



## OPPORTUNITIES FOR USING PULP MILL RESIDUES IN MINE REMEDIATION

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### Abstract

The pulp and paper industry produces organic wastes such as primary and secondary biosolids from water treatment, as well as bottom and fly ashes from energy production through combustion of biomass. We are investigating these residues for reuse in mine remediation; such as to support sulphate reducing bacteria and remove zinc and cadmium with secondary biosolids as the carbon and nutrient source, and treatment of acid mine drainage using green liquor and fly ash. Use of these residues is limited by transportation costs depending on the proximity of pulp mills and mine sites to each other. To expand the reuse of pulp mill residues, there is the opportunity to increase their value through fairly straight forward thermal, physical and or chemical transformations that functionalize them in order to sequester and recover specific values. In this paper, we provide the example where we recovered selenium for potential recycling from simulated mine impacted water using functionalized residues. Areas where this can be applied include the Elk Valley, East Kootenays, and the Cariboo region of British Columbia.

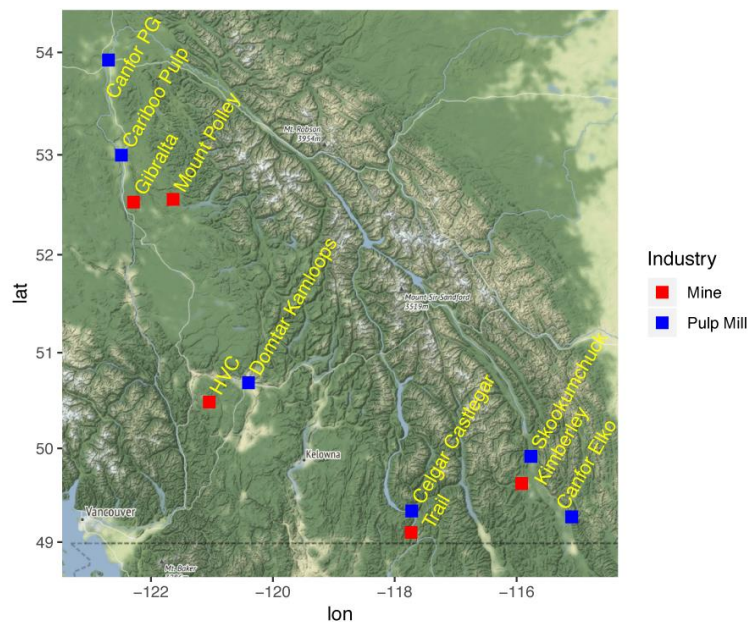
**Key Words:** wood ash, biochar, selenium, absorption, metal removal



### INTRODUCTION

There is increasing pressure from society towards the mining industry to eliminate wastewater release. A more sustainable approach is required in order to protect and make the most of the available natural resources, including water. It is important to mention that sustainable development was originally defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs (WCED, 1987). Applying the sustainability concept to water management means viewing wastewater as a potential resource, to be reused or recycled after suitable treatment. In addition, wastewater should also be seen for its potential value. More than just providing an alternative source of water for reuse, safe wastewater management will protect our ecosystems and provide energy, nutrients and other recoverable materials (UN-Water, 2019). Once a raw material is extracted, refined and produced with the usual costs, it makes economic and business sense to use the value produced as long as possible, i.e., keep the product

function/service and use-value in economic circulation as long as possible (Korhonen et al., 2018). Besides, landfilling of waste is restricted by the availability of space and costs. Industries such as mining, forestry and agriculture, important for Canada's economy and support the livelihoods of many Canadians can partner up and work towards a circular economy. Residues from one industry, presently regarded as liabilities, can be used to benefit another industry and thereby become valorized. For instance, organic and inorganic residues from pulp and paper mills, forestry or agriculture can be used to sequester metals from mine influenced waters (MIW) that can be recovered later. Areas in Elk Valley, East Kootenays, and the Cariboo region of British Columbia (Figure 1) have pulp mills and important mine sites which could potentially partner up to reduce residue landfilling and treat MIW.



