PASSIVE TREATMENT OF MINE DRAINAGE WATERS: THE USE OF BIOCHARS AND WOOD PRODUCTS TO ENHANCE METAL REMOVAL EFFICIENCY

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ABSTRACT

Passive biological treatments have been proposed as a possible efficient and cost effective treatment method for metal bearing water discharged from mine sites after closure. Several biofilters are under study in Yukon and have produced variable, but promising results up to now. However, concerns are typically expressed around biological treatments and their suitability in northern, colder climates. Biofilters allow for metal removal using a variety of chemical, physical and biological mechanisms. If biological processes are affected by a cold climate to some extent, chemical processes are typically not affected by the temperature the same way and can be reliable in cold waters. This study focused on metal sorption and metal removal by chemical mechanisms and assessed the sorption capacity of biochar and wood products which could be later introduced in bioreactors to help with metal removal from mine-impacted cold waters.

Biochars allowed for more than 90% removal of Cd, Cu and Zn from a metal-bearing effluent along with 35 to 69% removal of arsenic. Wood products displayed good removal capacity as well, in the range of 51 to 94% for Cd, Cu and Zn. However, arsenic and selenium removal by wood products was limited; Se also showed minimal sorption on biochars and was in one case released during sorption testing. Metal leaching from the materials was observed to some extent, including Cu and Zn from poplar and spruce products. Amongst spruce products, the chips from the trunk proved to be slightly more efficient than the needles. Overall, biochars and wood products showed potential for use in water treatment for metal sequestration in combination with other mechanisms such as sulfide precipitation in sulfate-reducing bioreactors. Such materials could be collected or produced on remote mine sites and could help with mine remediation.

Key Words: Water Treatment, Metal Removal, Metal Sorption, Adsorption, Bioreactors, Bioremediation.

INTRODUCTION

Water management in the mining industry has become a priority focus in our world, which has been increasingly concerned with sustainable development. To lower their footprint on the environment, mines are constantly working toward limitation of contaminant discharge to the environment. Hard rock mines have to closely control the concentrations of metals according to federal and provincial/territorial regulations, which leads to the treatment of mine-affected waters, including run-off waters, drainage from tailings or waste rocks pads, process waters, etc. Water treatment is required during operation of the mines as well as after closure for the long term. Current water treatment technology development is focused on long-term passive treatments that require low operation and maintenance. Various passive treatments are available, including chemical adsorption and bioremediation (Johnson and Hallberg 2005). Along with metals, mine waters commonly contain high sulfate content that results from the breakdown of sulfide minerals (Akcil and Koldas 2006; Kalin et al. 2006). There is an increased interest in the use of Sulfate-Reducing Bacteria (SRB) to help with metal removal from mine waters (Dar et al. 2007; Genty 2011; Jong and Parry 2003; McCauley et al. 2009; Neculita et al. 2010; USEPA 2002). Under anaerobic conditions, SRB reduce sulfate (SO_4^{2-}) into sulfide (S^{2-}) using electrons from organic matter. Sulfides, in turn, precipitate metals. The solubility of metal sulfides being generally very limited, it consequently lowers the concentration of metals in the effluent and provides a stable metal precipitate (Blais et al. 2008). To accomplish sulfide production, SRB catalyze the oxidation of organic carbon from the surrounding organic matter (eq. 1), where CH_2O represents organic carbon (Waybrant et al. 1998):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \text{ (eq. 1)}$$

Anaerobic bioreactors are being studied in the mining industry for effluent treatment. In these systems, the effluent passes through a biofilter (e.g., in trenches) filled with permeable solid support (gravel, sand) and substrate (organic matter). The substrate used to support SRB growth can be variable. Neculita and Zagury (2008) showed that cellulosic materials like wood waste have a beneficial effect on SRB treatment efficiency. Wood products (leaf mulch, wood chips, sawdust, wood compost, peat moss) mixed with sewage sludge or manure can be an excellent substrate for SRB and have been shown to achieve reduction of metals concentration in mine effluent (Neculita et al. 2010; Waybrant et al. 1998). Besides efficiency in the short-term, the ideal mixture of substrate should also last in the long term, i.e, not be too biodegrade and deplete before the end of the life time of the bioreactor, or to extend the useful life of the bioreactor before it would require replacement or refreshment of the media. Drury (2006) used a mathematical model and showed that organic matter with an older apparent age, less biodegradable, can sustain bioreactor efficiency for longer duration. Additionally, the residual organic products may improve the stability of the metal sulfide precipitate once the treatment system is closed.

