

## NM WRI Student Water Research Grant Progress Report

### Final Report

1. **Student Researcher:** Hengameh Bayat

**Faculty Advisor:** Dr. Catherine E. Brewer

2. **Project title:** Wastewater Treatment Using Food Waste Char Obtained from Hydrothermal Liquefaction as a Low-Cost Adsorbent Material

3. **Description of the research problem and research objectives?**

The presence of heavy metals in water poses a serious threat to human health and the environment (Furness, 2017). Rapid global industrialization and urbanization have led to surface and ground water contaminated with heavy metals from wastewater discharge of metallurgical, petrochemical, plumbing, mining, chemical, and battery manufacturing (Kobyas, Demirbas, Senturk, & Ince, 2005). Varieties of human disorders and diseases are caused by ingestion of heavy metals; therefore, the removal of heavy metals is a critical step in water treatment and remediation. The treatment methods reported in the recent literature are adsorption, membrane filtration, chemical precipitation, electrostatic interaction, ion exchange, and coagulation (Fu & Wang, 2011; Uddin, 2017; Wan et al., 2018). Among these methods, adsorption using carbonaceous materials has gained attention as one of the most cost-effective and efficient methods. Use of many commercial activated carbons is limited by the expensive carbon production processes.

There have been numerous attempts to use different types of low-cost adsorbents derived from lignocellulosic biomass, microalgae, dairy manure, and sewage sludge (Arun, Varshini, Prithvinath, Priyadarshini, & Gopinath, 2018; Audu et al., 2019; Liu, Zhang, & Wu, 2010; H. Lu et al., 2012). Thermochemical conversion processes, such as pyrolysis, gasification, and liquefaction, are promising for conversion of biomass into fuels and value-added products, including low-cost carbon adsorbents. Pyrolysis is an oxygen-free process that can convert a variety of feedstocks into bio-oil, non-condensable gases, and biochar (Cheng, Bayat, Jena, & Brewer, 2020). Most volatile compounds in the biomass are volatilized during pyrolysis process, resulting in biochars with high porosity and surface area that are good for adsorption, but also with reduced polar functional groups that are important for ion exchange capacity. Hydrothermal liquefaction (HTL) uses hot (250-375°C) compressed water to convert waste materials into energy-dense bio-crude oil, non-condensable gases, an aqueous phase, and HTL-char. The presence of cellulose and lignin in feedstocks promotes HTL-char formation (Cheng, Dehghanizadeh, et al., 2020). In order to increase the economic viability of bio-crude oil production through HTL, value-added uses of the co-products (HTL-char and aqueous phase) are needed. Recent studies showed that, compared with other carbonaceous materials such as activated carbon and biochar, HTL-char has some advantages such as higher yield at lower process temperatures, lower energy consumption in processing, and lower ash content (Fang,

Zhan, Ok, & Gao, 2018). Pyrolysis biochar and HTL-char differ widely in their physical-chemical properties (Bargmann, Rillig, Buss, Kruse, & Kuecke, 2013) with HTL-char usually having lower surface area and porosity while retaining oxygen-containing functional groups on its surface. Therefore, HTL-char may provide considerably higher adsorption capability for certain adsorbates, making it a potential adsorbent in wastewater treatment (Kambo & Dutta, 2015).

There are numerous studies regarding HTL-char as an adsorbent for removal of organic pollutants, such as methylene blue (Islam, Ahmed, Khanday, Asif, & Hameed, 2017), cationic dyes (Parshetti, Chowdhury, & Balasubramanian, 2014), and certain pharmaceuticals (Fernandez, Ledesma, Román, Bonelli, & Cukierman, 2015). Regmi et al. showed that HTL-char derived from switchgrass has better performance than pyrolysis biochar for Cu(II) and Cd(II) adsorption because of its abundant oxygen-containing functional groups (Regmi et al., 2012). HTL-char was also tested for adsorption of lead (Liu & Zhang, 2009), uranium (Kumar, Loganathan, Gupta, & Barnett, 2011), and copper (Liu & Zhang, 2011).

Use of food waste as a feedstock for biofuel production and resource recovery using an HTL process would not only reduce the feedstock cost challenges, but may also help in solving environmental problems, water scarcity, and reliance on fossil fuels. To the best of our knowledge, there is limited information on heavy metal adsorption using HTL-char produced from the organic fraction of food waste. The aim of this research is generally to evaluate the conversion of food waste into HTL-char for use as an adsorbent material for the removal of lead and copper from wastewater

- **Research Objectives**

The overarching objectives of this work are as follows:

- 1- Generate HTL-char at different HTL conditions and characterize them fully by laboratory methods.
- 2- Evaluation of the effect of appropriate pretreatment step on the surface properties and adsorption performance.
- 3- Evaluation of heavy metal (Pb and Cu) adsorption using HTL-char as a carbonaceous material in the treatment of metal-contaminated water.

#### **4. Description of employed methodology.**

- **Food waste collection**

Food waste was collected from New Mexico State University's Taos Restaurant dining hall. The organic fraction of the food waste was mixed with deionized water using a blender to create a slurry and then was frozen at -20 °C prior to conversion experiments.

- **HTL-char production**

All HTL experiments were conducted in a stainless steel 100 ml Parr batch reactor Model 4572. For each experiment, the reactor was loaded with 40 ml of food waste slurry (15 wt.% solids loading) and heated to the desired temperature (240 °C, 265°C, 295°C) and for the target residence time (0, 30, 60 minutes). Once the reaction was done, the gaseous, solid, and liquid

products were separated following the procedure described (Bayat et al., 2019). HTL-char was separated from the mixture using filtration and dried for 48 hr at 60°C. Figure 1 shows the HTL and product separation process for using food waste to produce bio-crude oil and HTL-char. Food waste HTL was performed in duplicate and ensuring measured yields agreed to within ± 3%. Yields (wt. %) of HTL-char and biocrude-oil were calculated as (Eq.1):

$$Yield \text{ (wt. \%)} = \frac{m_{product}}{m_{feedstock,db}} \times 100\% \quad (1)$$

where  $m_{product}$  and  $m_{feedstock,db}$  are the weights of the products and initial feedstock, respectively, on a dry basis.

