

NM WRRI Student Water Research Grant Final Report

Summer 2022

Student Researcher: Hengameh Bayat

Faculty Advisor: Dr. Catherine Brewer

1. Project title: Wastewater treatment and water recycling through use of byproducts from hydrothermal liquefaction of food waste

2. Description of the research problem and research objectives

The concept of the Food-Energy-Water (FEW) nexus collectively changes the way in which these resources are sustainably produced on an intersectional level. One technology suitable for the FEW nexus approach is hydrothermal liquefaction (HTL) to produce bio-crude oil, nutrient-rich aqueous phase (HTL-AP), and char (HTL-char) from food waste. Although HTL is a promising and integrated tool to treat wet biomass and produce biofuels simultaneously, implementation of HTL at a large scale has been hindered by the limited options for value-added use of the HTL-AP and HTL-char co-products.

HTL-char has attracted the interest of the scientific community because of its notable properties as an environmentally-friendly and cost-effective adsorbent for the removal of pollutants from waters [1, 2]. Nitrate is one of the main pollutants in surface and ground waters as a result of excessive use of nitrogenous fertilizers and the disposal of untreated municipal and industrial wastes. Drinking water with a high nitrate concentration can potentially cause health problems in people such as “blue-baby” syndrome (methemoglobinaemia) in infants [3] and stomach cancer in adults [4]. The nitrate concentration recommended by World Health Organization and the European Union is $< 50 \text{ mg NO}^{-3}/\text{L}$ [5]; the US Environmental Protection Agency has stipulated $< 44 \text{ mg NO}^{-3}/\text{L}$ [6]. In recent years, considerable increases in nitrate have been observed in the semi-arid portion of the Rio Grande River, wells in Albuquerque's South Valley, and on Kirtland Air Force Base, likely from fertilizers and wastewater effluents from

large cities. Commonly-used methods for nitrate removal are ion exchange, reverse osmosis, and electro dialysis, which can have high energy requirements and high capital costs [7]. Carbon-based adsorbents like biochar and hydrochar from agricultural byproducts have attracted attention because of their biodegradability, biocompatibility and renewability. The surface properties of char, which can be enhanced with activation, are key factors in its usability as an adsorbent [8]. Recently, magnetic chars have been developed as high-efficiency adsorbents for the removal of pollutants from aqueous solutions [9]. The introduction of a magnetic medium (such as maghemite, $\gamma\text{-Fe}_2\text{O}_3$) to carbon-based adsorbents by a pyrolysis activation (simultaneous activation and magnetization), or a chemical co-precipitation reaction enable, the adsorbent to be efficiently separated post-treatment with an external magnetic field. As an alternative to using chemical co-precipitation, researchers have begun to investigate red mud (RM), a byproduct generated during alumina processing from bauxite ore. Large volumes of RM are produced each year: approximately 1–2 tons of residue for every ton of alumina [10]. RM needs to be stored in large disposal areas which, if not maintained correctly, can lead to contamination of the surrounding soil, surface water, and groundwater. Typical RM is strongly alkaline, with pH in the range of 10–13, and contains high levels of a range of metals, such as aluminum (Al_2O_3 , 5–30 wt%), iron (Fe_2O_3 , 5–60 wt%), calcium (CaO , 2–14 wt%), silicon (SiO_2 , 3–50 wt%) and sodium (Na_2O , 1–10 wt%). Previous studies have reported the use of magnetic biochar obtained from pyrolysis of biomass and RM in wastewater treatment [11–13]. However, for a low-surface-area carbonaceous material, co-precipitation and pyrolysis are not efficient. In-situ modification of HTL-char through co-HTL of food waste and RM can simultaneously improve the physicochemical properties of HTL-char as an adsorbent and the bio-crude oil yield. This study aimed to evaluate co-HTL of red mud and food waste to produce magnetic HTL-char and to test its adsorption capabilities for nitrate.

The overarching research objectives of this work were to:

1. Produce and characterize surface properties and ion adsorption capacity of HTL-chars prepared through co-HTL of food waste and red mud
2. Quantify the effects of water pH, contact time, and initial nitrate concentration on adsorption performance and mechanisms for nitrate adsorption

3. Characterize food waste HTL-AP for compost-relevant properties, including pH, total carbon, total-N and ammonia-N, phosphorus, salinity, metals, and organics composition
4. Evaluate feasibility of HTL-AP addition to compost in terms of microbial activity, nutrient availability (C/N ratio), moisture, and quality of the finished compost

Research Methodology Employed

- **Co-HTL of food waste and red mud and product recovery**

Food waste was collected from New Mexico State University's Taos Restaurant dining hall in Las Cruces, New Mexico. HTL experiments were conducted in a stainless steel 1.8-L Parr reactor. Food waste slurry (75 g, 15 wt %) was loaded into the reactor, along with red mud (20 g when used). The reactor was purged with nitrogen and pressurized to approximately 140 kPa to remove air and prevent water evaporation during heating. Based on prior studies, the reaction conditions giving the highest bio-crude oil yield (240 °C and 30 min) were used. Once the reaction was finished and the reactor cooled, the gaseous products were vented. Hexane (300 ml) was added to the products and stirred for 3 min, then the mixture centrifuged at 9000 rpm for 4 min to extract the products. HTL char was separated from the mixture using filtration and dried for 48 h at 60°C. Hexane-soluble bio-crude oil was separated from the aqueous phase using a separatory funnel and the hexane was evaporated using a rotary evaporator. Food waste and red mud co-HTL were performed in triplicate, with measured yields agreeing to within $\pm 3\%$. Yields (wt. %) were calculated as (Eq.1):

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

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

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. Then, the HTL-char or red mud-modified HTL-char (RM-HTL-char) was dried for 48 h at 60 °C.