In northern climates, when the temperature is low, concerns have been expressed about the efficiency of SRB to sustain a sufficient level of biological activity during winter time to maintain treatment efficiency (Nordin 2010). The objective of this study is to assess if a range of substrates can also help with metal removal using chemical mechanisms, which are generally not as temperature-dependent as biological mechanisms. Besides providing feed to SRB, solid substrates can also act as a metal adsorbent. Cellulosic materials like sawdust and wood chips are known for their metal adsorption capacity (Argun et al. 2008; Keng et al. 2013; O'Connell et al. 2008) due to reactive groups within the substrate. Wood is an abundant resource in remote mine sites in northern Canada and other northern climates, and wood chips could easily be included in bioreactors to help metal removal by providing biodegradable organic matter and metals site adsorption. This study looked at the adsorption capacity of Spruce (trunk and needles) and Poplar (trunk) chips, as both species are very common in Yukon mine sites. In addition, biochars made from wood products were also studied. Biochar is defined as a carbon-rich material produced by thermal decomposition of organic material under limited supply of oxygen at relatively low temperature (<700°C) (Lehmann and Joseph 2009). On-going projects look at the construction of mobile pyrolysis ovens (personal communications with K. Stewart, Yukon Research Centre, M. Garcia-Perez, University of Washington). Hence biochars could be produced in remote locations, providing that the mine site has access roads. Due to the thermal decomposition, the remaining biochar is recalcitrant and is likely to persist in bioreactors on the long-term. Biochars are also capable of adsorbing metals on their surfaces and several biochars proved to have good potential for metal removal from effluent, although metal adsorption capacities can be very variable. Metal sorption by biochars depends largely on biochar characteristics, including feedstock, pyrolysis temperature, oxygen content, etc. Table 1 presents the adsorption capacity measured by various authors.

Table 1 Review of adsorption capacity of biochars from literature

Metal	**Adsorption capacity (mg/g)**	**Adsorption pH**	**Biochar feedstock**	**References**
Cd	1.5	5	Alamo switch grass	Regmi et al. 2012
Cu	4	5		
Cd	16.6	6	Pig manure	Kolodynska et al. 2012
Cu	6.3	5		
Pb	19.8	6		
Zn	4.2	5		
Pb	4.1	5	pinewood residues	Liu and Zhang 2009
Pb	2.4	5	rice husk residues	
Cr (VI)	3.0	2	Oak wood	Mohan et al. 2011
Cr (VI)	4.6	2	Oak bark	
Cu	0.04	5	peanut straw	Tong et al. 2011
Cu	0.09	5	canola straw	
Cu	12.5	5	corn straw	Chen et al. 2011
Zn	11	5	corn straw	
Cu	6.8	5	Hardwood	
Zn	4.5	5	Hardwood	
Cu	48.5	6	Salt-marsh plant	Li et al. 2013

Three different biochars, poplar wood chips, spruce wood chips and spruce branch mulch were studied as metal adsorbents in this study.

MATERIAL AND METHODS

Adsorbents Sampling and Preparation

Poplar and spruce trees were cut down in the Whitehorse region, Yukon Territory, Canada. Branches were removed from the tree before the trunks were were ground into chips using a log chipper (Bandit M65 XP, USA). Spruce branches were ground separately into mulch using the same equipment. Wood chips and mulch were used fresh, with less than a week of drying.

Three biochars were collected from different manufacturers. Biochar made from mixed spruce, pine, and fir was produced by Diacarbon Energy Inc. (Burnaby, BC, Canada) and named “BCD”. Biochar made of spruce, pine, fir, willow and poplar was produced by Zakus Farms ("BCZ"). The biochar collected from Titan (Saskatoon, SK, Canada) was made from Willow and fish bone meal ("BCT").

Adsorbents pH Measurements

Suspensions were made using 1:10 (w/w) ratio of biochar or wood with DI water. The pH of the suspension was measured at t=0 ($pH_{t=0}$) and after a week ($pH_{1\ week}$) at room temperature using an pH meter (Oakton pH5+, Vernon Hills, IL, USA) equipped with Ag/AgCl combination reference electrodes. pH calibration was done using certified pH 4, pH 7 and pH 10 standards (Fisher, catalogue number SB101-500, SB107-500 and B115-500).

