Community Scale Development of Manure Based Biochars for the Removal of Copper and Lead from Drinking Waters in Developing Countries

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***Abstract*—In many Bolivian Andes region alpaca farming communities, unregulated mining practices render surface water sources unusable due to toxic levels of heavy metal contamination. Biochar, a viable treatment option, is difficult to create due to lack of resources. Manure-based (MB) biochar was created through oxygen-limited pyrolyzation of alpaca feces for use as a water filtration media for the removal of stream level concentrations of lead (Pb) and copper (Cu). Contaminated water was introduced to varying amounts of the MB biochar for 1-hour to 4-hour periods. Biochar quantities between 0.5 and 8 g/L removed 98.9% and 99.6% of Copper (Cu) and Lead (Pb) concentrations of 8,400 ppb and 2,200 ppb, respectively. Final concentrations of 96 ppb for Cu and 9 ppb for Pb were recorded, which are 93% and 40% lower than EPA recommended national primary drinking water standards of 1,300 ppb and 15 ppb for Cu and Pb, respectively.**

Keywords—Biochar, Filtration, Pyrolysis, Alpaca Manure, Water Treatment, Adsorption

1. INTRODUCTION

Many communities in developing countries struggle daily with potable water and sanitation issues. Specifically, in the mountainous mining communities of rural Bolivia, vital organ bioaccumulation of heavy metals from drinking contaminated water is a serious problem. Also, concerns in the region regarding climate change, agricultural productivity, control of organic pollutants and reduction of heavy metal contamination within the environment prompted interest in the versatility and sustainability of biochars and their potential uses in localized remediation. Biochar feedstocks range from agricultural residues to manure and are typically produced using one of a multitude of thermochemical processes such as conventional carbonization, fast pyrolysis, slow pyrolysis, flash carbonization or gasification [1]. The result is a fine grained, porous substance with surface areas ranging from 253 to 548 m^2 g^{-1}, and similar in appearance to charcoal. Much like activated carbon, biochar is a carbonaceous residue with a strong sorption affinity for both organic (hydrocarbons) and inorganic (heavy metals) compounds. The significant difference being that biochar is less expensive and requires much less energy to produce [2]. The use of biochar for environmental remediation has recently produced a number of studies, including studies involving the use of biochar as a means of mitigating global warming [3]. Studies have also been conducted that involve the use of biochar as a strategy to manage soil health, increase agricultural productivity, and eliminate toxic heavy metals from industrial wastewaters [4-9].

Biochar innovations for the removal of heavy metals and organics from wastewater are rapidly gaining ground due to the versatility of biochars for multi-contaminant removal as well as the cost-effective nature of using biochar rather than more costly sorbents [4, 8, 10-13]. Heavy metal contaminated waters are mainly introduced into the environment through point sources such as discharges from metal plating, mining or battery development industries. Most metals introduced are carcinogenic in nature and therefore, have very strict maximum contaminant level goals associated with their occurrence in natural waters [5, 8]. Traditional water treatment technologies (precipitation, ion exchange, membrane filtration, etc.) are effective, but cost prohibitive. Experiments conducted using biochar created from anaerobically digested biomass for the removal of lead, copper, cadmium, and nickel produced results of greater than 97% removal of all contaminants using a digested whole sugar beet biochar, while a digested dairy waste biochar produced results of 99%, 98%, 57% and 26% respectively [4].

