Metal Retention Mechanisms in Pilot-Scale Constructed Wetlands Receiving Acid Mine Drainage

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ABSTRACT

Mining and metallurgical industries are critical to world's economy; however, their socio-environmental impacts are not negligible. Often, they have to deal with acid mine drainage (AMD), which is generated by sulfide oxidation in waste following the prolonged exposure to oxygen and water, if neutralizing minerals are insufficient. The AMD is characterized by low pH and high concentrations of dissolved metals and sulfates.

Environmental impacts of AMD can be minimized by passive treatment systems such as constructed wetlands (CWs). They represent an interesting approach, from technological, economic, environmental and regulatory points of view, for the efficient treatment of AMD impacted waters.

Wetlands have the capacity to increase pH and alkalinity, to remove dissolved iron and other metals, and to reduce sulfate concentration in AMD. Water treatment is accomplished by various physical (e.g. sedimentation, flocculation), chemical (e.g. sorption) and biological processes (e.g. sulfate reduction, phytoextration) acting independently, in some cases, or interactively, in others. However, cold climate could be challenging for CWs efficiency.

For the purpose of the present study, small-scale laboratory tests using cattail (*Typha latifolia*) were designed and carried out in 0.2 m^2 reactors filled with reactive mixtures, including substrates. The AMD, pH 4.2, contained an average 38.0 mg/L Fe, 2.6 mg/L Mn, 0.4 mg/L Ni, and 9.0 mg/L Zn, at pH 4.2. The AMD flow rate is 1.5ml/min.

CWs efficiency was evaluated during a 3 months period. Water chemistry analysis, as well as sequential extraction procedure (SEP) and microwave digestion of solids and plants were performed. Removal efficiency of Fe and Zn after treatment was up to 99%, at neutral pH. However, the removal of Mn and Ni, as well as of sulfate was negligible. The results of SEP performed on solids proved to be efficient tools for assessing metal fractionation and their potential mobility.

Keywords: Constructed wetlands (CWs), acid mine drainage (AMD), metal fractionation.

INTRODUCTION

Acid mine drainage (AMD) is one of the most significant environmental challenges faced by the mining industry worldwide. Its low pH and the high concentrations of dissolved metals and sulfates can severely impact surface and ground water making it harmful to human and aquatic life (Champagne et al., 2005). AMD is formed by a series of complex biogeochemical reactions that occur when sulfide minerals are oxidized in the presence of water and oxygen to form acidic, sulfate- and metal-rich drainage (Neculita et al., 2008; Genty, 2012). Passive systems, such as constructed wetlands (CWs), represent an interesting approach for the efficient treatment polishing of AMD. The CWs for secondary treatment of effluent are engineered systems specially designed to employ natural processes (vegetation, soil, and microbial activity), in order to treat the AMD (Vymazal, 2010). These systems are low-cost and low-maintenance, and are capable of removing heavy metals, nutrients, organic matters, and micropollutants (Neculita et al., 2007; Rötting et al., 2008; Yeh, 2009;). The CWs increase pH and alkalinity, remove the dissolved metals, and reduce sulfate concentration in AMD.

Water treatment is accomplished by a variety of physical (sedimentation, flocculation), chemical (oxidation, hydrolysis, reduction) and biological (sulfate reduction, phytoextration) processes acting independently, in some cases, or interactively, in others (Matagi et al., 1998; Stottmeimeister et al., 2003). However, the mechanisms governing the removal of metals (plants versus reactive mixture) are not well understood, hence the need to elucidate these processes in order to ensure treatment effectiveness and system sustainability (Stottmeimeister et al., 2003). In CWs, metals could exist in various particulate or dissolved forms (which can absorb onto particles), as complexes with inorganic and organic ligands or as free ions in water (Yeh et al., 2009). The toxicity of a given trace metal is largely controlled by its speciation, thus evaluation of metal partitioning (operational speciation), as well as the becoming and availability under conditions simulating natural processes (e.g. pH variation, reduction and oxidation) is crucial (Ryan et al., 2008). Sequential extraction procedure (SEP) is an important and widely applied tool for gaining information on potential mobility (hence, potential bioavailability and toxicity) of toxic elements in the environment (Bacon and Davidson, 2008). Basically, the ranking of metal mobility in SEPs is based on their concentrations in the water-soluble and exchangeable fractions, as well as the fractions that are reducible, bound to carbonate, and bound to organic matter or sulfides (Neculita et al., 2008). Assuming that bioavailability of heavy metals decreases with each successive extraction step in the SEP, consistent with the decreasing order of solubility, then the following ranking is obtained: water soluble > exchangeable > carbonate bound > Fe-Mn oxides bound > organic matter/sulfides > residual (Jong and Parry, 2004). In fact, bioavailability is a complex and evolving concept, but has recently been defined as the degree to which chemicals present in the soil may be absorbed or metabolized by a human or ecological receptor or is available for interaction with biological systems (Bacon and Davidson, 2008).

