) has been reported for periods varying from 260 days to more than 1,200 days (Degens, 2012; Biermann et al., 2014).

Nevertheless, the combined effects of high salinity and low temperature on alkalinity production (and acidity treatment) as well as on metal removal by PBR treatment are poorly documented and require further research. Thus, the present work aims to comparatively evaluate the effect of these two parameters on AMD and CND treatment using PBRs in column testing.

Methods

Mine drainage quality and column reactive mixtures

In the present study, two types of MD (AMD and CND) with two different salinities (0 and 20 g/L) were tested (tab. 1). The selection of AMD/CND chemistry was based on the compilation of surface water characterization data (pH, conductivity, sulfate and heavy metal concentrations) over 5 years of monitoring (2010-2014) for 2 sampling points at a nickel-copper mine located in a northern climate (average air temperature of -10.3°C).

Depending on the influent quality, columns were filled with two reactive mixtures (PBR#1 for AMD and PBR#2 for CND treatment) (tab. 2). All mixtures were fully characterized, before and after use (spent), and showed effective removal (>91%) of metals and sulfates during the treatment of highly contaminated MD in previous batch testing (Ben Ali et al., 2018).

Column design and experimental set-up

A parametric study was performed to evaluate the simultaneous effect of temperature and of salinity on sulfate reduction, metal removal, and acid neutralization. Experiments were performed with eight 11 L PBR columns (14 cm in diameter and 70 cm in height) for 8 months. Two types of MD (AMD and CND) with two different salinities (0 and 20 g/L) were tested at ambient temperature (22±0.5°C) during the first 3 months. The reactors were then transferred to a cold room at low temperature $(5 \pm 1^{\circ}C)$ for 5 months. Columns were operated at a HRT of 0.5 and 1 day for CND, and 2.5 and 5 days for AMD with vertically upward flow (fig. 1). For simplicity, columns were named according to the quality of the MD to be treated and the selected HRT (e.g., for saline AMD treatment with HRT of 2.5 days, column name is SAMD-2.5).

In each column, the mixture was placed between two layers of gravel (≈ 5 cm) and fine-mesh geotextiles, at the top and bottom, prior to being covered. All PBRs were saturated with the appropriate synthetic MD (tab. 2). Prior to starting the continuous feed of the columns, only the PBRs that treated acidic influent (AMD/SAMD) were incubated at room temperature for 1 week. Columns were fed with synthetic MD prepared weekly using peristaltic pumps (Masterflex).

Parameters	AMD	Saline AMD	CND	Saline CND	Salt used
рН	2.8-3.5	2.7-3.6	5.1-7.8	6.1-7.5	-
Fe2+	27 ±3.5	24.2 ±4.2	9.0 ±2.1	8.2 ±2.6	FeSO4•7H2O
Ni2+	49 ±3.7	40.8 ±5.1	28 ±3.4	24 ±4.9	NiSO4•6H2O
Cu2+	3.2 ±0.5	2.8 ±0.7	1.1 ±0.2	0.9 ±0.3	CuSO4•5H2O
	1612 ±121	1615 ±157	519 ±53	546 ±76	Na2SO4
Ca2+	-	19 000 ±1100	-	20 000 ±2500	CaCl2

Table 1 MD quality used in PBR column reactors (all concentrations are in mg/L, except for pH)



Mixture	PBR#1	PBR#2				
	(% dry weight)					
Carbon sources and porous material						
Wood chips / sawdust	48	0				
Sphagnum peat moss	0	50				
Nitrogen sources						
Leaf compost	10	20				
Neutralizing agent						
Ash	30	20				
Structural agent						
Sand	10	10				
Inoculum						
Sludge from the Rouyn-Noranda WWTP*	2	0				
Total	100	100				

Table 2 Components and proportions of reactive mixture composition

*WWTP: Wastewater treatment plant

Water sampling and analysis

Effluent water quality was monitored by weekly sampling and analysis of the physicochemical parameters, including pH, redox potential (ORP), alkalinity, acidity, sulfate () and total metals. The pH and ORP were measured with an Orion Triode sensor coupled with a Benchtop pH/ISE Meter Orion model 920 (relative precision +/- 0.01 pH) and with a Pt/ Ag/AgCl sensor linked to a Benchtop pH/ISE Meter Orion 920 (relative precision +/- 0.1 mV), respectively. The alkalinity and acidity were obtained by titration on non-filtered samples with a Metrohm Binkmann, 716 DMS Titrino titrator (APHA, 2012) (relative precision of 1 mg CaCO₃/L). Filtered samples (with a 0.45 μ m filter) used to quantify metal content were acidified with 2% (v/v) of nitric acid (70%) before analysis. The techniques used to analyze metal concentrations were Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Perkin Elmer



Figure 1 Laboratory schematic representation of PBR column treatment scenarios



3000 DV) and Inductively Coupled Plasma-Atomic Mass Spectrometry (ICP-MS; Agilent 7700X ICP-MS) for the non-saline and saline MD, respectively.

Results and discussion

The results will be discussed according to evolution of the treated water chemistry: 1) first period: 0-95 days, and 2) second period: 96-240 days, while highlighting the effect of temperature and salinity, as well as in combination for the treatment of each level of MD quality.