Of very recent interest is the development of manure-based (MB) biochars [2, 7, 9, 10,13]. Since manure is in such an abundant supply and can be labeled as a sustainable resource, research is beginning to surface on the use of MB biochars in environmental remediation. Specifically, research has been conducted on the conversion of animal wastes such as poultry and dairy manure to biochars for the purposes of heavy metal adsorption (Pb, Cu, Zn, and Cd) from aqueous samples [13]. Research has also been conducted on the use of manure-based (MB) biochars for the removal of organics such as PAHs, atrazine, pesticides (DDT), herbicides, dyes and non-aqueous phase liquids such as naphthalene and 1,3 – dinitrobenzene. All of the above experiments have provided favorable removal (i.e. - 77% - 100%) of organics and heavy metals from aqueous solutions [2, 10], however, most if not all of the experiments conducted thus far focus strictly on removal of these contaminants from aqueous wastewater streams. Very little work has been conducted on the use of MB biochars for the treatment of drinking water. This concept has the potential to revolutionize the sustainability of drinking water in developing countries and provide a preferential option for remote or disadvantaged populations struggling with sickness from water contamination issues. By using an abundant resource like MB biochars to clean water for the purposes of drinking, we are embracing the concept of sustainability.

2. THEORY

This work focuses specifically on the community of Pampoyo, Bolivia. The region has a very active mining component as a source of local income, and mine tailings waste streams are contaminating local water sources. Health survey data accumulated since 2011 suggests that many members of the community suffer or have died from liver and spleen issues associated with the bioaccumulation of metals from drinking the contaminated water. Completely safe sources are difficult to find in the region, and most sources are likely to be contaminated by the mining activity in the region. This is not an uncommon occurrence in many high elevation regions of south and central America. In fact, many mountainous mining regions suffer from contaminated drinking water sources [14, 15]. Activated carbon is known for its ability to remove heavy metals from drinking water, however, activated carbon is expensive to create, and is simply not sustainable in most developing communities. A more likely option is the use of biochars, a sustainable, easy to create form of carbon, capable of removing both heavy metals and organics from aqueous solutions. For these regions, the difficulty rests in the ability to find a sustainable organic material in ample supply to convert into biochar.

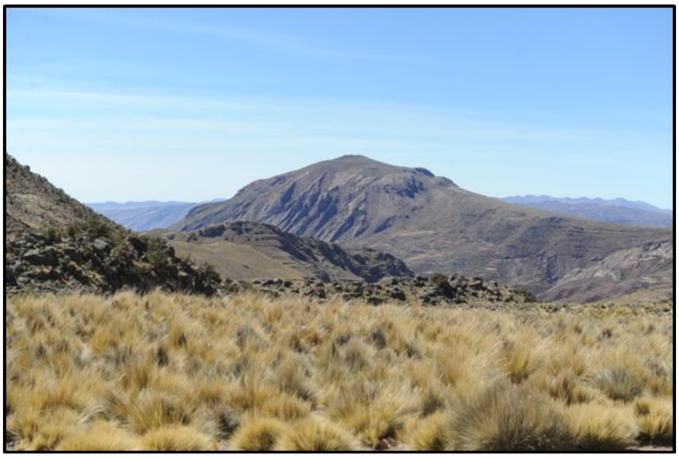


Figure 1.Pampoyo, Bolivia region, elevation ~14,000 feet. Arid conditions make typical biochars unsustainable.

In the mountainous regions of Bolivia as well as many low oxygen, high desert locations, woody organic material is at a premium, and using it to create carbon is far from sustainable (Figure 1). Other than mining as a means of support, local indigenous residents turn to farming of root vegetables such as potatoes, onions and carrots and the breeding of llama, alpacas, or other members of the camelidae family of animals (camels, alpacas, llama and vicugnas). Llama and alpacas, however, are the primary variety and are typically bred for many reasons, to include land cultivation, sustenance and use of fur for yarn and clothing. Llama and alpacas tend to feed on a diet of "brave grass", a type of hard, prickly grass as well as other plant material located in the high desert region. Consequently, their manure is composed of a significant amount of carbonaceous organic material, making it ideal for conversion to biochar. In these high desert regions, llama or alpaca manure is the most sustainable form of organic material for two reasons: (1) it is abundant in supply, and (2) that supply is constant and stable. Of great importance as well is that utilizing MB biochar in these regions does not swap one resource for another. Community members currently do not use llama or alpaca manure for soil fertilization because it has not been shown to improve crop growth in this region.