Batch Adsorption Studies

Synthetic drainage effluent was produced using sulfate metal salts (As_2O_5, $CdSO_4{\bullet}8/3H_2O$, $CuSO_4{\bullet}5H_2O$, $FeSO_4{\bullet}7H_2O$, SeO_2, $ZnSO_4{\bullet}7H_2O$ and $NaSO_4{\bullet}10H_2O$, all ACS reagents) dissolved in DI water at pH 6. Then 2, 4, 6, 8 and 10 g of adsorbent materials were mixed with 200 ml of synthetic drainage effluent in a 500ml baffled Erlen Meyer and shaken for 24 hours at room temperature to allow for metal sorption equilibrium. To assess metal leaching from the materials, 10g of adsorbent was mixed with DI in the same conditions. Supernatant was then filtered through 0.45µm porosity glass fiber filters (Cole Parmer, catalogue number RW03-04700) and stored for further analysis.

Analytical Techniques

Effluent pH was measured using Oaklon meter (Oakton pH5+, Vernon Hills, IL, USA with Ag/AgCl combination reference electrodes). Total Solids contents were measured according to APHA method 2540B. Biochar and wood products were partially digested using ACS grade nitric acid and hydrogen peroxide (method USEPA 3050b) to allow for determination of metal contents. Metal concentrations were measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Vista-AX CCO, by Varian (Palo Alto, CA, USA). Quality controls were performed with certified multiple element standards from SCP Science (Lasalle, QC, Canada) to ensure conformity of the measurement apparatus. Limit of Quantification (LQ) was calculated as 10 times the standard deviation measured obtained after measurement of 10 blanks.

RESULTS AND DISCUSSION

Material Characteristics

The material studied includes three biochars (BCD, BCZ and BCT) and three wood products (poplar chips, spruce chips and spruce needles). Table 2 presents the results of characterization. As expected, biochars displayed alkaline pH, initially between 9 and 10 and reducing down to close to 8.5 after a week. On the other hand, the wood products were acidic, with the poplar chips producing the most acidic conditions after a week, at pH 3.84. Arsenic and selenium contents in all materials were low, under the quantification limits of 0.9 mg/kg for As and 2.1 mg/kg for Se, except the biochar made of willow and bone meal (BCT) at 6.3 ± 0.7 mg/L Se. Overall, the BCT material, made of willow and bone meal, displayed higher concentrations of metals, including significant amount of Cd, Zn, Fe and Na. In general, higher metal contents were measured in biochars than in wood products. Biochars were made by pyrolysis, which involved volume reduction and subsequent concentration of the metals in the residual product.

Table 2 Measured adsorbent characteristics (1:10 water suspension was used for pH measurements; HNO_3/H_2O_2 digestion was used for metal contents analysis)

Material	**Total solids**	**$pH_{t=0}$**	**pH_{1week}**	**As**	**Cd**	**Cu**	**Fe**	**Na**	**Se**	**Zn**
	%			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
BCT	81.0	9.84	8.27	<0.9	11.0	3.3	3755.8	15814.5	6.3	164.2
BCD	81.1	9.91	8.51	<0.9	0.8	26	1362.3	1281.0	<2.1	55.8
BCZ	96.5	9.23	8.47	<0.9	0.2	15.2	939.1	123.0	<2.1	60.0
Pop. chips	93.7	6.06	3.84	<0.9	0.2	30.8	32.6	53.3	<2.1	30.0
Sp. chips	93.6	5.94	5.5	<0.9	2.0	67.9	54.5	111.4	<2.1	27.0
Sp. needles	89.9	5.28	5.11	<0.9	2.4	22.9	110.1	124.8	<2.1	51.1

Metal Leaching

Wood products and biochars contained heavy metals to some extent. Mixing of the materials with DI water for 24 hours was completed to assess the potential for metal leaching. The results are presented in Fig 1 along with the concentration measured in the synthetic drainage water for comparison. Wood products leached out more metals than biochar products, even if metals contents were generally lower (Table 2). The metals contained in pyrolysis products may be tightly bound and less available for leaching. Poplar chips and spruce needle leached significant amount of copper and zinc in the first 24 hours of being submerged in water, with concentrations 0.13 and 0.12 mg Cu/L and 0.13 and 0.17 mg Zn/L respectively using 5% S/L ratio. No selenium leaching was observed (< LQ of 0.021 mg/L) and arsenic leaching was observed only for BCT (0.012 mg As/L, otherwise < LQ of 0.0093 mg/L). Hence, the use of natural materials such as wood, in bioreactors should be managed carefully, with special attention to metal leaching potential in the initial operation period.