**Figure 1 – Location of Pulp mills and mine sites with potential of partnership**

Forest product industries contribute to the economic and social welfare of all Canadians as important employers nationwide and the main source of income for many living in rural and indigenous communities. Around 250 million ha in Canada are used for forestry applications. Moreover, harvested areas increased by 9% from 2014 to 2015, and the demand for Canadian forestry products is expected to continue to grow (Rancourt et al., 2017). The majority of the residues or by-products from this industry are from manufacturing processes, and they can be applied for different purposes, such as generation of energy. In order to remain competitive, the pulp and paper industry has taken measures to decrease energy costs. To reduce fuel costs, which account for about 25% of production costs, Canadian pulp and paper operations are using renewable biomass sources, such as by-products of their own production processes (NRCAN and CIPEC, 2008). This creates large amounts of ash residue from combustion of this biomass that has become a liability. Most of the ash is treated as a waste material and landfilled. Increasing volumes of ash

are raising concerns about storage, disposal and use, since this will demand landfill expansion, and increase costs of handling and transporting (James et al., 2012). For instance, in 2017, around 35000 m<sup>3</sup> of ash produced by pulp and mill activities in the Okanagan area ended up in landfills. Another material produced at pulp and paper mills is the biosolid residue from on-site treatment of wastes that can comprise 5-16% of the mass of the paper produced at the mill (Pervaiz and Sain, 2015). The primary and secondary treatment of pulp waste produces residual fibrous materials and biological sludge, which also mostly go to landfills, although some is used for energy generation or for land application depending on the local legislation. The same cited mill produces close to 2200 tons of primary sludge per year.

This study presents characteristics of ashes produced by two pulp mills in British Columbia and describes how they could be treated to make the most of their intrinsic characteristics, such as the char, unburned material.

## **MATERIALS AND METHODS**

### Chemical and physical analyses

Ash samples were analyzed for scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) in the Electron Microbeam & X-Ray Diffraction Facility at UBC using a Philips XL30 electron microscope (Bruker Quantax 200 energy-dispersion X-ray microanalysis system, XFlash 6010 SDD detector, Robinson cathodoluminescence detector). Raman spectra were collected with a Horiba XPlora Plus Raman Microscope system housed in the LaserSpot Facility at the Pacific Centre for Isotopic and Geochemical Research (PCIGR). The instrument is equipped with a 532 nm laser and 1800 gratings per millimeter. Horiba LabSpec 6 software was used to collect spectra between 100 and 1250 cm<sup>-1</sup>. Mathematical preprocessing of the raw data was performed in Origin Pro 2019 software (OriginLab, Northampton, MA). Baseline subtraction of each spectrum was carried out with the Asymmetric Least Squares Smoothing function, and each spectrum was normalized to its own standard deviation. Images from Fe-impregnated biochar were made using a Microscope Nikon Eclipse Ci POL.

Total dissolved selenium and iron in solution were analyzed using an inductively coupled plasma - optical emission spectrometry (ICP-OES Varian 725ES Optical Emission Spectrometer).

### Ash characterization and char separation

Different pulp mills located in the province of British Columbia (Canada) provided samples of fly and bottom ashes (Table 1). The as-received ashes were screened according to loss-of-ignition test (LOI - organic, inorganic, and minerals content) and SEM-EDX analysis. The chosen ashes were fractionated into 4 different size ranges (63-180, 180-500, 500-850, 850-1.7 μm) using sieves with different mesh sizes in a vibratory sieve shaker (Fritsch Analysette 3 PRO). Later, the fractions were characterized through gravimetric analysis for LOI. For the LOI test, the samples were weighed in porcelain crucibles, dried at 100°C overnight, followed by calcination at 550°C for 4h, and finally at 1000°C for 2h.