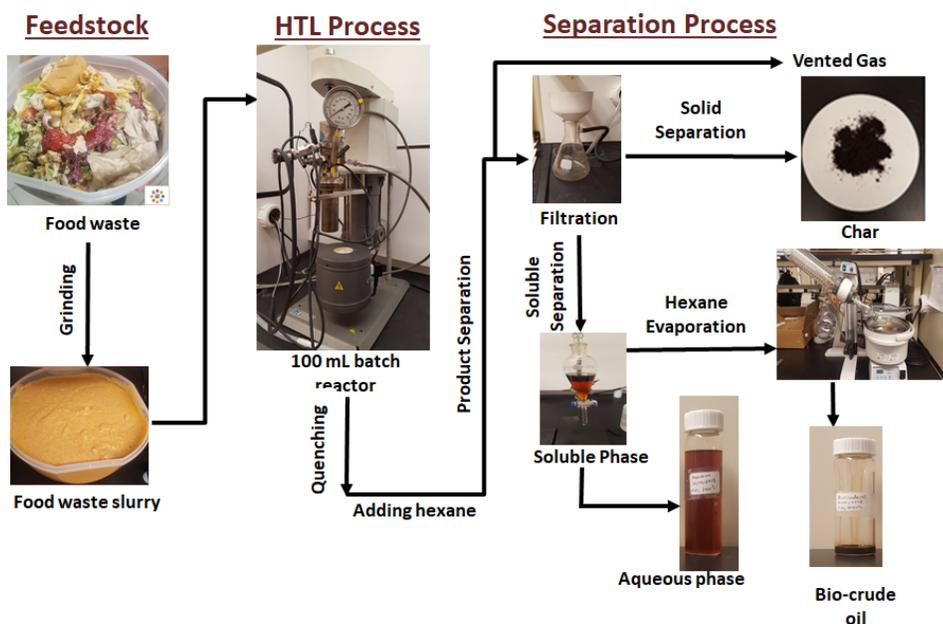


Figure 1. Food waste HTL experimental procedures

To generate sufficient HTL-char for treatment and adsorption experiments, a larger reactor (1.8 L Model 4572, Parr Instrument Co., Moline, IL) was used with 500 mL of food waste slurry at 240°C, 15% solids loading, and 30 min reaction time. The separation process was the same.

- **HTL-char characterization**

CHNS elemental content of the dry feedstock and HTL-char were measured using a Series II 2400 elemental analyzer (Perkin Elmer, Waltham, MA). Oxygen content was estimated by difference. Lead and copper concentrations in the solutions before and after adsorption were quantified using an Optima 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Waltham, MA). Surface area and pore size distribution of the HTL-chars were measured by nitrogen adsorption and desorption isotherms at 273 K on an ASAP 2050 analyzer (Micromeritics) over a relative pressure range of  $10^{-5} \leq P/P_0 \leq 0.99$ . Total surface area and average pore size were calculated using Brunauer-Emmett-Teller (BET) and Barrett–

Joyner–Halenda (BJH) analyses, respectively. Chemical functional groups on the HTL-char surface were characterized by Fourier transform infrared spectroscopy (FT-IR) using a Spectrum Two spectrophotometer (PerkinElmer, MA, USA) equipped with a crystal reflectance cell. The point of zero charge for the HTL-chars was obtained using the method in (Foo & Hameed, 2012). Briefly, the pH of lead or copper solutions (80 mg/L) was adjusted to values between pH = 2 and pH = 10 using 0.1 M nitric acid and 0.1 M potassium hydroxide. HTL-char (0.05 g) was added and the final pH of the solution was measured after 24 hr. using a pH meter (EcoScan, EUTECH Instruments, Singapore).  $pH_{pzc}$  was defined as the pH where  $pH_{final} = pH_{initial}$ .

- **Pretreatment and adsorption processes**

The solid residue after filtration was an asphalt-like sticky black residue, containing char and heavy bio-crude oil. Approximately half of the solid residue sample was Soxhlet-extracted with acetone (175 ml at 56 °C) to remove the heavy bio-crude oil until the acetone dripping from the thimble became clear. After extraction, HTL-char was dried for 48 hr at 60 °C.

As the adsorption performance of the HTL-char was expected to be very limited due to its low surface area, pretreatment using carbon dioxide (CO<sub>2</sub>) activation method was used to increase the surface area. HTL-char (1 g) was placed in a quartz boat in a horizontal tube furnace and heated to 700°C at a rate of 5°C/min under nitrogen. Once the furnace temperature reached the desired temperature, the nitrogen gas was replaced with CO<sub>2</sub> at a flow rate of 30 cm<sup>3</sup>/min for 20-45 minutes. At the completion of the reaction, the activated HTL-char was allowed to cool under nitrogen.

Prior to adsorption experiments, all prepared HTL-char samples were dried at 105 °C for 24 h in an oven and stored in a desiccator. Adsorption experiments were carried out in 50 mL Pyrex beakers using 25 mL of solution and 0.05 g of adsorbent each (HTL-char, activated HTL-char, and a commercial activated carbon). The initial concentrations of lead and copper were 5, 10, 20, 40, 80, and 100 mg/L. Contact between the solutions and the adsorbents was at room temperature (~ 23°C) for 24 hr. The quantity of the copper and lead retained by the char was calculated using Equation (2). Moreover, the capacity of each adsorbent was calculated using Equation (3).

$$\% \text{ Adsorption rate} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

$$Q_t = \frac{(C_0 - C_t)V}{M} \quad (3)$$

where  $Q_t$  is the adsorption of metal onto char (mg/g),  $C_0$  is the initial concentration of metal (mg/L),  $C_t$  is the final concentration of metal after 24 hr (mg/L),  $V$  is the volume of solution (L) and  $M$  is the mass of the char in solution (g).