- **Point of zero charge measurements**

The point of zero charge (pH_{PZC}) of HTL-char and RM-HTL-char samples were measured using solutions of deionized water with initial pH values ranging from 2 to 10. Briefly, a 50-mL centrifuge tube containing 20 mL of 0.05 M NaCl was pH-adjusted using 0.1 M HCl or NaOH solutions before the introduction of 0.05 g of char. The suspensions were agitated for 24 h in an orbital shaker at room temperature and the final pH of the solutions was measured. pH_{PZC} was determined as the intersection with the x-axis when plotting the difference between the final pH and initial pH against the initial pH.

- **HTL-chars and adsorption solution characterization**

The following characterizations of the HTL-char and RM-HTL-char were performed:

- ✓ Fourier transfer infrared spectroscopy (FT-IR) to identify char surface functional groups
- ✓ Brunauer-Emmett-Teller method (BET) gas adsorption analysis to measure the surface area and pore size distribution
- ✓ X-ray diffraction (XRD) to measure crystallographic features
- ✓ Inductively coupled plasma optical emission spectrometer (ICP-OES) to quantify inorganic element contents
- ✓ Technicon AutoAnalyzer analysis to measure nitrate (NO_3^-) and ammonium (NH_4^+)

- **Adsorption experiments**

Batch experiments were performed to determine the effect of solution initial pH, contact time, and adsorbate concentration on nitrate adsorption capacities of RM-HTL-char, HTL-char, and commercial activated carbon. To examine the adsorption capacity as a function of initial pH, 50-mL centrifuge tubes containing 25 mL of 40 mg/L NO_3^- solutions and 0.05 g of adsorbent with an initial pH between 2 and 10 were agitated at 150 rpm for 24 h at room temperature (~23°C) before the adsorbent was removed by filtration and the final concentration measured. The selection of initial concentrations was based on preliminary investigations. The capacity of the adsorbents was calculated using

$$q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where q was the mass of nitrate per mass of adsorbent (mg/g), C_0 was the initial concentration of metal (mg/L), C_e was the equilibrium concentration (mg/L), V was the volume of solution (L), and M was the mass of the adsorbent (g).

- **Composting experiments materials and configuration**

Hemp wastes and cattle manure were used as the raw materials for composting. Dry hemp wastes, consisting of primary dry stalk, leaves and flower materials (Figure 1a), were collected from the NMSU Agricultural Science Center, Farmington, NM. Hemp biomass was ground to < 2 mm using a cutting mill (Retsch® SM 300) (Figure1), located at the Leyendecker Plant Science Research Center. Manure compost (MC), collected from NMSU Animal Science range cattle pens, was incorporated as a nitrogen source. Hemp stalks, leaves, and manure were mixed at a C:N ratio of 25:1. Due to the high electrical conductivity (EC) of the HTL aqueous phase (14.38 mS/cm), the HTL-AP was diluted to 20% concentration (1:4) with water. The raw materials (~20 kg) were transferred into two-chambered commercial tumbling composters. Each composter had a volume of 140 L: 66 cm (width) × 91 cm (height) × 71 mm (length). At 30 cm from the bottom of both sides of the reactor, there were twelve 1 mm-diameter holes to enable aeration. One of the two treatment combinations (compost material + water and compost material + HTL-AP) were loaded into each chamber (such that each treatment was duplicated). The composters, kept in a shaded outdoor area, were turned every other day manually to provide fresh air to the composting mixtures for > 30 days.

- **Sampling, monitoring and analysis**

Compost temperatures were monitored twice daily (morning and afternoon) by thermometric sensors (Proster Digital Thermocouple, 12" Stainless Steel K-Type Thermocouple Insertion Probe) from the surface, middle, and bottom of the chambers, respectively, and the average were reported. Compost samples were collected after blending and turning. Sampling was performed at different depths (at two points from the surface, center, and bottom of the compost pile, respectively). Moisture content was determined by moisture meter (REOTEMP Garden and

Compost Moisture Meter) twice daily and by oven drying at 105 °C for 24 h once a week. Water extracts (1:10 w/v) of fresh compost were used to track pH, NH₃-N, NO₃-N, and EC. The suspensions were shaken 1 h, centrifuged at 12,000 rpm for 20 min, and filtered through 0.45 μm membrane filters. The pH and EC of the HTL-AP and the tap water were determined directly using a pH/EC meter (Orion4 Star, Thermo Fisher Scientific, MA, USA). NH₃-N and NO₃-N were analyzed by segmented flow analyzer (Technicon Autoanalyzer II System, Germany).



Figure 1. Initial compost materials and composters: (top from left to right) hemp leaves, hemp stalks, and cow manure; (bottom from left to right) tumbling composters, compost after three days

Results, Conclusions and Recommendations for Future Work

- **Characterization of adsorbents**

The elemental compositions of red mud, RM-HTL-Char, and HTL-char obtained from food waste are shown in Table 1. Compared to the HTL-char, the Fe₂O₃ and CaO contents were increased with the addition of the red mud to HTL.