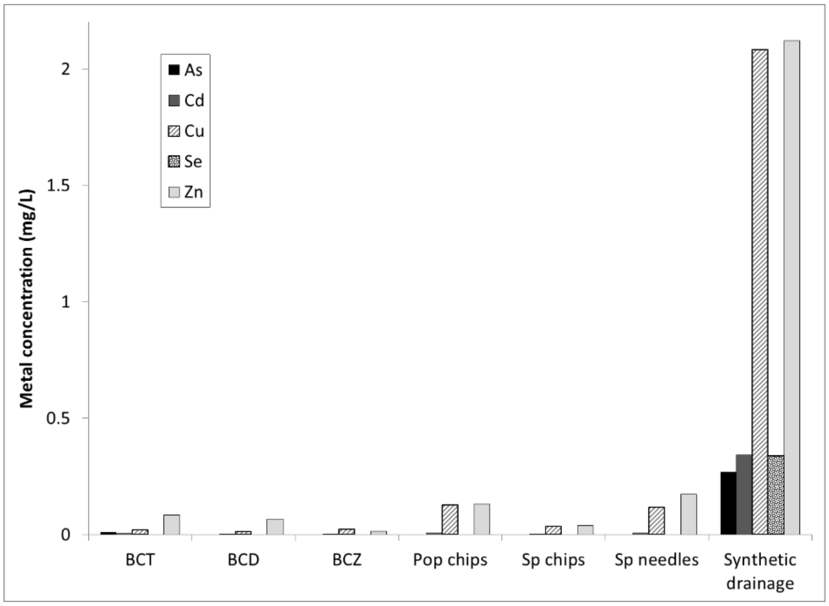

Figure 1 As, Cd, Cu, Se and Zn concentration observed after leaching from biochars BCT, BCD, BCZ, poplar chips, spruce chips and spruce needles and in the prepared synthetic drainage water (Solid to liquid ratio of 5% in DI water, 24 hours equilibrium, LQ are 0.009 mg/L for As).

<u>Metal adsorption</u>

The primary objective of this study was to assess the sorption capacity of materials which can be collected or produced on-site in many northern and especially Yukon mines, to help with metal sequestration. Three biochars and three wood products were mixed with pH 6 synthetic drainage water containing metals commonly found in mine impacted waters, namely As, Cd, Cu, Se and Zn. Figure 2 presents the relative concentration (C/C_o) of the different metals remaining in the effluent after exposure to each of the adsorbents for 24 hours. Biochars results (BCT, BCD and BCZ) are displayed in Fig 2a, b and c. The profiles are very similar for Cd, Cu and Zn, with more than 90% removal on average using 1% to 5% S/L ratio. Arsenic removal was lower, with 54, 69 and 35% respectively using BCT, BCD and BCZ. The selenium profiles were somewhat surprising. The three biochars studied were not able to remove more than 30% of selenium and the Biochar BCZ actually released selenium to a significant extent. Although 10 g of BCZ leached less than 2 µg of Se in DI water, when mixed with synthetic drainage the same amount of biochar released more than 80 µg of Se. Selenium initially bound to the biochars may have been displaced through an exchange process during sorption of other metals with higher affinities like Fe, Na, Zn, Cu, Cd on the biochar. The mechanisms of selenium release should be further studied.

Divalent metal removal by wood products was reasonably effective. Although not as efficient as biochar, poplar, spruce chips and spruce needles were able to remove Cd up to 87, 94 and 84% respectively, Cu up to 76, 81 and 66% respectively and Zn up to 83, 88 and 51% respectively. The spruce chips obtained from trunks displayed higher ability than the needles for metal removal. This difference may be due to the different structure, porosity, and surface chemistry of the needles versus the trunk chips. Amongst the three wood products, Spruce chips gave the best results.