## 5. Description of results; include findings, conclusions, and recommendations for further research.

### Effect of HTL conditions

HTL reaction temperature and time both affected HTL-char yield (Figure 2). The highest yield (37.8 wt.%) was obtained at 245 °C and 0 min; the lowest yield (21.7 wt.%) was obtained at 295 °C and 60 min. At the highest temperature condition, no HTL-yield reduction was observed with increased residence time, similar to results described by (Shakya, Whelen, Adhikari, Mahadevan, & Neupane, 2015). This was attributed to the inorganic compounds in the HTL-char not being able to be converted into other HTL-products (Watson et al., 2020).

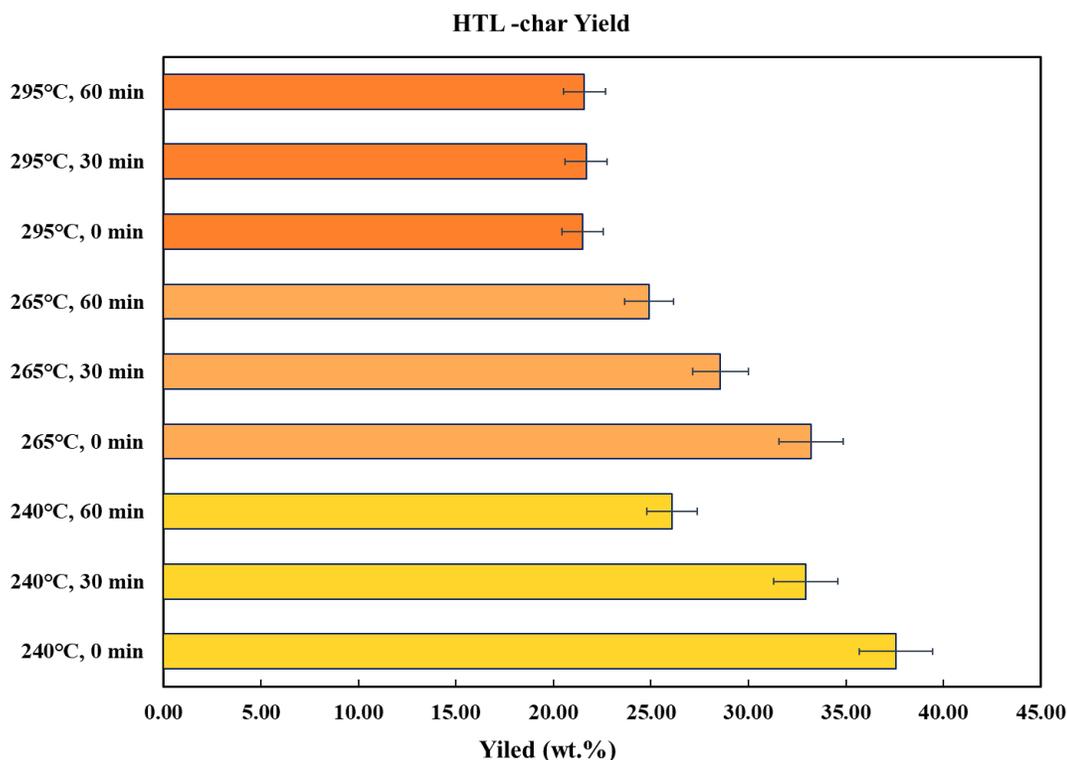


Figure 2. HTL-char yields as a function of HTL temperature and residence time

### HTL-char characterization

Elemental composition of food waste HTL-chars made at different operating conditions are shown in Table 1. As expected, the C content in HTL-chars was much higher, and the H and O contents were much lower, than in the food waste biomass. The higher H and O contents for HTL-char obtained at 240°C and 30 minutes implied the presence of carbon-oxygen complexes on the surface. Therefore, HTL-char from these conditions was selected for further surface morphology characterization and adsorption performance studies.

HTL-char characteristics from gas sorption analysis are summarized in Table 2. The results show that the BET surface area, Langmuir surface area, and total pore volume of activated HTL-char were greatly increased compared to HTL-char, implying the development of additional pores during CO<sub>2</sub> activation. These chars were classified as mesoporous materials according to

the International Union of Pure and Applied Chemistry (IUPAC) with average pore sizes (7.9 and 8.5 nm) between 2 and 50 nm.

**Table 1. Elemental analysis of food waste and HTL-char obtained at different operating conditions**

		C (%)	H (%)	N (%)	S (%)	O <sup>a</sup> (%)
Food waste		48.9	6.2	3.4	1.5	26.4
HTL-char (temperature (°C), time (min) and 15wt.%)	T=240, t=0	64.7	5.8	4.7	1.5	23.2
	T=265, t=0	68.4	6.3	4.2	1.6	19.5
	T=295, t=0	73.2	6.3	4.9	1.5	14.1
	T=240, t=30	68.9	6.6	4.4	1.6	18.5
	T=265, t=30	69.0	6.2	4.8	1.5	18.4
	T=295, t=30	73.4	6.3	5.0	1.5	13.8
	T=240, t=60	70.0	6.9	4.2	1.7	17.3
	T=265, t=60	72.8	6.3	5.3	1.6	13.9
T=295, t=60	74.4	6.5	5.0	1.7	12.4	

**Table 2. The results of surface area, pore size, and pore volume parameters of char samples from BET analysis**

	HTL- char	Activated HTL-char	Commercial activated carbon
BET surface area (m <sup>2</sup> /g)	10.1	54.5	776
Langmuir surface area (m <sup>2</sup> /g)	10.0	67.2	1148
Average pore size (d, nm)	7.9	8.6	11.8
Total pore volume (cm <sup>3</sup> /g)	0.02	0.06	0.01

FTIR spectra for the HTL-char, activated HTL-char, and commercial activated carbon are shown in Figure 3. Abundant peaks were observed in the HTL-char spectrum, whereas the spectra for the activated carbons were similarly lacking in any identifiable peaks. Peaks at 3000–2700 cm<sup>-1</sup> and 1690–1600 cm<sup>-1</sup> correspond to C-H and C=O stretching vibrations, respectively. C=O peaks indicate the presence of carboxyl groups on the adsorbent surface, which is expected to be positively correlated with adsorption of heavy metal ions (Deng et al., 2019).