This research focuses on the development and use of camelidae MB biochars for the removal of stream level concentrations of copper (Cu) and lead (Pb). These metals are known to cause nervous system disorders, as well as inhibit the transport of necessary minerals causing permanent damage to vital systems of the human body [16-19]. Experimental concentrations were chosen based on typical stream level concentrations noted from source water collection locations within the Pampoyo region. Concentrations of Cu and Pb ranged from 8,400 ppb to 2,200 ppb, respectively. Future testing and research of camelidae MB biochars will provide for optimization of the biochar for 100% removal of Pb and substantial adsorption of other heavy metals noted at source water locations within the region (i.e. - cadmium, zinc, chromium). Further testing and research of camelidae MB biochars will include equilibrium and kinetic studies [20, 21] and biochar optimization through the development of field applicable thermochemical conversion devices and community or household scale filtration devices. Community education and implementation scheduling will also be addressed in future research campaigns. Through this research, the use of MB biochar for localized treatment of drinking water will substantially benefit resource poor locations.

3. METHODS

3.1 Preparation of the biochar

Biochar samples were developed through controlled pyrolysis of alpaca manure. Raw samples (1 kg), were placed in an oxygen free, stainless steel vessel. The vessel was then placed in a DT-31-THA-AE-12 Top Hat Atmosphere Envelope Furnace (AEF)with a temperature ramp of 10°C/min until temperatures reached a sustained 350°C for three hours. Prior research has shown that temperatures ranging from 300°C to 600°C provide the best levels of biochar yield [10, 22, 23]. The temperature limit of 350°C was determined as the best temperature for field reproducibility in developing regions [24].

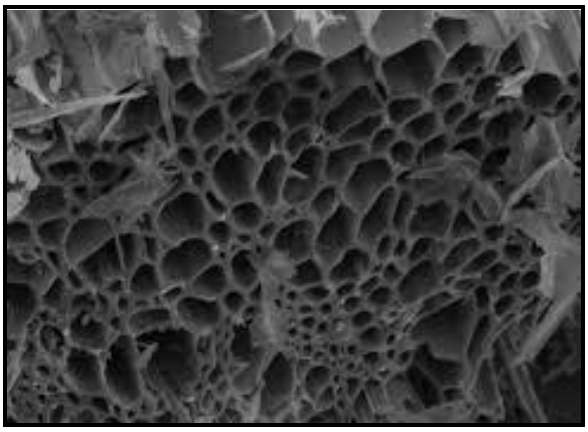
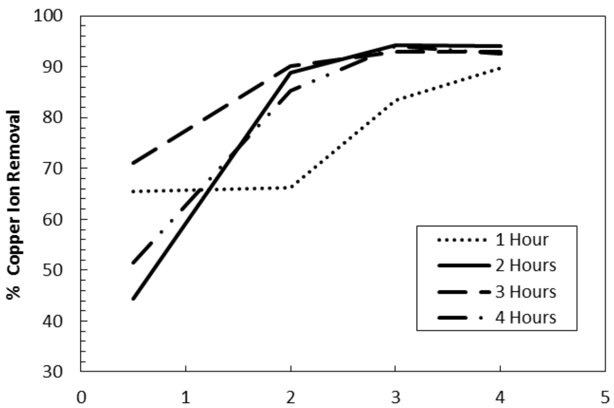


Figure 2. Post conversion 2000x magnification of camelidae MB biochars created in the AEF.

Once cooled, biochar samples were double rinsed with deionized water and dried at 105°C. Biochar was ground into powder form prior to execution of experimental procedures to increase surface area exposure. Physicochemical analyses were conducted to determine biochar composition. Carbon, Hydrogen, Nitrogen and Sulfur content was determined using the LECO CHN 628 elemental analyzer both pre- and post-pyrolysis. Calorimeter analysis was found using the LECO AC-600 and moisture content using the oven-dry method. Moisture content was determined to be 68% for raw manure and cooking undried manure produced the most effectively porous biochar (Figure 2).