**Table 1 – List of the different tested ashes provided by company A and B**

Sample name	Industry	Ash type
PPTA_002	A	Fly ash
MCA_003	A	Fly ash
BTA_004	A	Bottom ash
PPTA_007	B	Fly ash
MCA_008	B	Fly ash
GBA_009	B	Fly ash

#### Iron impregnation onto biochar

The biochar provided to us by a third-party industry was made from Douglas-Fir, Hemlock and Western Red Cedar wood chips through pyrolysis at 550°C. Two different biochar samples were used, regular (RB) and steam activated biochar (STB) and both were impregnated with iron (10% w/w). For impregnation, a solution of iron (III) nitrate nonahydrate and acetone was poured onto the biochar (RB or STB), and pasted for 10min, followed by heating in the oven at 120°C for 24h. The impregnated samples were called FeRB and FeSTB, respectively.

#### Adsorption tests

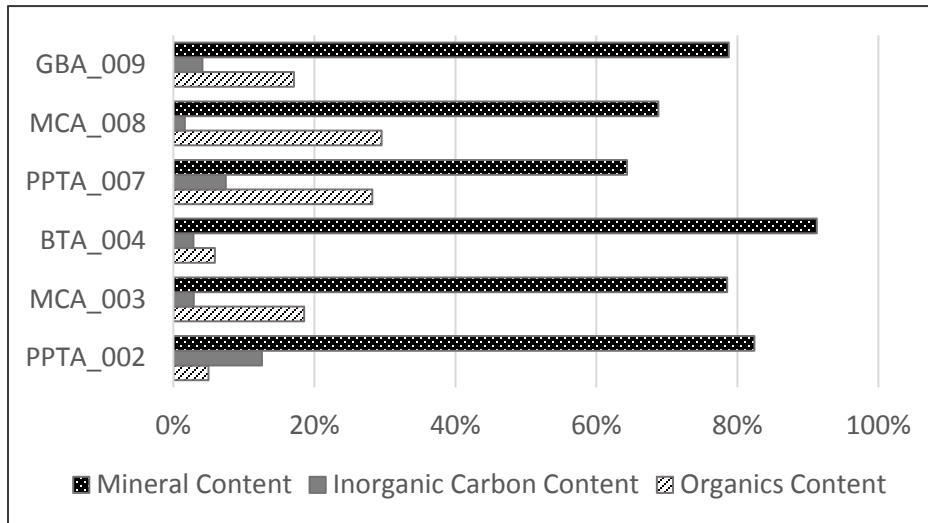
The biochar samples were tested for Se (VI) adsorption using solutions at 500ppm prepared with sodium selenate (Sigma-Aldrich, Na<sub>2</sub>SeO<sub>4</sub>). RB, STB, FeRB and FeSTB were used at a load 50mg·L<sup>-1</sup>, and tests were carried out using 20mL glass tubes placed in a shaker (250rpm) for 4h at constant temperature (25°C).