As surface properties are important for biochar reactivity, SEM images for food waste, HTL-chars before and after activation are shown in Figure 4. Hydrolysis is the primary reaction for biomass during hydrothermal treatment; changes from hydrolysis can be seen between the food waste and HTL-char as structural degradation occurred and products were released into solution. The activated HTL-char shows more pore structures than the untreated HTL-char from the release of additional volatiles with CO<sub>2</sub> reactions with the carbon surface (Figure 4).

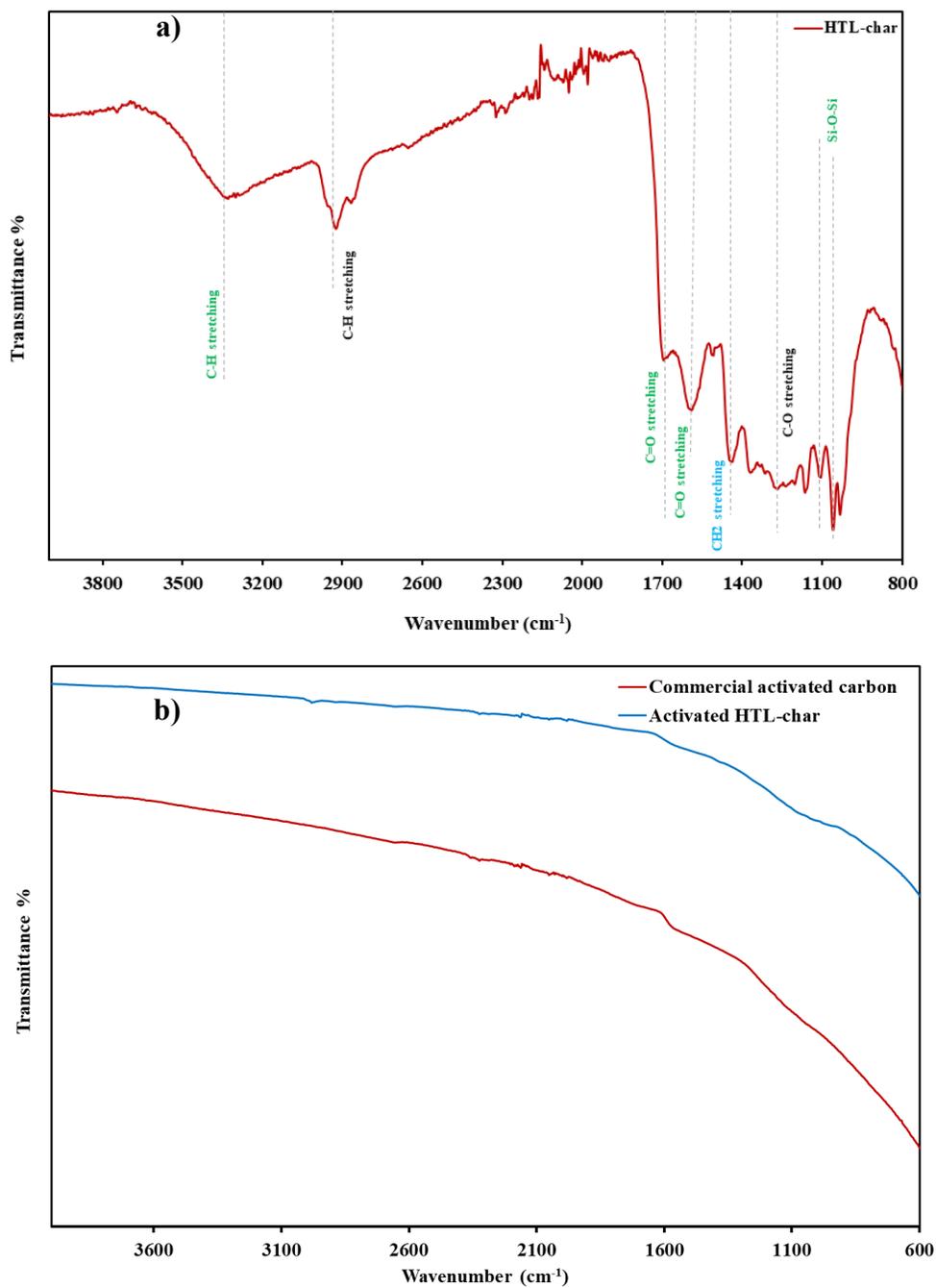
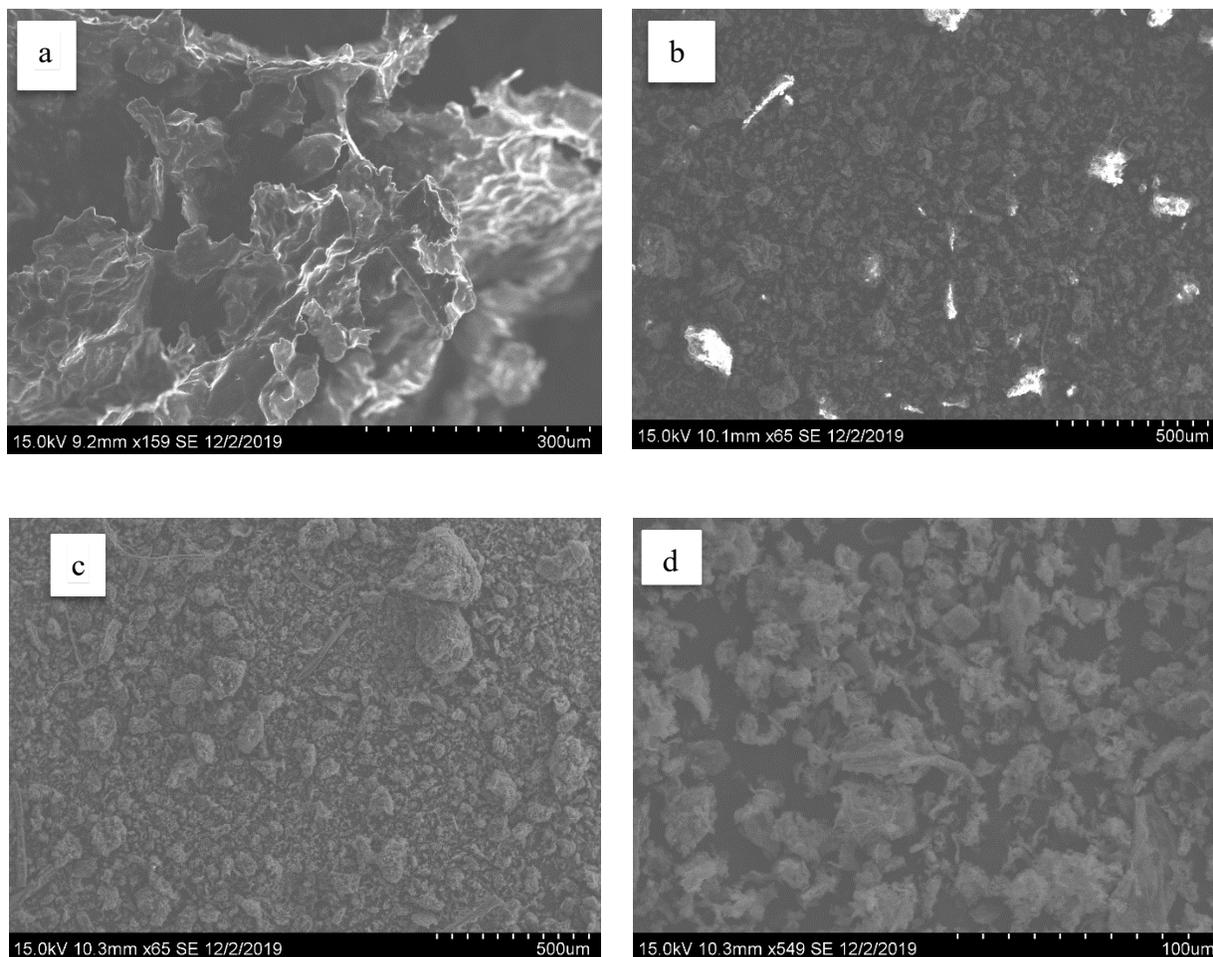