Table 1. Elemental composition of original red mud and char samples

Samples	Elemental content (wt.%)						
	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SiO ₂	Na ₂ O	TiO ₂
Red mud	9.79	22.98	2.45	0.04	0.01	4.30	0.03
RM-HTL-char	0.02	0.03	0.46	0.06	0.15	0.14	0.002
HTL-char	-	0.01	0.12	0.05	-	0.52	-

FTIR spectra to identify the functional groups of the HTL-char and RM-HTL-char are shown in Figure 2. Peaks around 3420 and 3140 cm⁻¹ were attributed to the O-H stretching and deformation vibration of O-H groups (e.g., water, alcohols, and phenols) [14]. The peaks at 1100-1000 cm⁻¹ were attributed to the Si-O or Al-O bonds, while those at 570, 550 cm⁻¹ originated from Fe-O bonds of Fe-OH or Fe₂O₃ and Fe₃O₄, respectively, indicating that Fe compounds exist in the adsorbents [11]. Strong peaks of Si-O and Fe-O were observed in the RM-HTL-char, while the intensities of these peaks were weaker in the HTL-char (Figure 2).

BET surface areas, pore volumes, and BJH pore size distributions from N₂ gas sorption analysis are presented in Table 2 and Figure 3. The RM-HTL-char had larger BET surface area (15.4 vs 10.1 m²/g) and larger average pore size (8.5 vs 7.9 nm) compared with HTL-char. Kazak et al. [15] reported that the addition of red mud during co-hydrothermal treatment of vinasse increased surface area from 9 to 23 m²/g and enhanced the development of hydrochar pores.

Table 2. Gas adsorption analysis results for adsorbents

Parameter	HTL-char	RM-HTL-char	Commercial activated carbon
BET Surface Area (m ² /g)	10.1	15.4	776.0
Total Pore Volume (cm ³ /g)	0.02	0.02	0.01
Average Pore Diameter (nm)	7.9	8.5	11.8

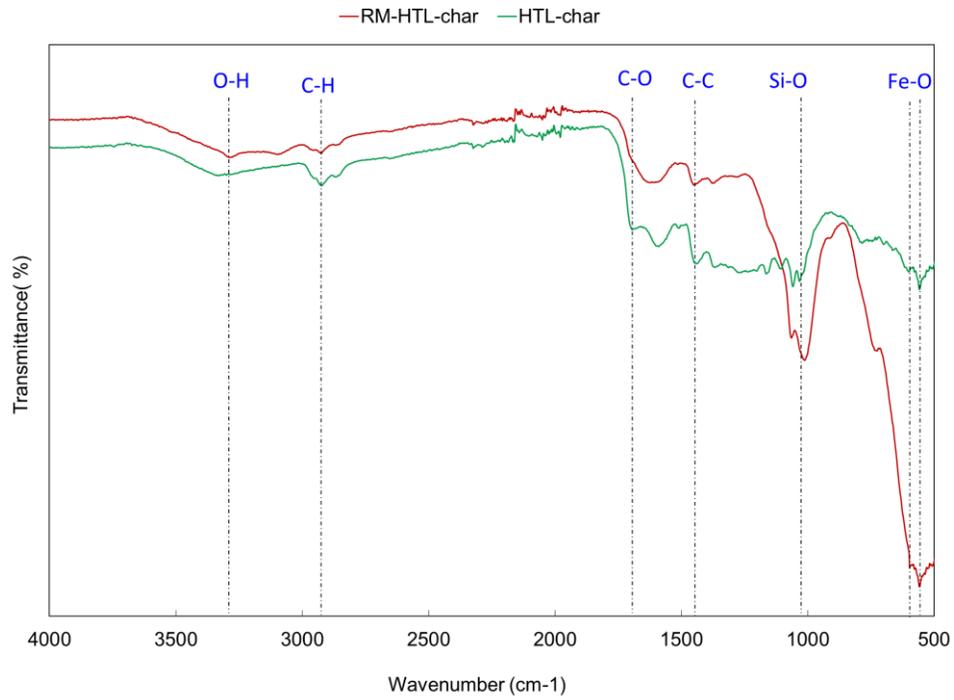


Figure 2. FTIR spectra of the HTL-char and RM-HTL-char

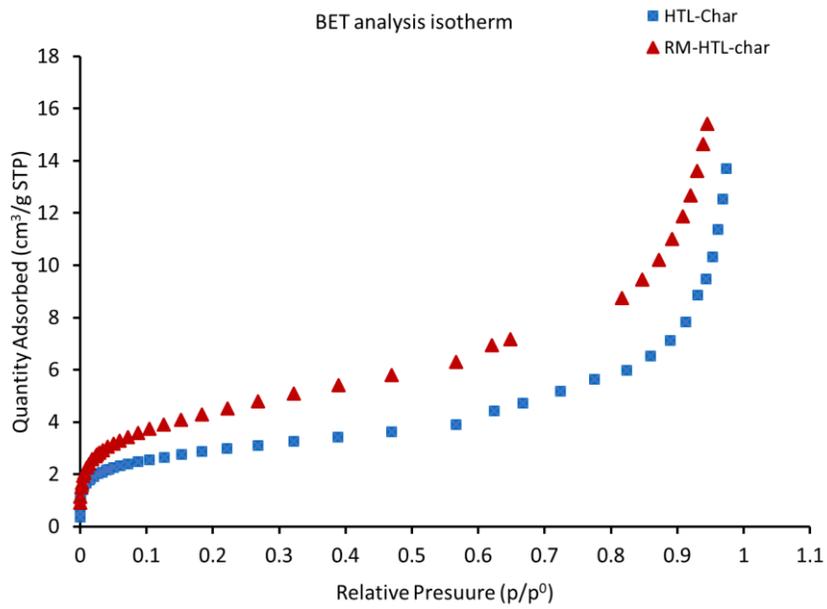


Figure 3. Nitrogen adsorption isotherms

The diffraction patterns of HTL-char, red mud, and RM-HTL-char are shown in Figure 4. Both amorphous and crystalline structures, and the presence of some inorganic minerals, such as SiO₂ and Al/Si oxides in the HTL-char and RM-HTL-char, with the typical peaks at $2\theta = 21.22^\circ$, 26.44° , 29.12° , and 39.45° , were observed. The diffraction peaks of the red mud representing AlO-OH ($2\theta = 14.2^\circ$, 18.7° , and 35.4°), FeO-OH, ($2\theta = 20.3^\circ$), Fe₂O₃ ($2\theta = 24.4^\circ$, 33.1° , 40.8° , 49.6° , and 54.5°), TiO₂ ($2\theta = 27.4^\circ$), and SiO₂ ($2\theta = 27.6^\circ$)[13], were also observed for the RM-HTL-char. This result indicates that red mud particles were successfully introduced into the HTL-char during HTL.