## **RESULTS AND DISCUSSION**

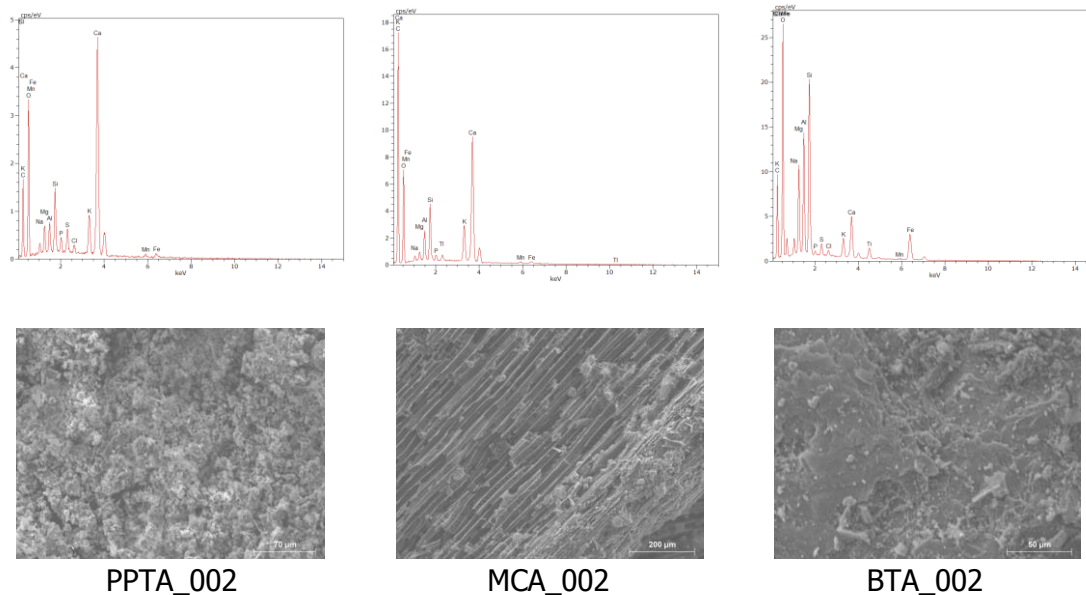
#### Ash characterization

The samples were analyzed as received for LOI (Figure 2) and SEM-EDX (Figure 3 and 4). LOI tests indicated that mineral content in the samples is between 64.3 and 83.4 %, with the bottom ash having the highest percentage. The organic carbon content varies from 5.0% to 29.5%.

SEM-EDX analysis provided some insights about the composition of each ash and its morphology. Fly ashes PPTA\_002 and PPTA\_007 differ in organic carbon content, 5.0% and 28.2% respectively (Figure 3) but both presented calcium in their composition (Figures 3 and 4). Fly ashes MCA\_003, MCA\_008, and GBA009 presented similar organic carbon content, 18.5, 29.6 and 17.1 %, and composition, Al, Si, Na, K and Fe. Moreover, it is possible to observe that the carbon in these samples has the same morphology as biochar samples (Figure 5). Biochar is a carbon-rich solid material produced by thermal decomposition of sustainable sourced biomass in the presence of limited oxygen and at temperatures between 350 and 700°C, which is also called pyrolysis (Lehmann and Joseph, 2009). It has been shown that biochar has a relatively large specific surface area, highly porous structure, and stable carbon matrix, which makes it a high capacity adsorbent for nutrients as well as metals (Abdelhadi et al., 2017; Dehkhoda et al., 2016; Ding et al., 2016; Qian et al., 2016).