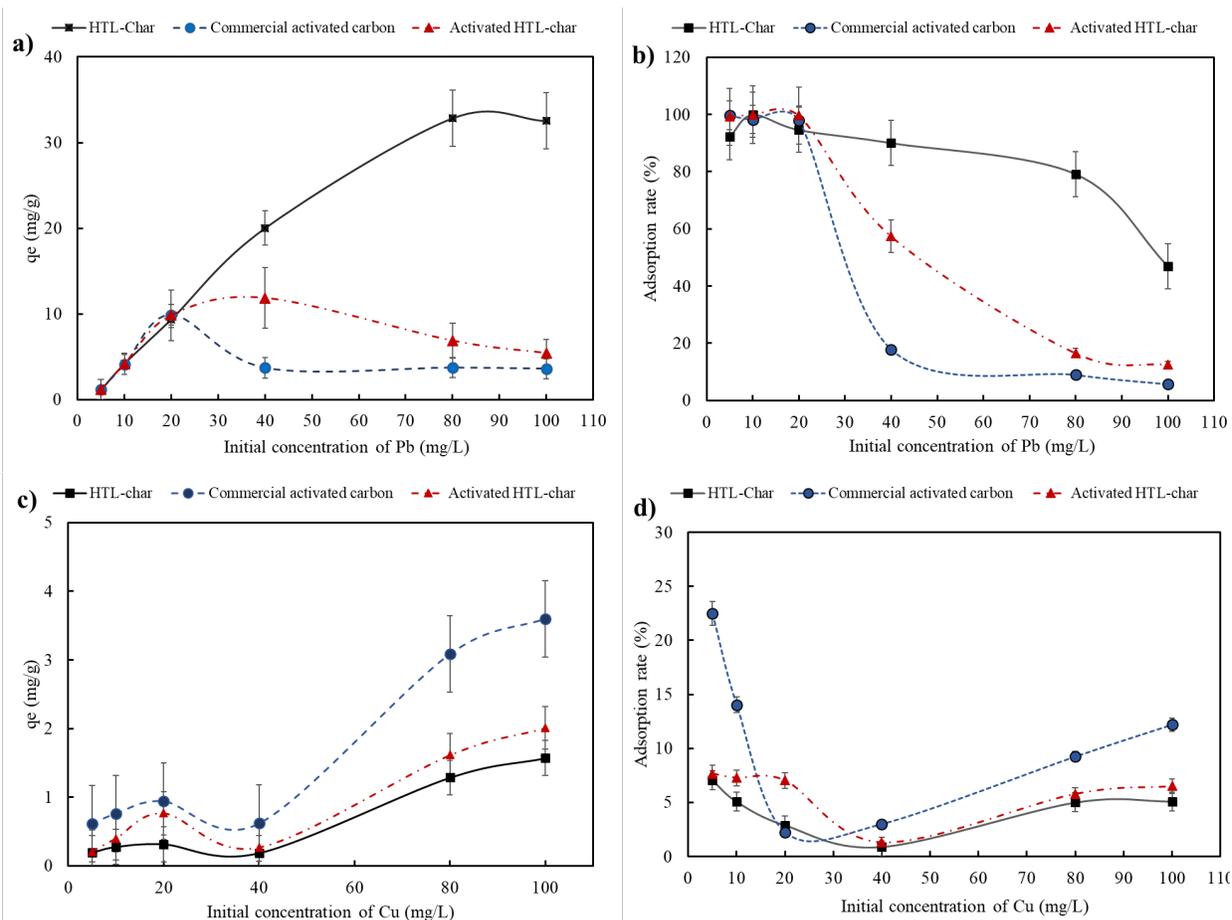
Figure 3. FTIR spectra of a) HTL-char b) activated HTL-char and commercial activated carbon