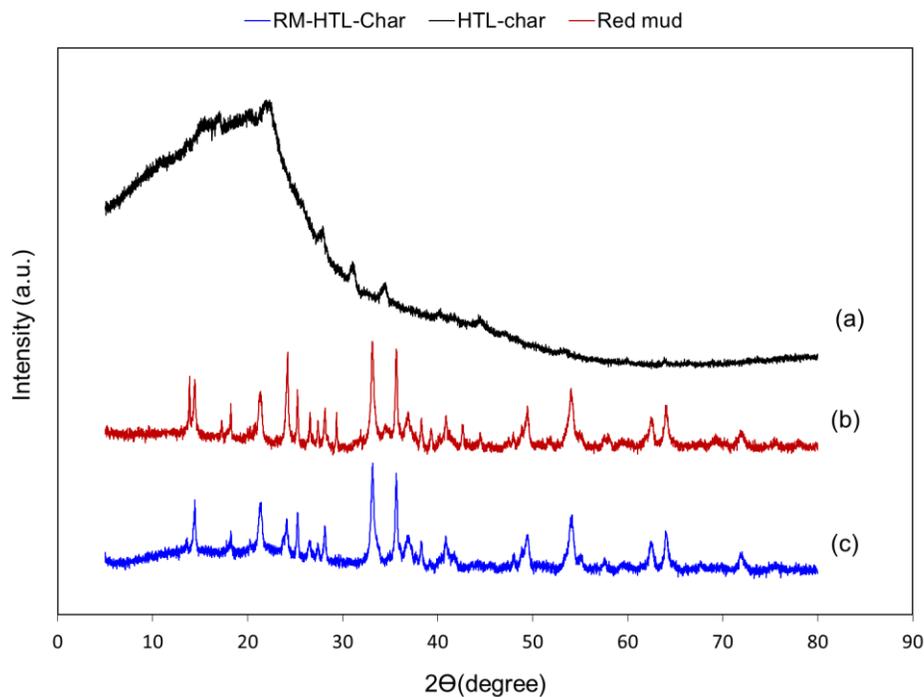


Figure 4. XRD diffractograms of HTL-char (a), red mud (b) and RM-HTL-char (c)

Figure 5 shows the pH_{PZC} results for the adsorbents: 5.62 for HTL-char and 6.11 for RM-HTL-char, which were similar to that of the commercial activated carbon. When solution $pH < pH_{PZC}$, HTL-char exhibits positive surface species while can attract negatively-charged nitrate ions. When solution $pH > pH_{PZC}$, excess hydroxyl ions on the HTL-char and RM-HTL-char surfaces create repulsive forces between the negative surface of the adsorbent and negative charge of nitrate ions, resulting in a lower nitrate adsorption capacity.

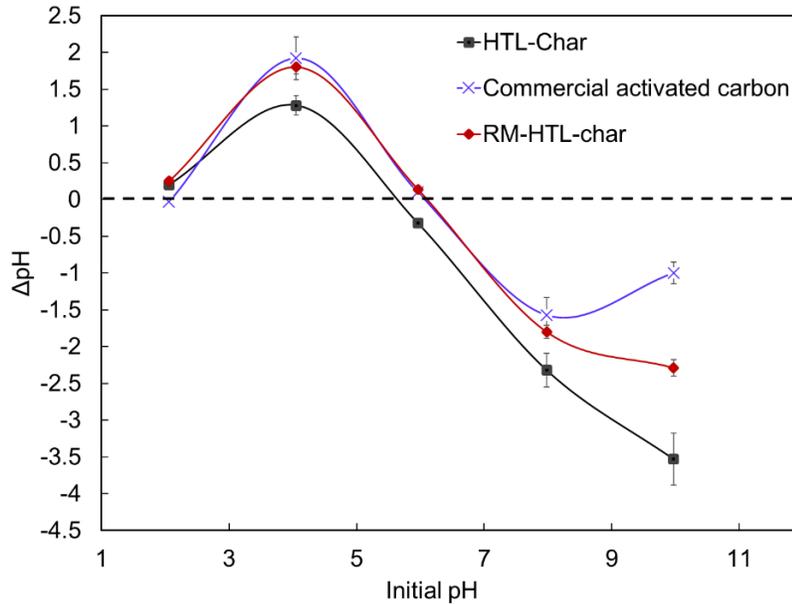


Figure 5. Point of zero charge of HTL-char, RM-HTL-char, and commercial activated carbon

Adsorption studies

Figure 6 shows the amounts of nitrate adsorbed by HTL-char, RM-HTL-char, and commercial activated carbon as a function of pH, solution initial nitrate concentration, and adsorbent-solution contact time. In general, RM-HTL-char showed higher adsorption capacity than unmodified HTL-char, which had minimal adsorption capacity for nitrate. Zhang et al. [16] reported that the majority of unmodified chars had no or minimal adsorption capacity. Similar results were also reported by Gai et al. [17], where no nitrate removal from aqueous solution was observed using biochars obtained from three biomass. These negligible nitrate removal efficiencies are most likely due to the electrostatic repulsion between the negatively-charged biochar surfaces and the nitrate anions. At higher concentrations (Figure 6 a), a decrease in adsorption capacity typically represents saturation of adsorption sites. Solution pH has an important role in the adsorption process of nitrate, as illustrated in Figure 6b. The maximum adsorption capacity of nitrate for RM-HTL-char was 5.7 mg/g at pH 2. However, the adsorption capacity dropped sharply to 0.28 mg/g as the pH was raised to 10. Ozturk and Bektas reported that the maximum adsorption of nitrate on activated char (about 92%) occurred at pH 2 due to an increase in the number of positively-charged sites on the surface of activated char [18].