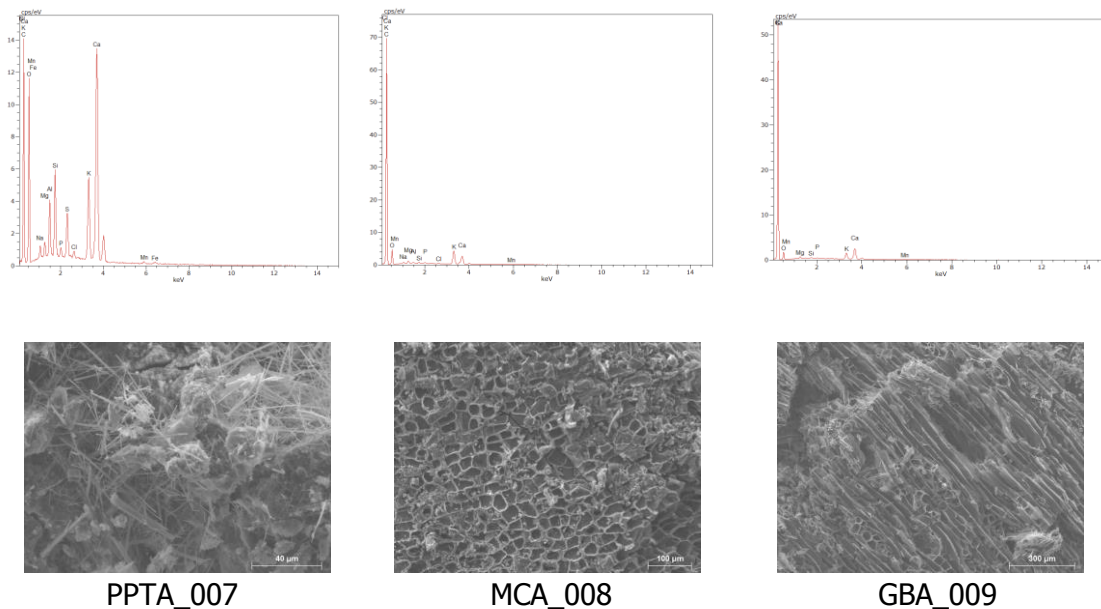


**Figure 2 – LOI analysis for the different ash samples as received (dry weight). Organic carbon content**

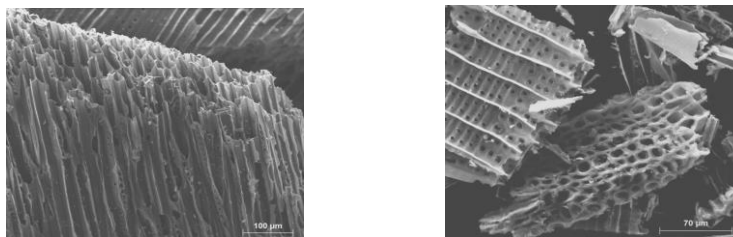


**Figure 3 – SEM-EDX analysis from wood-based fly and bottom ashes provided by pulp mill industry A**

One possible way to reuse the ash residues is to separate the char from the ash and use the char fraction for treating MIW by adsorbing metals such as selenium. Different methods are available to achieve char separation from the ash, such as float-sink, oil agglomeration and froth flotation (Hwang et al., 2008; Izquierdo and Rubio, 2008), but all are arduous processes, which can also interfere with char quality. For this reason, an attempt to separate char from the ash was done by size selection using sieves and a vibratory shaker.



**Figure 4 – SEM-EDX analysis from wood-based fly and bottom ashes provided by pulp mill industry B**

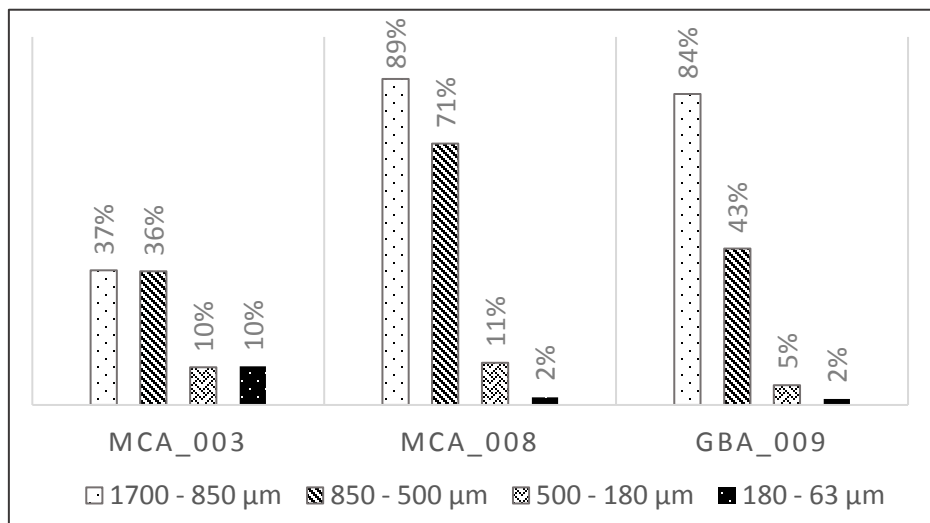


**Figure 5 - SEM image from regular (RB) and steam activated (STB) biochar**

#### Separating char from ash

The samples MCA\_003, MCA\_008 and GBA\_009 were sieved and divided into four different fractions so that the char could be separated from the ash. In order to evaluate if size selection did enrich certain fractions with char, each fraction was analyzed for LOI (Figure 6) and the results were compared to LOI values for the as-received ashes (Figure 2).

It is possible to observe that fractions with larger particles have higher organic content. There is a slight difference between the fraction 1700-850 and 850-500 for MCA\_008 and almost no difference was found in MCA\_003 among the same fractions. For MCA\_003 the sieving could be done from 1700-500  $\mu\text{m}$ . The organic content was twice as much in the fraction 1700-850 than 850-500 for GBA\_009. In all samples the fractions smaller than 500  $\mu\text{m}$  were low in organic content, between 11 – 2 %, and consisted mostly of just mineral matter. Comparing the results from before (Figure 2) and after (Figure 6) sieving, it is noticed an enrichment of the organic content, which is most likely char material. In conclusion, the sieving process can separate char from the ash due to the larger size of the char particles.

