Magnetochemistry

Novel Production of Magnetite Particles via Thermochemical Processing of Digestate From Manure and Food Waste

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Abstract—Sustainable management of food waste has become a global priority because of the significant environmental impacts associated with conventional disposal methods, including landfilling. Thermochemical processing is a food-waste-to-energy conversion technology in which food waste materials are converted to biofuel in a reduced O_2 environment at elevated temperatures. Another conversion technology is anaerobic digestion, in which microorganisms digest biodegradable material, producing biofuel and solid byproducts "digestate." We measured the physical properties of "biochar" produced by combining these approaches: digestate was used as feedstock for a commercial-scale thermochemical processing system. Magnetite (Fe_3O_4) particles were produced during the food-waste-to-energy conversion process. This was particularly unexpected because none of the input materials were ferromagnetic, and no specific Fe precursors were introduced in the process. The Fe_3O_4 was identified through a combination of X-ray fluorescence and dc magnetometry. Zero-field cooled magnetization-temperature curves reveal a Verwey transition at ∼125 K across samples prepared under various conditions. Room temperature magnetization-field loops show a Langevin-like curve, technical saturation, and coercive fields of $H_C = 98$–130 Oe across various samples. Clear Verwey transition, room temperature hysteresis, and an irreversibility temperature well above room temperature indicate that particles are multidomain. We attribute the presence of Fe_3O_4 to the relatively high concentration of Fe naturally present in the solid digestate and the operating parameters of the thermochemical conversion process. High surface area magnetic biochar has a variety of potential applications, including the adsorption of heavy metals, wastewater treatment, supercapacitors, and conductive polymer composites.

Index Terms—Magnetochemistry, magnetism in solids, biomagnetic particles, nanomagnetics, soft magnetic materials.

I. INTRODUCTION

A biorefinery consists of processing biomass through a combination of different technologies to produce energy and other valuable products with low environmental impact and reduced waste. This idea is based on the design of a petroleum refinery, where many value-added products are recovered during the multistep process. This product diversification enhances the commercial viability of biomass treatment [Cherubini 2010, FitzPatrick 2010]. Inspired by this concept, this letter explores the integration of anaerobic digestion (**AD**) and thermochemical processing as a sustainable option for manure and food waste management. AD is a well-established technology used for processing animal manure and other types of biomass into biogas, a fuel mainly composed of methane [Ebner 2016]. Another product of the AD process is an effluent, often referred to as "digestate." Solids from the digestate are separated and used as bedding for cattle, whereas the liquid fraction is spread on crop fields as an alternative to conventional chemical fertilizers. However, land application of liquid digestate can lead to nutrient run-off and cause surface and groundwater contamination, as well as eutrophication that has resulted in toxic algae blooms in many parts of the country [Nkoa 2014]. Therefore, with the proliferation of AD, managing its digestate has become a concern, and thermochemical processing is one possible solution to this problem.

Thermochemical processing involves exposing biomass to elevated temperatures (500–1000 °C) under reduced oxygen concentrations to produce biochar [Mohan 2014]. Biochar is a carbon-rich material conventionally used as a soil amendment [Lone 2015], but also known for its potential as an adsorption medium [Ahmad 2014]. Biochar made from the solid fraction of digestate can be used to remove nutrients (nitrogen, phosphorous, potassium, etc.) present in the liquid fraction. The "enriched" biochar thus produced can then be applied as a more stable solid fertilizer, replacing land application of liquid digestate and reducing potential water contamination. In addition, this practice returns nutrients once harvested from the soil as food or cow feed and brings them back to the soil in a circular model.

In this letter, a commercial-scale thermochemical processing system was used to convert solid digestate into biochar. We found that it is possible to obtain magnetic biochar from solid digestate. Magnetic biochar has previously been produced from a variety of feedstocks, mainly agricultural waste [Thines 2017]. This material has been studied for its capacity of removing contaminants from water, like organics and heavy metals, although it has other potential applications in polymer composites and supercapacitors [Thines 2017] and as a catalyst in dyeing wastewater treatment [Zhang 2018]. Typically, this material is synthesized by exposing the feedstock to an

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iron precursor, such as ferric salts [Faulconer 2012, Zhang 2013, Han 2016]. Using our approach, magnetic biochar was obtained without the need of an iron precursor, hence the novelty of the reported results.