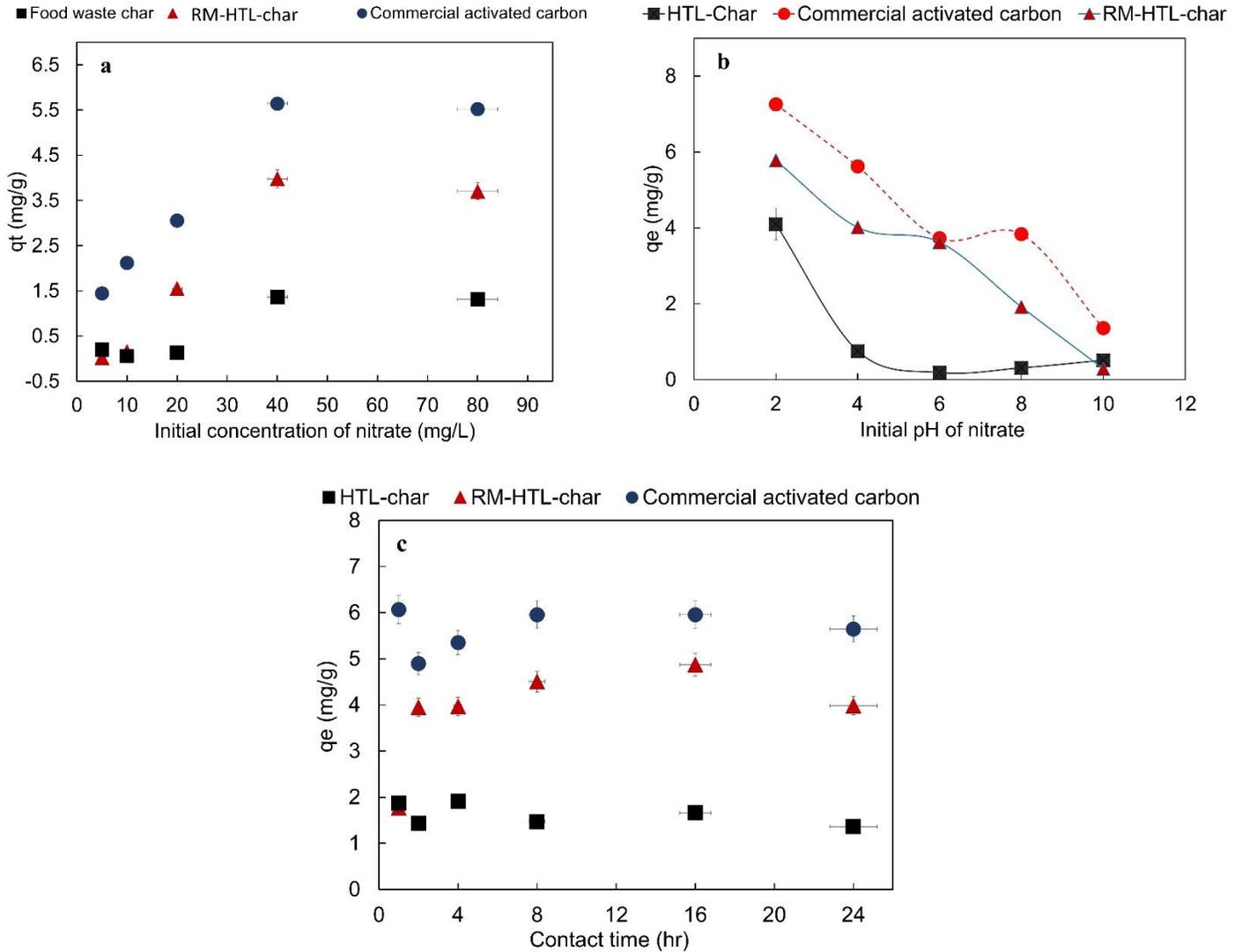


Figure 6. Effect of a) the initial concentration of nitrate (pH = 5, adsorption time = 24 h), b) initial pH of nitrate (initial concentration = 40 ppm, adsorption time = 24 h); and c) effect of contact time (pH = 5, initial concentration = 40 ppm) on nitrate adsorption capacity

To understand adsorption kinetics, adsorption studies were conducted over time periods ranging from 1 to 24 h. Figure 6c shows that the adsorption was rapid in the first hour, which was attributed to a large number of active sites on the surface of char samples being available initially. After that, the nitrate adsorption rate was approximately constant with time, reaching equilibrium before 8 h.