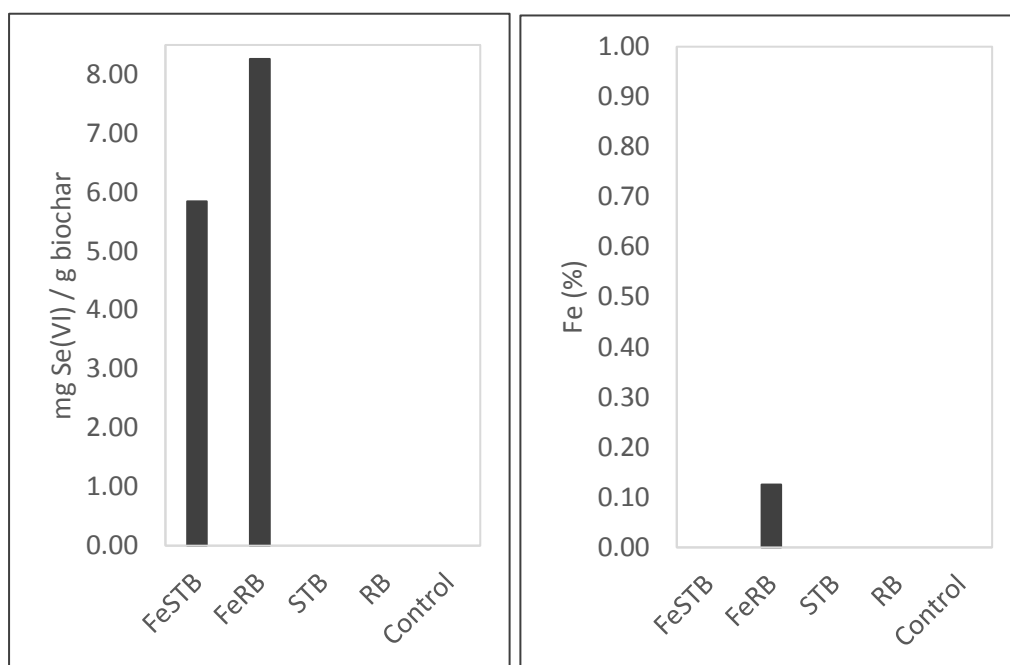


**Figure 6 - LOI results from different particle size fractions in 3 different fly ash samples**

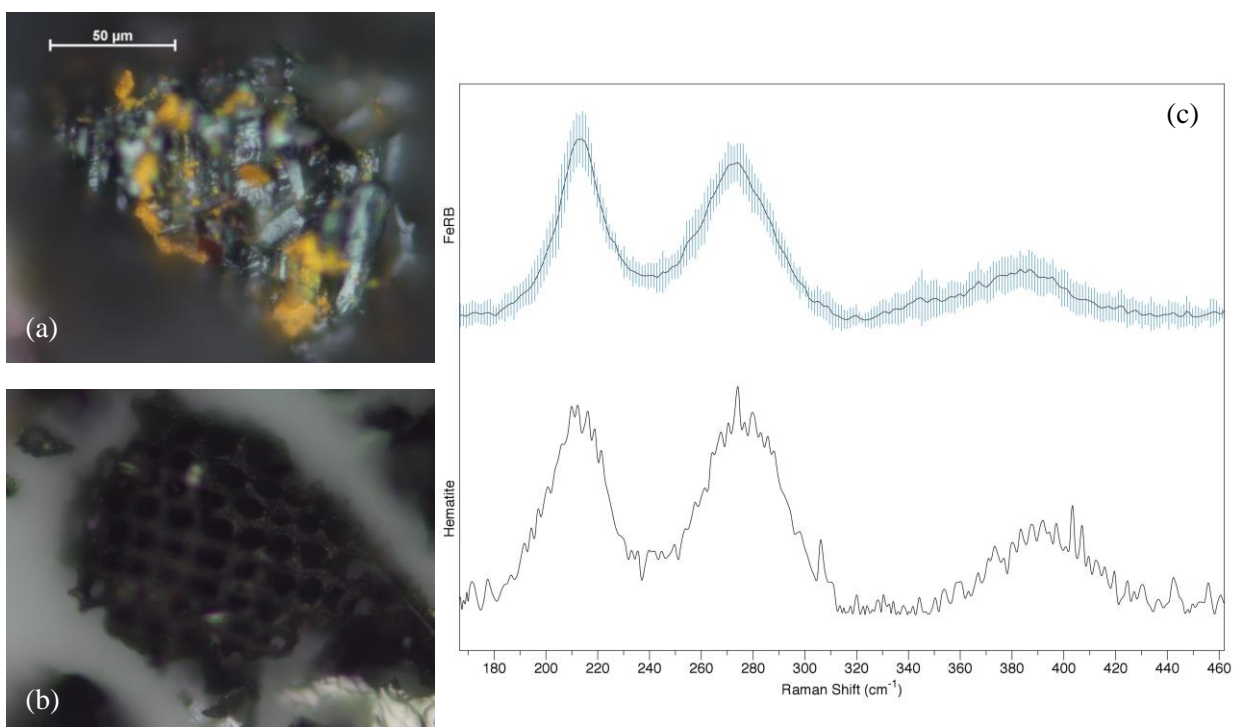
#### Selenium adsorption into biochar

Once separated from the ashes, there is the potential for the char portion to be used as an adsorbent and applied for metal removal (Ignácio et al., 2018) from MIW. The benefit of removing metals, potentially selectively with an adsorption process, is that this allows their value to be eventually recovered through recycling or reuse. Studies in the literature reported removal of selenium with Fe-impregnated granular activated carbon (Dobrowolski and Otto, 2013; Zhang et al., 2008). No studies reported Se removal through a similar process on biochar. For the purpose of testing the capacity of metal removal from water, wood-based regular biochar (RB) and steam activated biochar (STB) samples were tested. Both RB and STB were functionalized through Fe-impregnation (FeRB and FeSTB), and all the four materials were tested for Se (VI) removal from water (Figure 7).

As seen in the Figure 7, selenium was not removed when RB or STB were used. On the other hand, Fe-impregnated biochar, FeRB and FeSTB, removed 59.7 and 84.3%, respectively, which corresponds to adsorption capacities of 5.85 and 8.26mg of selenium per each gram of impregnated biochar. At the same time, none or less than 0.20% of the impregnated iron was leached during the selenium adsorption, in the case of FeRB sample. There is some