II. MATERIALS AND METHODS

A. Feedstock Material

Solid digestate was collected from a full-scale anaerobic digester located in upstate New York. This plant processes more than 360 t (∼400 short tons) of organic material per day, comprised roughly of 70 v/v% cow manure, and the remaining 30 v/v% a mixture of industrial food wastes. The methane-rich biogas produced is supplied to an engine-generator set rated at 1.4 MW.

The collected digestate samples were sundried until their moisture content was less than 35 wet wt%. Moisture measurements were obtained on site using a moisture scale (Data Support Company, Inc., Panorama City, CA, USA, model DSC 500) with 50 g capacity and 1 mg resolution. Feedstock characterization was performed by an external laboratory, as described ahead. Moisture, ash, and volatile matter values were determined based on the standard test method for chemical analysis of wood charcoal (ASTM D1762-84) [ASTM 2013]; organic carbon and total nitrogen were determined by dry combustion based on the standard test method for rapid determination of carbonate content of soils (ASTM D 4373) [ASTM 2014]; iron, potassium, and phosphorus values were determined using EPA method 3050B: acid digestion of sediments, sludges, and soils in combination [EPA 1996] with EPA method 6010C: inductively coupled plasma-atomic emission spectrometry [EPA 2000].

B. Thermochemical Processing

A commercial-scale thermochemical processing system, the "Biogenic Refinery" manufactured by the Biomass Controls (Putnam, CT, USA), was used to produce biochar. This system was designed for treating biogenic waste, including wood chips, human solid waste, corn, and cardboard. It is comprised of a forced air heat exchanger, a pollution control assembly containing a catalytic converter, a pyrolysis box (or carbonizer), a biochar collection box, and a custom controller that monitors and records conditions during operation (see Fig. 1). For the test runs conducted to produce biochar, digestate was fed through a hopper and fuel auger at an average flow rate of approximately 5 kg/h. Experiments were performed under different combinations of carbonizer temperature and input air flow rate that dictated the oxygen concentration within the zone where thermochemical conversion occurred. For the biochar materials reported here, the temperature setpoint was 800 °C and was maintained within ±25 °C over the course of each approximately 4 h experiment duration. Input air flow was varied by adjusting fan speed between 25% and 50% of its maximum setting. Once the converted feedstock fell by gravity to the bottom of the carbonizer section, a dual auger assembly transported the final solid product to the biochar collection box, where samples were collected every 15 min. Immediately after acquiring samples, they were quenched with fine water spray to cool the biochar material and avoid any further reaction with the ambient air.

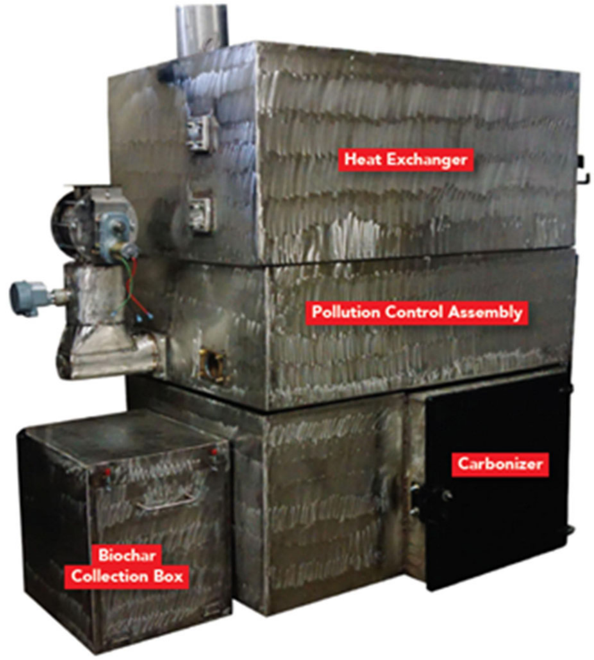

Fig. 1. Commercial-scale "Biogenic Refinery" used to produce biochar from digestate.