The main objective of this study is to design a CW, which can be used in the polishing step of a multi-units passive system for the treatment of AMD contaminated by Fe, Mn, Ni, and Zn. The evaluation of removal mechanisms and of metal speciation in the reactive mixture and the plants of the CW is also performed. For this purpose, small-scale laboratory tests were carried out. The overall results improved the understanding of the processes governing the treatment and the evaluation of design criteria for a CW. This knowledge would allow the transfer of this technology on active, closed or abandoned mine sites, contaminated by the AMD. The research focuses also on hydrology, effect of plants, substrate or filter media that should not be neglected, since they are key elements, especially in a northern climate such as Abitibi-Témiscamingue.

METHODOLOGY

Bench-scale testing of CWs for AMD treatment

Bench-scale CWs were built in polypropylene (48 x 33 x 33 cm). Two different support media and two configurations (vertical and horizontal flow) were tested. Limestone (up to 20 mm in size) was

placed on the bottom of the vertical flow cells and was covered then with a mixture of gravel (8-16 mm) and peat, whereas free surface flow cells were filled with a mixture of sandy soil (0-4 mm), cattle manure, peat and granular dolomitic limestone. Once filled with the reactive mixture, 45 five month old *Typha latifolia* (cattail) were planted in tested wetland modules at a density of $2,84/m^2$.

In parallel, unplanted CWs (control) were also set-up. The testing was carried out for a 3-month period (July to October, 2013).

Tap water was added to the plants for 3 weeks, before starting the artificial AMD feed. Continuous flow of AMD was then applied to the CWs, at a flow rate of 1.5ml/min, for a 5-day retention time. The artificial AMD, at pH 4.2, was constituted with Fe, Mn, Ni and Zn sulfates salts, at average concentrations of 38.1, 2.6, 0.4 et 9 mg/l, respectively.

Water sampling and analysis

Influent and effluent samples were collected from each wetland daily for the 3 months duration. The following parameters were measured in the laboratory: pH, redox potential (Eh) and sulfate. For the dissolved metal analysis, 10 ml of filtered samples were preserved using 2 % (by volume) of 70 % nitric acid and then analyzed (ICP-AES type: Vista AX CCO Simultaneous ICP-AES - Palo Alto) with detection limits of 0.39, 0.006, 0.004 and 0.008 mg/l, for Fe, Mn, Ni and Zn, respectively.

Media sampling and analysis

In addition to water samples, solid media from the top (0-5 cm) and middle (15 cm, for vertical-flow only) layers were collected from each CWs, toward the end of the testing. Sediments (solid media) were dried in an oven at 70 $^{\circ}$C and digested (0.200g) via microwave digestion by $HNO_3:HCl$ (7:1) solution for the analysis of total metal concentration. The fractionation of heavy metals was evaluated using the SEP developed by Jong and Parry (2004), which is based on the classical method of Tessier *et al.* (1979). The SEP was performed to evaluate the partitioning of four heavy metals (Fe, Mn, Ni and Zn) into six operationally defined fractions. Dried sediment samples were used for the separation of the following metal fractions: soluble (extracted with water), exchangeable (extracted with 1 M $MgCl_2$, pH 7.0), carbonate bound (extracted with 1 M NaOAc buffered with HOAc, pH 5.0), reducible or bound to Fe–Mn oxides (extracted with 0.04 M NH_2OH-HCl in 25% (v/v) HOAc), oxidable or bound to organic matter (digested by HNO_3, H_2O_2, and 3.2 M NH_4OAc in 20% (HNO_3), and residual fraction (dissolved by acid attack with HNO_3 and HCl).