evidence that during the Fe-impregnation, hematite ( $\text{Fe}_2\text{O}_3$ ) is formed in the surface of the biochar (Dobrowolski and Otto, 2013). Indeed, Raman analysis confirmed the presence of hematite in our Fe impregnated samples. Raman spectra of a hematite standard (RRUFF Database, 2019) and from yellow precipitates on our FeRB (Figure 8a) have a similar profile, with the main peaks existing at 213 and 274 Raman shift ( $\text{cm}^{-1}$ ). We postulate that one possible mechanism for removal of Se from solution seen in our experiments was the interaction of hematite and selenium through complexation on the surface of the biochar (Rovira et al., 2008).



**Figure 7 – Absorption capacity of Se(VI) in biochar (7a). Iron leaching during Se (VI) adsorption (7b)**



**Figure 8 – FeRB (8a) and RB (8b) image in microscope. (8c) Raman spectra from precipitates on the surface of FeRB and hematite (RRUFF Database, 2019)**



## CONCLUSION

Ash residues from pulp mills that presently have no use and end up in landfills can be repurposed and used for metal recovery from MIW. The char found in these residues can be easily separated by a simple sieving method followed by a straightforward Fe-impregnation method, which can functionalize the char for the removal of selenium in MIW. The mechanism of removal is still under investigation and the impregnation method should still be optimized, and the adsorbent tested for environmental relevant selenium concentrations.

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