C. Characterization of Biochar

Biochar samples were characterized by two external labs based on the International Biochar Initiative (**IBI**) (Watsonville, CA, USA and Tucson, AZ, USA) standardized product Definition and Product Testing Guidelines for Biochar That Is Used in Soil [International Biochar Initiative 2015]. Moisture, total ash, and volatile matter were determined based on method ASTM D1762-84 [ASTM 2013]; organic carbon, hydrogen, and total nitrogen were determined through dry combustion based on method ASTM-D4373 [ASTM 2014]; finally, pH and electrical conductivity were based on the test methods for the examination of composting and compost [USDA 2001] with dilution from Rajkovich [2012].

In addition to the surface area correlation provided by the external laboratory, which uses the butane activity correlation method, we performed surface area analysis in-house, using the multipoint Brunauer–Emmett–Teller (**BET**) method. These measurements were done based on N_2 adsorption using a Quantachrome Nova 4200e surface area and pore size analyzer. Samples were dried under vacuum for 6 h at 120 °C and tested in quadruples.

A scanning electron microscope (**SEM**) (AMRAY 1830) coupled with an X-ray fluorescence (**XRF**) system (IXRF Systems 550i) was used to analyze the surface of the biochar samples and to determine the distribution of iron in each sample. Samples were prepared using carbon conductive double-faced adhesive tape (Nisshin EM Co., Ltd., Tokyo, Japan) and sprayed with a graphite lubricating resistance coating (PELCO).

D. DC Magnetometry

Magnetic measurements were carried out using a Quantum Design VersaLab system with the vibrating sample magnetometer option.

Table 1. Representative characteristics of solid digestate.

Parameter	Value	Units
Moisture	24.5	% wet wt.
Organic Carbon	37.8	% dry wt.
H:C$_{org}$	1.91	Molar Ratio
Ash	7.1	% dry wt.
Volatile Matter	72.9	% dry wt.
Total Nitrogen (N)	1.09	% dry wt.
Total Potassium (K)	3,194	mg/kg dry wt.
Total Phosphorus (P)	5,880	mg/kg dry wt.
Iron (Fe)	8,705	mg/kg dry wt.

Magnetization versus magnetic field $M(H)$ measurements were taken at 300 K in externally applied fields of up to ±3 T. Magnetization versus temperature $M(T)$ curves were taken under the zero-field-cooled (**ZFC**) (samples cooled with zero field) and field-cooled warming (**FCW**) (samples cooled with a 0.01 T field) protocols in the temperature range of 50–350 K and measured with an externally applied field of 0.01 T upon warming.

III. RESULTS AND DISCUSSION

A. Feedstock Characterization

Table 1 presents the characteristics of solid digestate examined in this letter. The iron content of this feedstock is what provides the inherent magnetic characteristics of the biochar made from it. Although the exact source of the Fe is yet to be determined, we have disregarded manure as a potential source, since samples of the solids of manure were analyzed and its Fe content was between 316–461 mg/kg dry, which is significantly lower than the 8705 mg/kg dry that we observed in our samples. The other potential source that we examined was the industrial food waste (**IFW**) that is treated through anaerobic digestion. The type of food waste treated in this facility includes waste from dairy processing and expired dairy products, fat, oil, and grease and some grain waste product of the manufacturing of rice drink. We took representative samples of each source of IFW for a given month, and some of the samples presented high Fe concentrations ranging from 1170–105 600 mg/kg dry. Although broader sampling should be performed to confirm so, we consider that IFW is likely to be the source of the high Fe concentration of the digestate.

B. Biochar Characterization

Fig. 2 shows an SEM image of the surface of the digestate biochar. In this image, we see how the fibrous structure given by the lignin contained in the sample remains even after thermal processing. Fig. 3 shows an XRF image of the Fe distribution in the sample. Fe is distributed throughout the sample, including some Fe-rich clusters.