The SEP was conducted with 1 g of solid accurately weighed in 50 mL polypropylene centrifuge tubes. Between each two extraction steps, the supernatant was separated from the solid-phase residue by centrifugation (Thermo Scientific Sorvall ST-16) at 1000 rpm for 30 min. The supernatant was then carefully removed, filtered through a 0.45 μm filter and preserved in 50 mL vials. The remaining residue was washed twice with 8 mL deionized water, centrifuged for 30 min, and the filtered supernatant mixed with the initial extract and stored at 4°C before analysis for metal concentrations by ICP-AES.

RESULTS AND DISCUSSION

Evolution of pH and sulfate concentration

Results showed the effectiveness of CWs for increasing the pH, all along the 3-month testing period (Fig. 1). The data indicate that there was a significant increase in the pH at the outlet of both configurations. The effluent had, in average, pH of 8.0, for vertical-flow, and pH of 7.6 for surface-flow wetlands. The processes responsible for pH increase were probable (1) the dissolution of carbonate substrate materials, which generate alkalinity and consume protons, and (2) bacterially-mediated sulfate reduction producing carbonate alkalinity in anoxic conditions (Mayes *et al.*, 2009).

As a result, SO_4^{2-} concentration in VSS-flow planted and unplanted and HS-flow CWs halved over the time (292-138; 377-193; 309-146 mg/l), excepting for HS unplanted one (320-301 mg/l). It is reasonable to assume that SO_4^{2-} were released from the substrate material after the start-up (Zagury et al, 2006; Song et al., 2012).
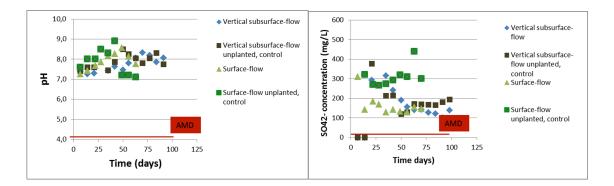
Figure 1 Evolution of pH and sulfate concentration over time in CWs

Metal removal efficiency

Results on bench-scale testing showed that CWs are efficient for Fe and Zn removal in AMD, with values up to 98.6%. The VSS-flow were more efficient than the HS-flow wetlands for contaminant removal (probable due to larger surface of contact), as well as the planted test cells. However, the removal of Mn and Ni was negligible, especially for HS-flow wetlands. Noteworthy, Mn is among the most difficult metals to remove due to the complexity of the interactions governing its solubility (Karathanasis *et al.*, 2009; Song *et al.*, 2012). Kinetics of Mn chemical oxidation are slow, whereas due to the high reduction potential of Mn(IV), parallel reactions, such as organic matter and Fe^{2+} oxidation, induce excessive oxidant consumption. Therefore, iron removal is required prior to manganese oxidation (Sylva *et al.*, 2010).

Table 1 Removal of Fe, Mn, Ni and Zn in AMD by CWs

Wetland design	Removal of metals (%)			
	Fe	Mn	Ni	Zn
Vertical subsurface-flow planted	98.6	75.5	88.5	96.7
Vertical subsurface-flow unplanted	92.7	23.1	46.4	95.7
Horizontal surface-flow planted	89.8	-20.3	58.1	96.3
Horizontal surface-flow unplanted	86.9	-35.2	-6.0	91.2

Fractions that contain most of Fe (5.01-5.04 mg/l) and Zn (1.01-4.43 mg/l) in planted and unplanted subsurface were bound to Fe-Mn oxides, whereas most of the Mn (0.84-0.47 mg/l) and Ni (0.28-0.27 mg/l) were found bound to carbonates. In surface-flow wetlands substrate, Fe was concentrated mostly to Fe-Mn oxides (4.43-3.95 mg/l) and residual fraction (6.57-6-40 mg/l) in planted and unplanted cells respectively, Zn to organic matter and sulfides (0.01-0.01 mg/l), Mn was found bound to carbonates (1.16-0.47 mg/l) and in the residual fraction (0.39-0.39 mg/l) and Ni was essentially found in the residual fraction (0.97-1.31 mg/l). These results indicated that metals were successfully immobilized in the microcosms. However, the availability of heavy metals within sediments can change over time, as a result of changes in redox potential, pH, organic material content (Yeh et al., 2009). Low pH could increase metal solubility, while low redox potential (more reducing conditions) could dissolve iron and manganese oxides, resulting in the mobilization of oxide-sorbed metals. On the contrary, increasing the redox potential (more oxidizing conditions) could mobilize metals by oxidation of metal sulfides (Hodda and Alloway, 1998).