Influence of temperature on MD treatment

During the first period (0-95 days-22°C), pH increased from 5.5–6.2 to 6.4–8.2 in all CND columns which was essentially maintained when the temperature was decreased (to 5°C) during the second treatment period (96-240 days). For the AMD columns, pH increased from 2.8-3.5 to 7.3-8.4 at room temperature and then slightly decreased at 5°C (6.8-7.9). Oxidizing conditions (ORP between 200 and 414 mV) were found in the CND columns with low HRTs (0.5 and 1 day) at both tem-



Figure 2 Evolution of pH, ORP, alkalinity and SO₄2- removal during CND/AMD treatment in column reactors

peratures. Nevertheless, for the AMD columns with 2.5 and 5 days of HRTs, anoxic conditions were noted (ORP from 200 to -400 mV) for 0–95 days, at room temperature, in contrast to the low temperature where slightly oxidizing conditions were maintained (>80 mV) (fig. 2). The lower HRTs used for CND treatment relative to AMD could explain these results.

Alkalinity increased from 0-20 to over 200 and 700 mg CaCO3 /L, for CND and AMD columns, respectively, at room temperature. However, alkalinity deceased significantly at low temperature to reach 100 mg CaCO3 /L (fig. 2). These findings are consistent with the evolution of acidity removal (results not shown). For SO42- removal, the results showed a release during the first three days, for both CND and AMD columns. A low removal efficiency (<27%) was noted for CND columns, regardless of the temperature and the HRT, as an indication of limited microbial reduction. However, for AMD reactors, better removal efficiencies were observed at room temperature, especially for AMD-5 (25-100%), contrary to low temperature, where efficiency decreased to <10%. One explication could be related to the low microbial activity at low temperature. For metal removal (Cu, Ni and Fe), results showed that, unlike copper which was efficiently removed (80%-99%) during the first and second periods, Fe and Ni removal was a function of HRT and temperature. Higher metal removal was found with 1-day HRT for the CND columns. More than 99% of Ni was removed in CND-1, at room temperature, relative to 70%, at 5°C. However, Fe removal was maintained at >95% for CND-1, regardless of the temperature. In the AMD columns, metal removal was better at room temperature (>97%) and no HRT dependent. Efficiency dropped to 80% for Fe but remained high for Ni at 5°C for AMD-5. Higher HRTs (1 day for CND and 5 days for AMD) showed better results for all parameters.

Influence of salinity on MD treatment

The effect of increased salinity will be dicussed only for the first period (0-95 days-22°C), period during which the pH and ORP showed similar evolution to non-saline CND and AMD columns. However, produced alka-

linity was three times less. For SO₄²- removal, only from saline AMD, efficiency significantly increased at room temperature (from 25%) to 100% for AMD-5). This can be explained by sulfate microbial reduction, in addition to precipitation, especially of gypsum (CaSO₄), the formation of which is favored at sulfate and calcium concentrations greater than 1500 mg/L and 500 mg/L, respectively (Fernando et al., 2018). Metal removal from SCND-1 also showed less efficiency compared to CND-1 (65 and 70 % for Ni and Fe, respectively) at room temperature. The competition of major ions (especially Ca²⁺) with metals on the sorption sites could be responsible for it (Warrender and Pearce, 2007). For the AMD columns, salinity has practically no effect on metal removal efficiencies which were even higher than 95% for AMD-5.

Combined effect of low temperature and high salinity on MD treatment

The evolution of the physicochemical parameters (pH, ORP, acidity and alkalinity) in the CND and AMD columns at low temperature and high salinity (96-240 days) were similar to non-saline MD over the same period. For $SO_4^{2^-}$ removal, no significant variation was noted for CND, but for AMD, $SO_4^{2^-}$ removal decreased significantly for SAMD-5 (<40%) and was absent for AMD-5. These results indicate that mineral precipitation takes over in the absence of any microbial activity. At low temperature, Ni, Fe and Cu removal did not change for SCND-1, whereas for SAMD-5 metal removal decreased to 74% and 80% for Ni and Fe, respectively.

Conclusion

The objective of the study was to evaluate the influence of temperature (22°C and 5°C) and salinity (0 g/L and 20 g/L as CaCl2) on the performance of PBR in the treatment of mine drainage (AMD and CND). Eight PBR columns were tested either at 2.5 and 5 days of HRT (for AMD) or 0.5 and 1 day of HRT (for CND), for a 8-month period. Results showed that, at room temperature, acidity neutralization and metal removal efficiency were maintained for saline/non-saline CND and AMD for more than 90 days, at HRTs of 0.5 and 2.5 days, respectively. However, better efficiency was found at a HRT of 1 day and 5 days



for Ni, Cu, Fe and SO₄²⁻ removal from CND and AMD, respectively. At low temperature, metal removal efficiency decreased, especially for Ni, from 99% to 36% and 66% for the CND and the AMD, respectively. Regardless of the MD quality (CND vs AMD, saline vs non saline), biological sulfate reduction was severely hampered at low temperature. The simultaneous effect of low temperature and high salinity decreased the overall efficiency of the treatment system, especially when used to treat AMD. Moreover, metal and sulfate removal mechanisms depend on MD quality. Sorption could be the main mechanism for CND treatment, while precipitation as oxy-hydroxides, carbonates or sulfides and co-precipitation with iron oxy-hydroxides could be the main ones for AMD treatment with PBR. Nonetheless, a physicochemical (e.g. leaching) and mineralogical (e.g. scanning electron microscope and X-ray diffraction) characterization of the post treatment solids would allow a better understanding of the treatment mechanisms.

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