Table 2 presents characteristics of biochar made from solid digestate. After thermochemical processing, the organic carbon (C$_{org}$) content of the samples increased when compared to the unprocessed feedstock material, reducing the H:C$_{org}$ ratio, which is related to the biochar's stability. The maximum ratio according to IBI is 0.7, since a lower H:C$_{org}$ ratio defines a more stable biochar in soil [International Biochar Initiative 2015].

An assessment of the toxicant substances present in the biochar material is presented in Table 3. This evaluation includes heavy metals that could be contained in the feedstock material. In addition, samples were tested for polycyclic aromatic hydrocarbons (**PAH**s) that can

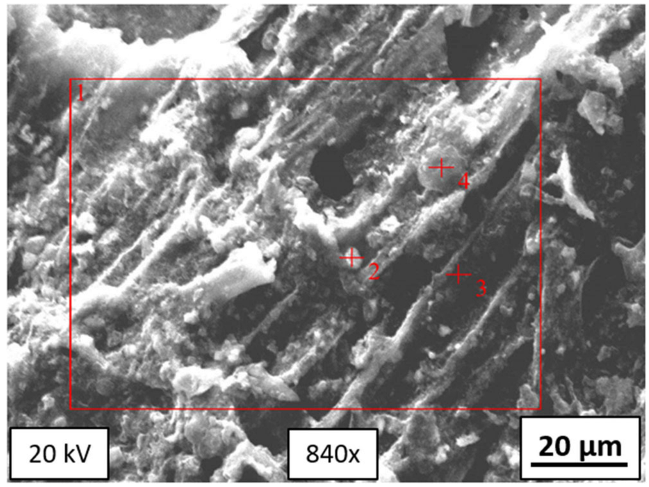

Fig. 2. SEM image of digestate biochar. Magnification 840×. Scale: 20 µm.

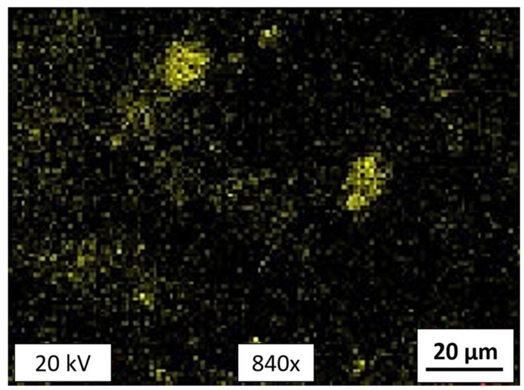

Fig. 3. XRF image of the iron distribution in the sample. Magnification 840×. Scale: 200 µm.

Table 2. Characteristics of biochar made from solid digestate.

Parameter	Value	Unit
Moisture	3.65 ± 1.52[a]	% wet wt.
Organic Carbon	58.99 ± 2.38[a]	% dry wt.
H:C$_{org}$	0.55 ± 0.06[b]	Molar Ratio
Total Ash	26.76 ± 5.50[a]	% dry wt.
Total Nitrogen	1.25 ± 0.22[a]	% dry wt.
Total Potassium (K)	13,376.7±943.7	mg/kg dry wt.
Total Phosphorus (P)	22,033.7±8,143.4	mg/kg dry wt.
Iron (Fe)	31,078.61 ± 7,107.19[a]	mg/kg dry wt.

[a]Average of five samples.
[b]Average of three samples.

Table 3. Toxicant assessment of digestate in biochar.