CONCLUSION

The efficiency of bench-scale laboratory CWs was evaluated during a 3-month period for the treatment of AMD contaminated by Fe, Mn, Ni, and Zn. Results showed that the wetland test cells have the capacity to increase pH, to remove Fe and Zn, whereas they proved inefficient for Mn and Ni treatment. However, metals were immobilized in the substrate of CWs. The findings of the study include also the fact that the design and the substrate have no significant influence on the treatment effectiveness in laboratory.

Results from microcosm experiments must be interpreted with care due to edge and container effects but they are especially useful in determining broad patterns and investigating mechanisms. In order to investigate the "patterns" found in this bench-scale study and to understanding the processes governing the treatment of AMD, the overall results will be used to evaluate landscape-scale design criteria.

This knowledge would allow the transfer of this technology on active, closed or abandoned mine sites, contaminated by the AMD.

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Stability of metal precipitates and their potential mobility

As mentioned, the SEPs are currently used to assess the geochemical fractionation of metals in soils (Claff *et al.*, 2010). Partitioning patterns of heavy metals in CWs are shown in Table 2.

Table 2 Partitioning of Fe, Mn, Cd, Ni, and Zn in spent reactive mixtures from bench-scale CWs

Wetland design	Fraction	Fe (mg/g)	Mn (mg/g)	Ni (mg/g)	Zn (mg/g)
	F4	4.43 ± 022)	0.26 ± 0.22)	<LDD	<LDD
Vertical subsurface-flow planted	F5	0.44 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
	F1	<LDD	<LDD	<LDD	<LDD
	F6	6.57 ± 0.01	0.39 ± 0.01	0.97 ± 0.65	<LDD
	F2	<LDD	0.05 ± 0.00	<LDD	<LDD
	Sum	11.47	1.83	1.29	0.01
	F3	<LDD	0.84 ± 0.08	0.28 ± 0.02	<0.14
	MT	10.12	0.22	0.00	0.00
	F4	5.01 ± 4.21	0.41 ± 0.07	<LDD	1.01 ± 0.08
Horizontal surface-flow unplanted	F1	<LDD	<LDD	<LDD	<LDD
	F5	0.50 ± 0.07	0.03 ± 0.00	0.04 ± 0.00	0.04 ± 0.00
	F2	<LDD	<LDD	<LDD	<LDD
	Sum	5.51	1.34	0.33	1.05
	F3	<LDD	0.47 ± 0.18	0.27	<LDD
	MT	5.95	0.79	0.00	0.34
	F4	3.95 ± 0.00	0.11 ± 0.00	<LDD	<LDD
Vertical subsurface-flow unplanted	F1	<LDD	<LDD	<LDD	<LDD
	F5	0.40 ± 0.23	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
	F2	<LDD	0.03 ± 0.00	<LDD	0.00
	F6	6.40 ± 2.41	0.39 ± 0.05	1.31 ± 1.25	<LDD
	F3	<LDD	0.47 ± 0.19	0.27	0.00
	Sum	10.75	0.99	1.59	0.01
	F4	5.04 ± 0.13	0.28 ± 0.06	<LDD	1.43
	MT	8.41	0.13	0.00	0.00
	F5	0.38 ± 0.03	0.03 ± 0.00	0.04 ± 0.00	0.04
	Sum	5.42	0.81	0.31	1.47
	MT	2.88	0.6075	<LDD	0,32
Horizontal surface-flow planted	F1	<LDD	<0.0063	<LDD	<LDD
	F2	<LDD	<0.06	<LDD	<LDD
	F3	0.02 ± 086	1.16 ± 0.86	0.31 ± 0.02	<LDD

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