**Figure 4. SEM images of a) food waste, b) HTL-char, c) and d) activated HTL-char**

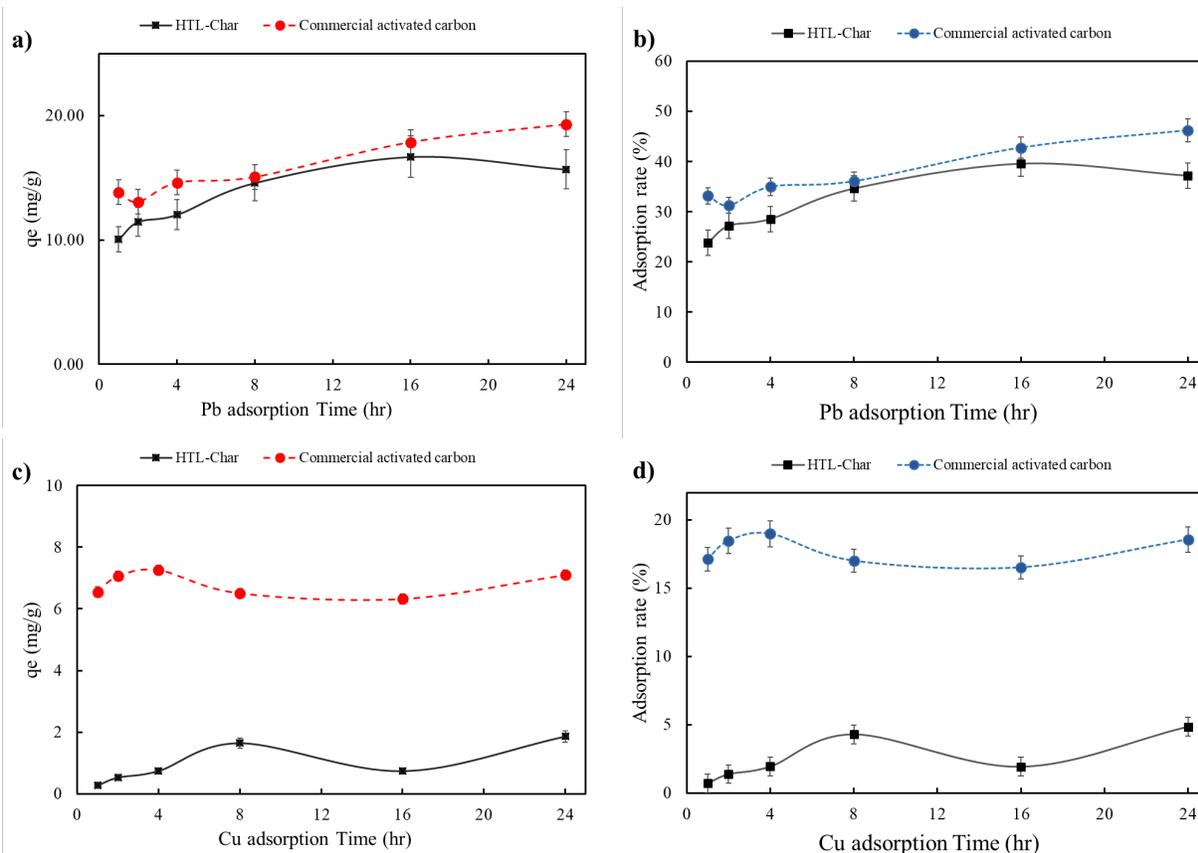
### **Adsorption studies**

Figure 5 shows the effects of initial concentration on lead and copper adsorption on HTL-char, activated HTL-char, and commercial activated carbon. In general, the adsorbents had higher capacity for lead than for copper. The increase in heavy metal adsorption capacity stems from the phenomena that an increase of adsorbate concentration leads to increase the mass transfer driving force between solution and surface to overcome transfer resistances (Liu & Zhang, 2009). At higher concentrations, a decrease in adsorption capacity typically represents saturation of adsorption sites. HTL-char had the highest Pb adsorption capacity ( $32.9 \text{ mg g}^{-1}$  at  $80 \text{ mg/L}$ ) even though it had the lowest BET surface area (Table 2). This suggests that  $\text{CO}_2$  activation does not significantly improve adsorption capacity of these carbonaceous materials for heavy metal adsorption. None of the three adsorbents showed substantial adsorption capacity or removal percentage for copper. Adsorption of charged ions with surface functional groups is highly pH dependent (L. Lu et al., 2020). Copper (II) adsorption increases considerably at higher pH due to the increased deprotonation of the functional groups and thus more coordination with copper (Liu & Zhang, 2011). In this study, the pH of the copper solution was very low ( $\text{pH} \approx 2$ ), explaining the low adsorption capacities observed.