Compost temperature evolution

The temperatures for both composts followed typical patterns: a heating stage (days 1-3), a thermophilic stage (days 3-7), and a cooling stage (days 7-20) (Figure 7). The first mesophilic stage for both composts was very short. The temperature increased sharply to a thermophilic value ($> 50\text{ }^{\circ}\text{C}$) after 3 days, reaching maximums of 57.9°C and 54.6°C for compost + HTL-AP and compost + water, respectively. The thermophilic stage was the main phase for water loss and microbial degradation for all composts. The faster increase of temperature in the heating stage and longer thermophilic phase (4 days vs 2 days) indicated that addition of HTL-AP improved the performance the composting process. Higher temperature and longer thermophilic phase accelerate organic matter decomposition and shorten the time required for maturity. After reaching their maximum temperatures, temperatures in both composters remained at similar mesophilic values ($35\pm 2\text{ }^{\circ}\text{C}$), just above the ambient summer temperatures, for 10 days.

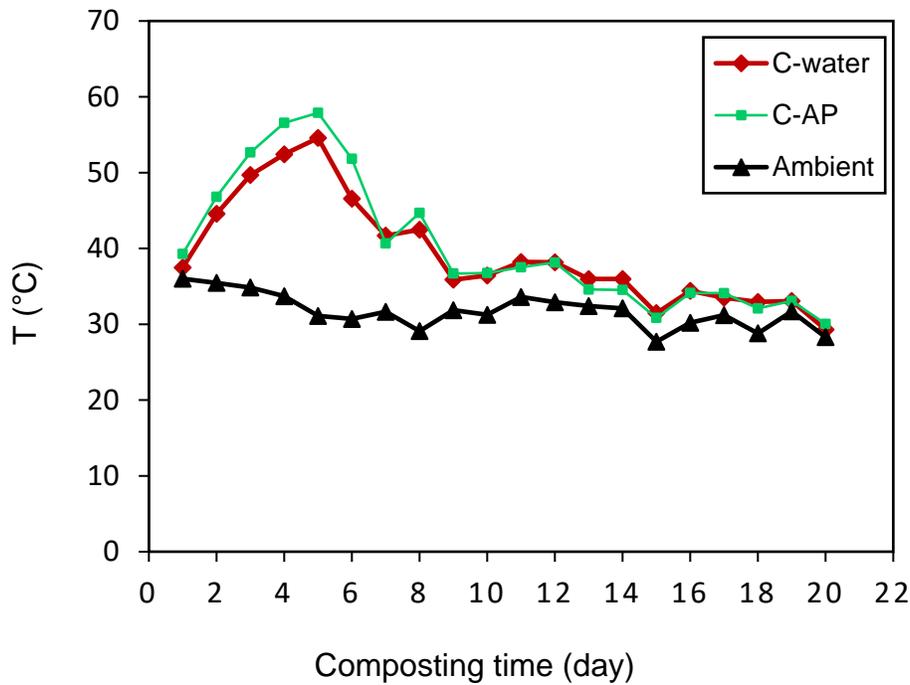


Figure 7. Ambient temperature and temperature evolution of composters for composts containing water (C-water) or HTL aqueous phase (C-AP) treatments to maintain moisture content

Impact of HTL-AP on physical-chemical characteristics during composting

The moisture content, pH, and EC of composts for the first 20 days (d1- d20) are shown in Table 3. The change in moisture content, which is mainly affected by compost temperature, was faster in the HTL-AP than that in the water-treated compost during the thermophilic phase (Figure 7). After that initial period, the moisture content showed similar high and stable values.

The biodegradation of organic matter is affected by the extreme pH levels. pH levels at the initial stage of composting for water and HTL-AP-treated chambers ranged between 5.34 and 6.20, respectively (Table 3). Increases in pH are attributed to organic matter degradation and ammonization of the contained nitrogen. The pH of the compost + HTL-AP was consistently lower than that of the water-treated, probably owing to the acidic nature of the added HTL-AP.

The EC value reflects the degree of salinity and the potential inhibitory effect on plant growth if the compost is applied for agricultural use. The changes in EC values showed a similar pattern for both treatments during composting (Table 3): EC values significantly increased during the initial stage and then slightly decreased or remained stable until the end. Pan et al. (2018) reported a similar increase in the EC value during the initial stage of apple pomace composting; calcium super-phosphate and pig manure may be related to the biotransformation of organic material into simpler compounds and the release of water-soluble mineral ions such as phosphate, sulphate, ammonium, sodium, and potassium [19].

Table 3. Variation in moisture content, pH and EC of water-treated and HTL aqueous phase-treated materials during composting

Day	1	5	9	13	20	1	5	9	13	20	1	5	9	13	20
Compost Treatment	Moisture Content (wt.%)					pH					Electrical Conductivity (mS/cm)				
Water	65.0	71.7	72.9	73.6	51.5	6.2	9.6	8.2	8.2	7.0	1.4	5.1	5.4	4.2	2.2
HTL-AP	65.4	62.6	66.0	71.1	69.7	5.3	8.1	7.7	8.1	7.1	3.3	6.8	5.6	4.2	3.8

Impact of HTL-AP on available nitrogen in compost

Ammonium levels are typically high during initial stages of composting, then decrease as compost matures. This pattern was observed here (Figure 8) for both treatments. Addition of HTL-AP into the compost swiftly reduced NH₃ emissions. Peak levels of extractable-N were 52.8 mg/kg and 32.9 mg/kg for compost + water and compost + HTL-AP, respectively. The

initial nitrate concentration was < 1 mg/kg for both mixtures and increased to 5.1 and 5.8 mg/kg, suggesting that the addition of HTL-AP increased the gross nitrification rate.