3.2 Biochar Testing Procedures

Cupric Chloride (CuCl2) and Lead Nitrate (Pb(NO3)2) stock solutions were developed for dilution in accordance with EPA method 200.8. Stock solutions were diluted to 8,400 ppb and 2,200 ppb for Copper and Lead, respectively. Concentrations of test solutions were chosen based on concentrations obtained from source water collection locations in the Pampoyo region 6b. Research conducted in South American mining communities suggests that high altitude region heavy metal concentrations of Cu and Pb from mining waste range from 600-2,880 ppb to 217-2,290 ppb for Cu and Pb, respectively 6a.



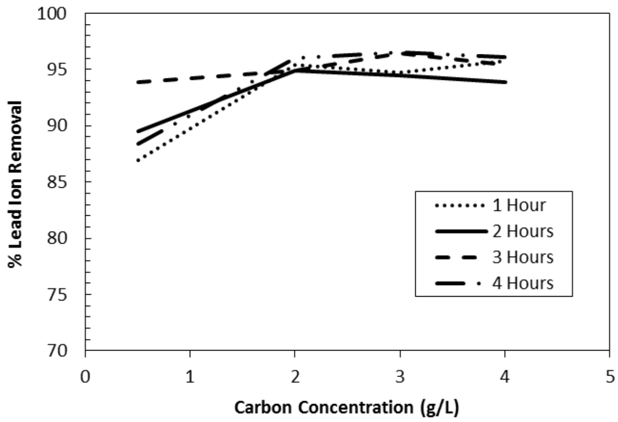


Figure 3. Preliminary carbon effectiveness testing using the Hach DR 5000 with Cu and Pb TNT kits

Adsorption experiments were conducted in 100 mL reagent bottles containing 50 mL of 8800 ppb Cu or 2400 pbb Pb and dilutions, respectively. Initial MB biochar dose concentrations ranged from 1 to 4 g/L. After the addition of MB biochar to the contaminated solutions, reagent bottles were placed on a mechanical shaker for 1 to 4 hours. Following agitation, solutions were filtered through a 0.45 µm glass fiber filter. Using a Hach DR 5000 spectrophotometer, preliminary experiments were conducted to assess the effectiveness of the camelidae MB biochar prior to launching a full testing campaign. Cu and Pb removal was assessed at 1 to 4-hour carbon agitation periods (Figure 3). Preliminary results show that a 2 to 4 g/L biochar concentration and a contact time of 1-hr was sufficient to remove >95% of Pb in most cases. Cu adsorption did not occur as quickly with maximum adsorption levels of >93% occurring with 3 to 4 g/L of biochar for 2 to 3-hr contact times. In all cases, a 2-hr contact time achieved sufficient results and was therefore used as the optimal contact time for all subsequent testing. 2-hr contact time testing was conducted using an iCAP 6500 ICP spectrophotometer. All tests were conducted in triplicate and averaged. MB Biochar concentrations in all 2-hr tests varied from 1 to 8 g/L.

4. RESULTS AND DISCUSSION

Table 1. Pre-Conversion Physicochemical Properties of Camelidae Manure-Based Biochars

	Alpaca Manure	StDev
Energy (btu/lb)	7002.4	72.4
%C	40	0.39
%H	5.27	0.178
%N	1.94	0.03
%S	0.344	0.0062
Moisture ct (w%)	68.3	0.97

Table 1 provides physicochemical data for the camelidae manure used for conversion. Data is presented on the MB biochar prior to thermochemical conversion. Energy content of the camelidae manure is similar to energy contents found in many manure based biomass species. Most importantly, we can see that prior to conversion, the carbon content of the manure is relatively high (40%) with minimal amounts of nitrogen and sulfur (1.94 and 0.344%, respectively). Low-oxygen conversion of the manure was conducted during pyrolysis in an effort to reconstruct field level scenarios likely experienced in the remote Andes region. Pyrolysis enhancement has been shown to greatly improve post conversion carbon content [4, 9, 11,13]; however, this research focuses on the conversion of alpaca manure using materials readily available in resource poor regions. For similar reasons, pH was not adjusted to determine its effect on the sorption of Cu and Pb [25] since pH adjustment would not be feasible in a field scenario.