**Figure 5. Effect of the initial concentration of Pb and Cu on the equilibrium adsorption capacity,  $Q_e$ , (a and c) and adsorption rate (% of initial metal adsorbed) (b & d). Cu  $pH_{initial} = 1.6$ , Pb  $pH_{initial} = 3.4$ , temp. = 25 °C, adsorption time = 24 hr, adsorbent dose = 2 mg/mL**

To gain an initial understanding of the adsorption kinetics, adsorption studies were conducted over multiple time periods ranging from 1 to 24 h. Figure 6 shows that the ratio of adsorption of heavy metals is approximately constant with time, meaning that the equilibrium was reached before 4 h. This result is consistent with the results obtained by (Al-Tohami, Ackacha, Belaid, & Hamaadi, 2013), who observed equilibrium between 2 and 4 h. The short time is attributed to the decrease in the number of active sites as adsorption occurs (Al-Anber, 2011).



**Figure 6. Effect of contact time of Pb and Cu on the equilibrium adsorption capacity,  $q_e$ , (a and c) and adsorption rate (% of initial metal adsorbed) (b & d). Cu  $pH_{initial} = 5$ , Pb  $pH_{initial} = 4.5$ , temp. = 25 °C, heavy metal concentration = 80 ppm, adsorbent dose = 2 mg/mL**

Assuming that the point of zero charge correlated with a turning point for adsorption performance, where the carbon's surface would be more negatively charged and more favorable for cation adsorption when  $pH > pH_{pzc}$ , adsorption on the HTL-char and the commercial activation would have been favored at 4.2 and 5.6 for lead, and 5.6 and 8.5 for copper, respectively (Figure 7). The HTL-char had lower  $pH_{pzc}$  than the commercial char, which leads to the more negatively charged surface, attributed to the more abundant oxygen-containing functional groups on the surface of HTL-char (Yao et al., 2011). Since the  $pH_{pzc}$  for the copper solutions were  $> 5.5$  for both adsorbents (Figure 7b), future copper adsorption experiments need to be conducted at higher pH values.

The effect of pH on lead and copper adsorption using HTL-char and commercial carbon was investigated over an initial pH range between 2 and 10 (Figure 8). Generally, there was a significant increase in the adsorption capacity and fraction adsorbed for both Cu and Pb, where the adsorption removal increased to 98% for both adsorbents. According to Al-Senani et al., metal adsorption increases due to an increase of  $H^+$  ions and more available exchangeable cations for metal binding capacity (Al-Senani & Al-Fawzan, 2018).

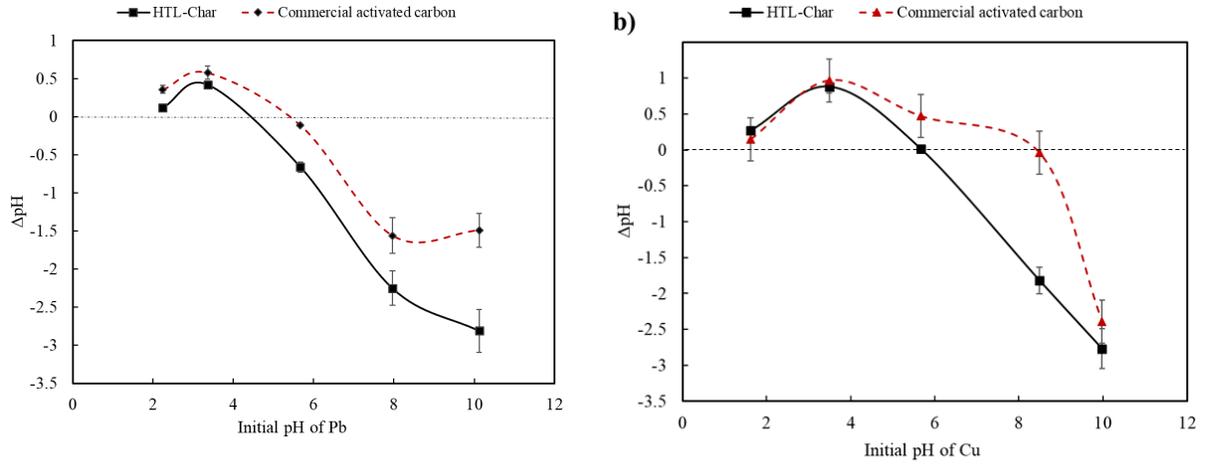


Figure 7. Point of zero charge of HTL-char and commercial char in a) Pb and b) Cu solutions (80 mg/L)