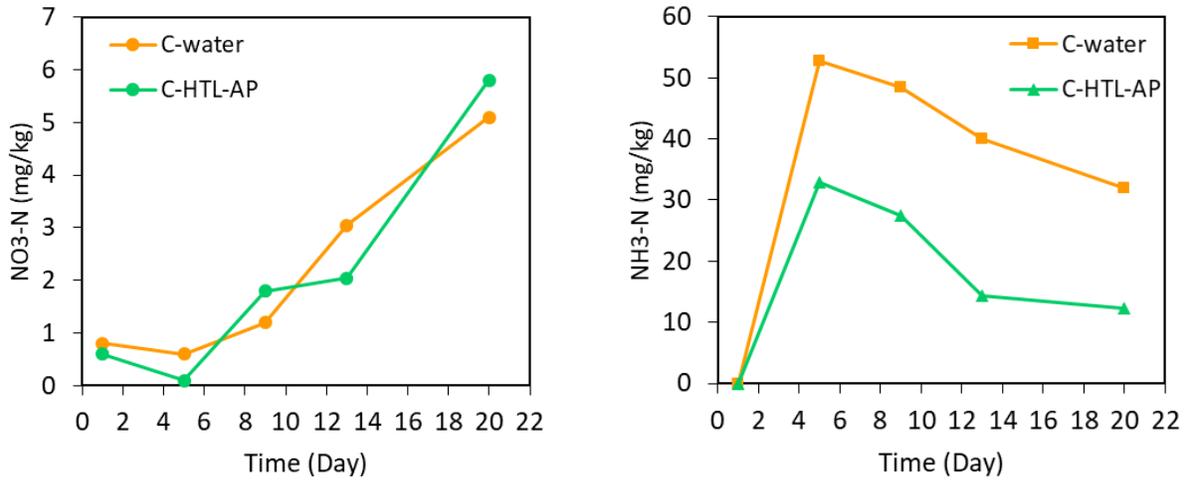


Figure 8. Effect of HTL-AP addition on NH₃-N and NO₃-N

3. Conclusions

This study has demonstrated the potential value-added use of HTL byproducts for wastewater treatment and composting. HTL-char obtained from co-HTL of food waste and red mud showed great potential for nitrate removal from wastewater. Nitrate adsorption capacities were significantly improved using the red mud-modified HTL-char because of the char’s composition and structural properties. The maximum adsorption capacity of nitrate for RM-HTL-char was 5.7 mg/g at pH 2. The results offer significant potential due to it being derived from readily-available waste materials: food waste and red mud. To facilitate HTL-char implementation in future, testing in a lab/large-scale column for adsorption of nitrate is needed.

This study also demonstrated that the addition of food waste HTL-AP, another HTL process byproduct, to compost of hemp waste and cow manure is a viable process that increases re-use of water and available nutrients. HTL-AP in compost led to faster increase in temperature and maturation. More research on ammonia volatilization and greenhouse emissions, the fate and balance of heavy metals, and pathogen removal in this compost would be of great interest.

4. Beneficiaries of research results

This research provides information about downstream energy recovery from food waste and the ability of byproducts like HTL-char for removal of nitrate from aqueous solutions. The results of this research are interesting for the Food and Agriculture Organization of the United Nations (FAO), who support a FEW-nexus approach for the transition to a Green Economy. This approach can generate additional revenue streams for operators, thereby contributing to the sustainability of the water system. The U.S. Environmental Protection Agency (EPA) and the National Association of Clean Water Agencies (NACWA) provide funding to improve water and wastewater systems in small and rural communities using less expensive methods. Solid waste management organizations, like the Solid Waste Association of North America (SWANA) and the National Waste & Recycling Association (NWRA), continuously seek ways to reuse and recycle materials and can benefit from the results of this research.

5. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds.

Description	Amount Spent (as of 07/30/22)
Undergraduate salary	\$785
Fringe benefits	\$5
Health insurance	\$600
Travel	\$400
Supplies	\$1019
Services	\$4058
Total	\$6867

6. List presentations you have made related to the project.

- “Use of the aqueous phase and char from hydrothermal liquefaction of biomass in compost and heavy metal adsorption applications,” oral presentation, *2021 AIChE Annual Meeting*, Boston, MA, November 7-12

- “Wastewater treatment using char derived from co-hydrothermal liquefaction of food waste and red mud,” poster, *66th Annual New Mexico Water Conference*, Virtual Conference, October 26-28, 2021.
- “Nitrogen management using byproducts from hydrothermal liquefaction of food waste,” *2022 Annual International Meeting*, Houston, Texas – July 17-20.

7. List publications or reports that you are preparing. For all publications/reports and posters resulting, please attribute the funding to NM WRRI and the New Mexico State Legislature, including account number: NMWRRI-SG-2021.

We are preparing two papers on:

1. “Removal of heavy metals and nitrate ions from wastewater using a red mud modified HTL-char” to submit to *Bioresource Technology*.
2. “Comparative evaluation of the use of aqueous phase obtained from hydrothermal liquefaction process on composting process” to submit to *Waste Management*.

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

- Mark Chidester (lab manager), Mostafa Dehghanizadeh, Hanah Rheay (PhD students), Nicholas Soliz, Nicolas Carrera-Little, Justice Armijo, Andrea Loya Lujan Hannah Severns (undergraduate students), Chemical and Materials Engineering
- Barbara Hunter (Lab Coordinator), Plant and Environmental Sciences
- Carlos Armenta (XRD analysis coordinator), Physics

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

- Outstanding Graduate Assistant Award 2021-2022

10. 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 the PhD comprehensive exam in Summer 2021 and plan to graduate in Fall 2022.