Parameter	Value	Maximum Allowed Thresholds
	mg/kg dry wt.	
Polycyclic Aromatic Hydrocarbons (PAHs)	ND[c]	6-300
Arsenic (As)	ND[a]	13-100
Cadmium (Ca)	ND[a]	1.4-39
Chromium (Cr)	33.8 ± 19.3[a]	93-1,200
Cobalt (Co)	8.0 ± 2.2[b]	34-100
Copper (Cu)	332.3 ± 96.1[a]	143-6,000
Lead (Pb)	2.6 ±1.0[b]	121-300
Mercury (Hg)	ND[b]	1-17
Molybdenum (Mo)	6.4 ±1.6[b]	5-75
Nickel (Ni)	23.7 ±9.1[a]	47-420
Selenium (Se)	1.2[b]	2-200
Zinc (Zn)	279.0 ±71.4[a]	416-7,400
Boron (B)	46.3 ±7.6[b]	NS
Chlorine (Cl)	2,572.0 ±739.8[b]	NS
Sodium (Na)	7,528.3 ±1,335.8[a]	NS
Manganese (Mn)	496.8 ± 168.1[a]	NS

ND: Non detected.
[a] Average of five samples.
[b] Average of three samples.
[c] Two representative samples tested.
NS: Non specified.

be formed during the thermal conversion processes; this includes the 16 PAH priority compounds identified by the IBI Standard [International Biochar Initiative 2015]. All toxicants tested were found within the allowable thresholds proposed by the IBI standard, making this biochar suitable for agricultural application.

C. DC Magnetometry

$M(H)$ measurements taken at $T = 300$ K indicate that samples show a Langevin-like curve, technical saturation, and coercive fields of $H_C = 0.0098$–0.0130 T across various samples (see Fig. 4 bottom). The ZFC curve of the $M(T)$ plot (see Fig. 4 top) reveals what appears to be a Verwey transition at $T \approx 125$ K [Walz 2002, Chandra 2017] across samples prepared under all processing conditions. The Verwey transition is a property unique to magnetite and is only seen in highly crystalline samples. There is a possibility that our samples contain mixed magnetite (Fe_3O_4) and hematite (γ-Fe_2O_3) particles, in which case, the signal from magnetite tends to dominate [Ahmadzadeh 2018].

We note that the magnetization in these samples is fairly low for magnetite particles. Since the biochar samples have various materials intertwined, it is not feasible to separate the ferrimagnetic materials from paramagnetic and diamagnetic materials in each sample. Therefore, the mass that each magnetization is measured by includes mostly "nonmagnetic" material. Despite the majority of the mass of the sample being comprised of nonmagnetic materials, the $M(H)$ and $M(T)$ plots still show remarkably clean curves, indicating a sample of well-formed magnetic material.

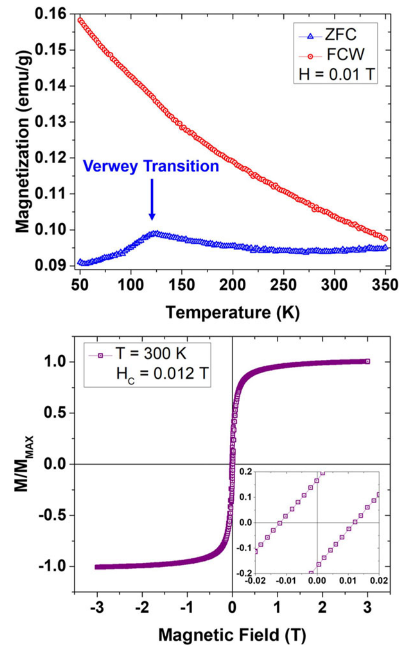

Fig. 4. Magnetization versus temperature taken using ZFC and FCW protocols showing Verwey transition (top). Magnetization versus magnetic field taken at room temperature with inset showing a close-up of the origin to see coercivity (bottom).

Although there are many phases of iron oxide, clear Verwey transition, room temperature hysteresis, and lack of irreversibility temperature indicate that most magnetic particles are likely large Fe_3O_4 rods [Walz 2002, Lee 2015, Chandra 2017, Ahmadzadeh 2018].

IV. CONCLUSION

These findings demonstrate the first known instance of iron oxide produced without the addition of an iron-based precursor during thermochemical processing of biomass to produce magnetic biochar. Furthermore, iron oxide that is present in the samples is magnetite, which is useful for a variety of applications, particularly for sustainable waste management. Future work aims to identify the source of iron present in the digestate and to produce biochar under pure pyrolysis (i.e., zero-oxygen) conditions.

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