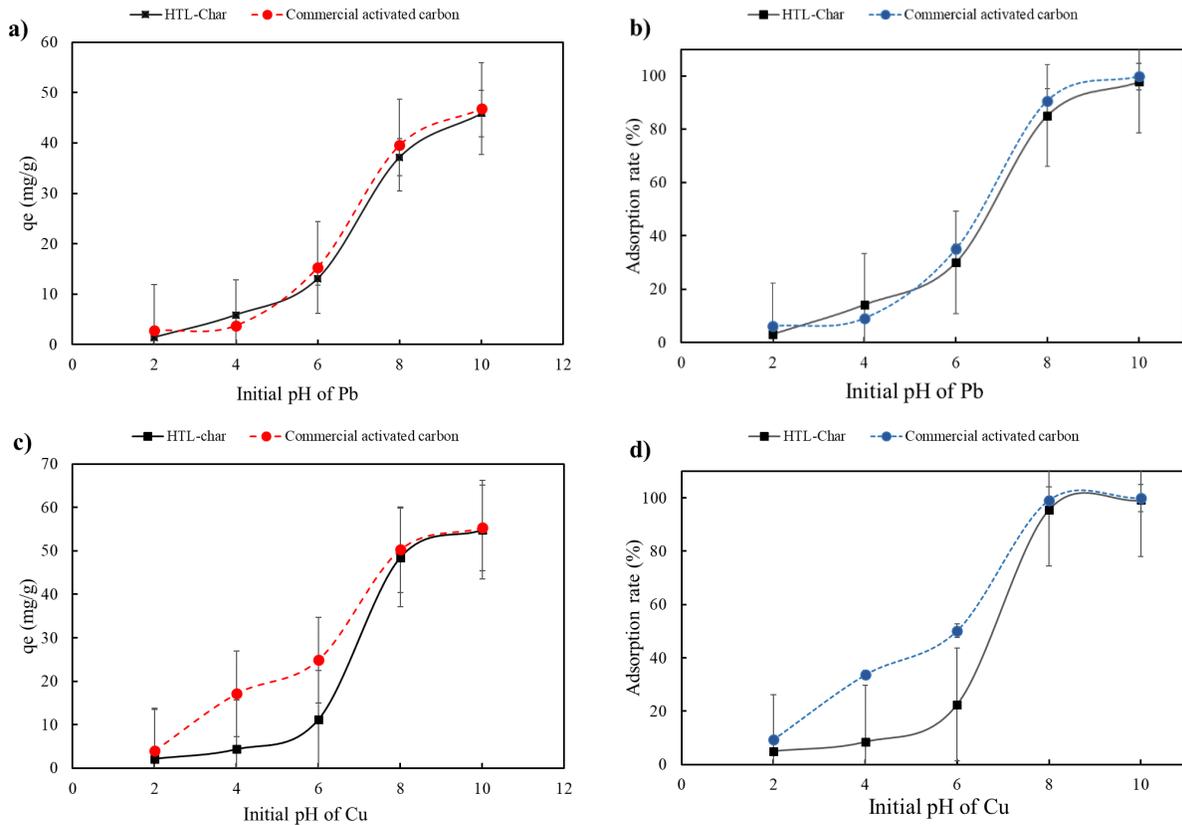


Figure 8. Effect of initial solution pH solution on equilibrium adsorption capacity,  $q_e$ , (a and c), and adsorption rate (fraction of initial metal adsorbed) (b and d). Heavy metal (Pb or Cu) initial concentration = 80 ppm, temp. = 25 °C, adsorption time = 24 h, adsorbent dose = 2 mg/mL

- **Conclusions**

Preliminary results showed that food waste HTL-char has significantly higher lead adsorption capacity compared to commercial activated carbon and CO<sub>2</sub>-activated HTL-char by almost three-fold. Although HTL-char did not show the significant adsorption capacity for Cu removal at low solution pH, increasing the pH showed a significant increase in heavy metal adsorption, especially at pH values above 7. Higher pH creates a more negatively-charged char surface, resulting in enhanced complexation and metal removal. Although activation of HTL-char did increase the char’s porosity and surface area, adsorption results showed that functional groups played a more important role in adsorption of heavy metals than adsorbent porosity. Overall, food waste-derived HTL-char may be an effective adsorbent for the remediation of metal contaminated water and its use for such applications are worth investigating to add value to the products from HTL.

**6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results?**

This research provides information about downstream energy recovery of food waste, and HTL-char has the ability for wastewater treatment. Among various metal ions present in contaminated water, lead (Pb) is a highly toxic element and its effects on biological systems are of great concern. For instance, Pb can accumulate in bones, brain, kidney, and muscular tissues, while exposure to high levels of Pb can cause anemia, encephalopathy, hepatitis, and nephritic syndrome. Chronic exposure to Pb has been observed to cause hyperactivity, irritability, headaches, and learning difficulties. Thus, it is necessary to remove aqueous Pb from metal-contaminated water before discharge. So that remediation of this heavy metals like Pb and copper form water not only is important for animal and human health, the using HTL-char produced from biowaste would be economical and environmentally friendly which is interesting for the United States Environmental Protection Agency (EPA) and the National Association of Clean Water Agencies (NACWA).

**7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after May 31, 2020, please contact Carolina Mijares immediately. (575-646-7991; [mijares@nmsu.edu](mailto:mijares@nmsu.edu))**

Description	Expenses
Summer 2019 & winter 2020 salary	\$3480.01
Fringe Benefits	\$34.10
Fall 2019-spring 2020 tuition	\$2138
Travel (WRRRI conference to Santa Fe)	\$230.53
Supplies/Chemicals/Analytical Instrument	\$617.36
Total	\$6500

**8. List presentations you have made related to the project.**

H Bayat, U Jena, "Removal of heavy metal ions from aqueous solution using char derived from hydrothermal liquefaction of food waste" 64th Annual New Mexico Water Conference, November 7-8, 2019, Santa Fe, NM

H Bayat, M Dehghanizadeh, F. O. Holguin, U. Jena, C. E. Brewer, "Removal of Heavy Metal Ions from Wastewater Using Food Waste Char", 2020 ASABE Annual International Meeting, July 12-15, Virtual meeting.

**9. List publications or reports, if any, that you are preparing. For all publications/reports and posters resulting from this award, please attribute the funding to NM WRRRI and the New Mexico State Legislature by including the account number: NMWRRRI-SG-2019.**

Conference proceeding paper:

H Bayat, M Dehghanizadeh, F. O. Holguin, U. Jena, C. E. Brewer, "Removal of Heavy Metal Ions from Wastewater Using Food Waste Char", DOI: 10.13031/aim.202001062, paper to be presented at the *2020 ASABE Annual International Meeting*, St. Joseph, MI.

**10. List any other students or faculty members who have assisted you with your project.**

Dr. Umakanta Jena, Mark Chidester (Lab Manager), Mostafa Dehghanizadeh (PhD), Nicholas Soliz, Nicolas Carrera-Little, April Wright, and Alan Moya (undergraduate students) from the Department of Chemical & Materials Engineering

Barry Dungan (Senior Ag Research Assistant), Jacqueline Jarvis (Research Assistant Professor), and Omar Holguin (Associate Professor) from the Department of Plant and Environmental Sciences.

**11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.**

- 2019 Jacqueline Shields Memorial Scholarship for waste management research and study

**12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.**

I passed my PhD qualifying exam in summer 2019 and I plan to take the comprehensive exam in Fall 2020.

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