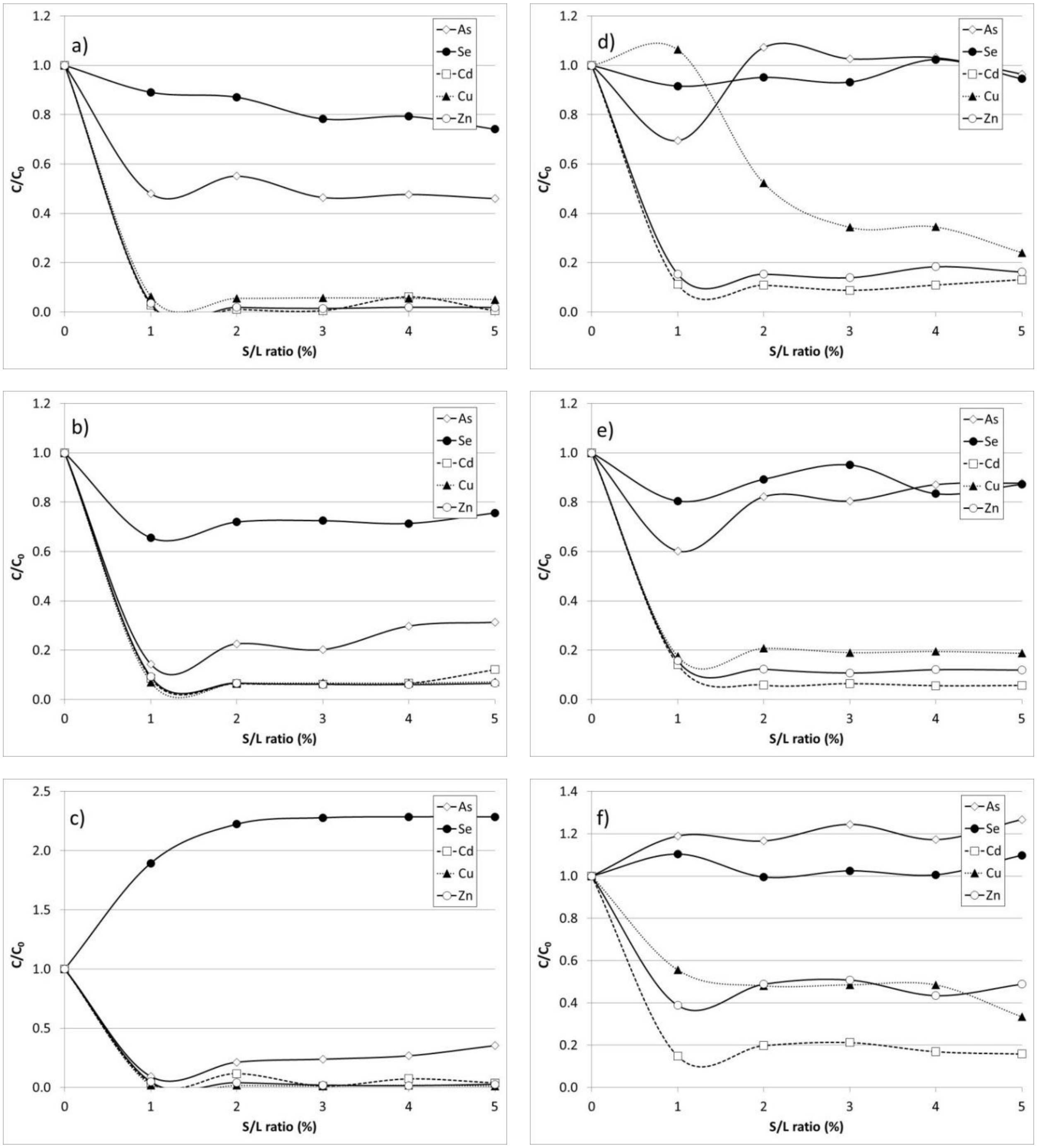

Figure 2 Relative concentrations (C/Co) of As, Se, Cd, Cu and Zn after 24 hours equilibrium with variable solid to liquid ratio using a) BCT, b) BCD, c) BCZ, d) poplar chips, e) spruce chips and f) spruce needles (initial concentrations of 0.27 mg As/L, 0.34 mg Cd/L, 2.08 mg Cu/L, 0.34 mg Se/L and 2.12 mg Zn/L).

CONCLUSION

Natural wood products and biochars were studied for metal removal from a synthetic drainage effluent. Biochars exhibited alkaline properties whereas wood products generated acidity however, both materials displayed good capacity for divalent metal removal like Cd, Cu and Zn although biochars were slightly more efficient than wood products. As and Se were less amenable to adsorptive removal than divalent metals but biochars helped to remove arsenic to some extent. Overall, this study gave evidence of the potential of wood products and biochars for water treatment and metal sequestration, providing that metal leaching from the material itself is controlled. Further study should investigate the effect of using such materials on sulfate-reducing bacteria growth and bioreactor efficiency, and these tests are planned using some of the same media as was tested in this study.

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