References

- [1] J. Deng *et al.*, "Sulfamic acid modified hydrochar derived from sawdust for removal of benzotriazole and Cu(II) from aqueous solution: Adsorption behavior and mechanism," *Bioresource Technology*, vol. 290, p. 121765, 2019/10/01/ 2019, doi: <https://doi.org/10.1016/j.biortech.2019.121765>.
- [2] S. Kumar, V. A. Loganathan, R. B. Gupta, and M. O. Barnett, "An assessment of U (VI) removal from groundwater using biochar produced from hydrothermal carbonization," *Journal of environmental management*, vol. 92, no. 10, pp. 2504-2512, 2011.
- [3] L. Fewtrell, "Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion," (in eng), *Environmental health perspectives*, vol. 112, no. 14, pp. 1371-1374, 2004, doi: 10.1289/ehp.7216.
- [4] H.-F. Chiu, S.-S. Tsai, and C.-Y. Yang, "Nitrate in Drinking Water and Risk of Death from Bladder Cancer: An Ecological Case-Control Study in Taiwan," *Journal of Toxicology and Environmental Health, Part A*, vol. 70, no. 12, pp. 1000-1004, 2007/04/30 2007, doi: 10.1080/15287390601171801.
- [5] F. Edition, "Guidelines for drinking-water quality," *WHO chronicle*, vol. 38, no. 4, pp. 104-108, 2011.
- [6] M. J. Pennino, J. E. Compton, and S. G. Leibowitz, "Trends in Drinking Water Nitrate Violations Across the United States," *Environmental Science & Technology*, vol. 51, no. 22, pp. 13450-13460, 2017/11/21 2017, doi: 10.1021/acs.est.7b04269.
- [7] D. A. Sanchez Hernandez, "Determining sources of nitrate in the semi-arid Rio Grande using nitrogen and oxygen isotopes," 2017.
- [8] B. Ghanim, J. G. Murnane, L. O'Donoghue, R. Courtney, J. T. Pembroke, and T. F. O'Dwyer, "Removal of vanadium from aqueous solution using a red mud modified saw dust biochar," *Journal of Water Process Engineering*, vol. 33, p. 101076, 2020/02/01/ 2020, doi: <https://doi.org/10.1016/j.jwpe.2019.101076>.
- [9] M. Zhang, B. Gao, S. Varnoosfaderani, A. Hebard, Y. Yao, and M. Inyang, "Preparation and characterization of a novel magnetic biochar for arsenic removal," *Bioresource Technology*, vol. 130, pp. 457-462, 2013/02/01/ 2013, doi: <https://doi.org/10.1016/j.biortech.2012.11.132>.
- [10] M. Wang and X. Liu, "Applications of red mud as an environmental remediation material: A review," *Journal of Hazardous Materials*, vol. 408, p. 124420, 2021/04/15/ 2021, doi: <https://doi.org/10.1016/j.jhazmat.2020.124420>.

- [11] J. S. Cha *et al.*, "Performance of CO₂ and Fe-modified lignin char on arsenic (V) removal from water," *Chemosphere*, vol. 279, p. 130521, 2021/09/01/ 2021, doi: <https://doi.org/10.1016/j.chemosphere.2021.130521>.
- [12] A. I. Casoni, P. Mendioroz, M. A. Volpe, and V. S. Gutierrez, "Magnetic amendment material based on bio-char from edible oil industry waste. Its performance on aromatic pollutant removal from water," *Journal of Environmental Chemical Engineering*, vol. 8, no. 2, p. 103559, 2020/04/01/ 2020, doi: <https://doi.org/10.1016/j.jece.2019.103559>.
- [13] O. Kazak, Y. R. Eker, and A. Tor, "In-situ magnetization of porous carbon beads by pyrolysis of waste red mud doped polysulfone beads for efficient oil sorption," *Chemical Engineering and Processing - Process Intensification*, vol. 158, p. 108190, 2020/12/01/ 2020, doi: <https://doi.org/10.1016/j.cep.2020.108190>.
- [14] Z. Guo, G. Bai, B. Huang, N. Cai, P. Guo, and L. Chen, "Preparation and application of a novel biochar-supported red mud catalyst : Active sites and catalytic mechanism," *Journal of Hazardous Materials*, vol. 408, p. 124802, 2021/04/15/ 2021, doi: <https://doi.org/10.1016/j.jhazmat.2020.124802>.
- [15] O. Kazak and A. Tor, "In situ preparation of magnetic hydrochar by co-hydrothermal treatment of waste vinasse with red mud and its adsorption property for Pb(II) in aqueous solution," *Journal of Hazardous Materials*, vol. 393, p. 122391, 2020/07/05/ 2020, doi: <https://doi.org/10.1016/j.jhazmat.2020.122391>.
- [16] M. Zhang *et al.*, "Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water," *Water Research*, vol. 186, p. 116303, 2020/11/01/ 2020, doi: <https://doi.org/10.1016/j.watres.2020.116303>.
- [17] X. Gai *et al.*, "Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate," (in eng), *PloS one*, vol. 9, no. 12, pp. e113888-e113888, 2014, doi: 10.1371/journal.pone.0113888.
- [18] N. Öztürk and T. E. I. Bektaş, "Nitrate removal from aqueous solution by adsorption onto various materials," *Journal of Hazardous Materials*, vol. 112, no. 1, pp. 155-162, 2004/08/09/ 2004, doi: <https://doi.org/10.1016/j.jhazmat.2004.05.001>.
- [19] J. Pan *et al.*, "Comparative evaluation of the use of acidic additives on sewage sludge composting quality improvement, nitrogen conservation, and greenhouse gas reduction," *Bioresource Technology*, vol. 270, pp. 467-475, 2018/12/01/ 2018, doi: <https://doi.org/10.1016/j.biortech.2018.09.050>.