Table 2 presents equilibrium concentrations of Cu and Pb following addition of MB biochar and 2-hr agitation cycles with MB Biochar concentrations ranging from 1 to 8 g/L. Agitation cycles showed varying results, likely due to variability in available sorptive capacity from the inconsistencies associated with the modified pyrolysis method used in this research. MB biochar concentrations of ≥1 g/l for Cu and 8 g/l for Pb provided the best results with final equilibrium concentrations ranging from 96 to 559 ppb and 9 to 30 ppb for Cu and Pb, respectively (Table 2).

Table 2. Pb and Cu initial and equilibrium concentrations (ppb) and removal (%) following agitation with MB biochar

Initial Concentration (ppb)	
Cu	8800
Pb	2400

	Cu		**Pb**	
Carbon (gm/L)	**Final Concentration (ppb)**	**Removal (%)**	**Final Concentration (ppb)**	**Removal (%)**
1	540.88	93.85	10.10	99.58
2	218.03	97.52	29.69	98.76
3	113.01	98.72	22.89	99.05
4	136.82	98.45	29.48	98.77
5	148.51	98.31	32.34	98.65
6	119.80	98.64	22.94	99.04
7	108.20	98.77	16.44	99.32
8	96.01	98.91	8.85	99.63

These final concentrations prove the effectiveness of a modestly developed MB biochar and show that drinking water quality heavy metal MCLs can be achieved with minimal contact time (≤ 2-hr). Removal efficiencies ranged from 93.6-99.8% for Cu and 98.7-99.6% for Pb with initial concentrations of 8,400 ppb and 2,200 ppb, respectively (Figure 4). Final concentrations of 96 ppb for Cu and 9 ppb for Pb are 93% and 40% lower than EPA recommended national primary drinking water standards of 1,300 ppb for Cu and 15 ppb for Pb. These results provide a preferential option for resource poor communities such as Pampoyo, Bolivia through the conversion of manure to a usable and effective filtration media.

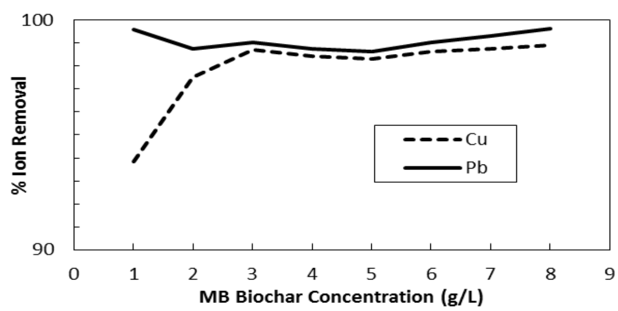


Figure 4.MB biochar dose (1 to 8 g/L) vs. % removal (Pb and Cu) for 2-hr agitation cycle

5. CONCLUSION

Results clearly show that using modestly developed camelidae MB biochars, we can achieve removal of >8,700 ppb of Cu and >2,390 ppb of Pb with <2-hr contact time from heavily contaminated water samples. MB biochar removal of Cu and Pb in resource poor settings is a good option provided additional testing is completed to achieve near 100% removal of Pb. Cu and Pb solution concentrations modeled those found in source water collection points around the Pampoyo region and MB biochars were created

with field level reproducibility in mind for future sustainability in developing regions.

ACKNOWLEDGMENT *(Heading 5)*

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