



Hydrothermal carbonization of food waste for nutrient recovery and reuse



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ABSTRACT

Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. Laboratory-scale experiments evaluating the hydrothermal carbonization of food wastes collected from restaurants were conducted to understand how changes in feedstock composition and carbonization process conditions influence primary and secondary nutrient fate. Results from this work indicate that at all evaluated reaction times and temperatures, the majority of nitrogen, calcium, and magnesium remain integrated within the solid-phase, while the majority of potassium and sodium reside in the liquid-phase. The fate of phosphorus is dependent on reaction times and temperatures, with solid-phase integration increasing with higher reaction temperature and longer time. A series of leaching experiments to determine potential solid-phase nutrient availability were also conducted and indicate that, at least in the short term, nitrogen release from the solids is small, while almost all of the phosphorus present in the solids produced from carbonizing at 225 and 250 °C is released. At a reaction temperature of 275 °C, smaller fractions of the solid-phase total phosphorus are released as reaction times increase, likely due to increased solids incorporation. Using these data, it is estimated that up to 0.96% and 2.30% of nitrogen and phosphorus-based fertilizers, respectively, in the US can be replaced by the nutrients integrated within hydrochar and liquid-phases generated from the carbonization of currently landfilled food wastes.

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1. Introduction

Concerns associated with anticipated future nutrient demands required to satisfy projected increases in food production due to the growing population are well documented (e.g., Cordell et al., 2009; Dawson and Hilton, 2011). Alexandratos and Bruinsma (2012) estimate worldwide fertilizer requirements will reach approximately 263 million tonnes in 2050. Challenges associated with achieving this level of fertilizer production stem from dwindling nutrient (particularly phosphorus) availability, inefficient nutrient use and/or recovery from residual materials, and/or high energy demands associated with fertilizer production (Cordell et al., 2009; Dawson and Hilton, 2011). Developing effective strate-

gies to overcome these challenges is critical for meeting future food demands.

One promising and potentially sustainable approach to alleviating some of these challenges is to recover nutrients from food waste using hydrothermal carbonization (HTC). Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. In 2014, 38.4 million tonnes food waste were generated in the United States (US) (USEPA, 2016), which contain significant amounts of available nitrogen, phosphorus, and potassium. HTC is a thermal conversion process in which wet feedstocks are converted into value-added liquid, solid (also referred to as hydrochar), and gaseous products (Berge et al., 2011; Funke and Ziegler, 2010; Libra et al., 2011; Sevilla and Fuertes, 2009; Titirici and Antoniette, 2010) without the need for feedstock drying prior to conversion, at relatively low temperatures (<350 °C), and with relatively low input energy requirements (Berge et al., 2011, 2015; Funke and Ziegler, 2010;

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Li et al., 2013; Libra et al., 2011). Managing food wastes using HTC has the potential to reclaim nutrients from these food wastes in a form that may be directly used as a fertilizer/soil amendment, potentially reducing the need for acquisition of virgin nutrients and thus reducing energy demands associated with fertilizer manufacturing.

The feasibility and environmental benefits associated with the HTC of different food wastes (e.g., corn, artichoke waste, onion, fish, mixed urban food waste) and food-related residues (e.g., corn-cob, grape seeds, rice hull, tomato peels) have been previously reported (e.g., Benavente et al., 2015; Cao et al., 2013; Li et al., 2013; Lu and Berge, 2014; Oliveira et al., 2013; Reza et al., 2013; Sabio et al., 2016). Understanding the fate of nutrients as a result of food waste carbonization is necessary to develop a nutrient recovery and recycling strategy. The fate of nitrogen, phosphorus, and/or potassium has been evaluated for a variety of feedstocks, including animal manures (e.g., cow, horse), bamboo, various digestates, straws, algae, and sewage sludge (e.g., Ekpo et al., 2016; Erdogan et al., 2015; Funke, 2015; Funke et al., 2013; Heilmann et al., 2014; Reza et al., 2016; Smith et al., 2016; Zhang et al., 2014). Nutrient fate reported in these studies varies significantly because of changes in feedstock composition/properties and process conditions, complicating the extension of such information to that of different feedstocks.

Relatively little information associated with the fate of primary (e.g., nitrogen, potassium, and phosphorus) and secondary (e.g., calcium, sodium, and magnesium) nutrients as a result of the carbonization of mixed restaurant-generated food wastes exists. Benavente et al. (2015) and Reza et al. (2013) evaluated the fate of nutrients of specific food wastes, reporting that between approximately non detectable levels to 50% and 5–55% of initially present phosphorus and potassium, respectively, ultimately reside in the hydrochar following the carbonization of olive mill, canned artichoke, and orange juice wastes and rice hull. The reported variability associated with nutrient fate in these studies suggests that information specific to the carbonization of restaurant-generated food waste is needed before an appropriate strategy for reclaiming nutrients from this waste stream can be developed.

The purpose of this work is to evaluate the fate of nutrients resulting from the carbonization of food waste collected from local restaurants and to ultimately use such information to determine the potential impact associated with offsetting the need for virgin nutrient acquisition and fertilizer production if using the generated solids as a fertilizer. The specific objectives of this work include to: (1) understand how changes in feedstock composition (e.g., food waste with and without packaging materials) and carbonization process conditions (e.g., reaction time and temperature) influence primary (e.g., nitrogen, phosphorus, and potassium) and secondary nutrient fate (e.g., calcium, magnesium, sodium), (2) determine the total leachable mass of primary nutrients from the solids, and (3) investigate the reduction of virgin primary nutrient requirements if food wastes were hydrothermally carbonized and nutrients subsequently recovered from the solid and liquid-phases.

2. Materials and methods

2.1. Food and packaging material acquisition and properties

Food waste was periodically collected from restaurants located near the University of South Carolina (Columbia, SC), following procedures outlined by Li et al. (2013). Briefly, this food waste consisted of a variety of different components, including seafood, meats, bread, pasta, potatoes, vegetables, and condiments. Immediately following collection, the waste was weighed and non-food materials (e.g., packaging) and food containing bones were removed. Packaging materials were subsequently separated into three categories: (1) paper, (2) cardboard, and (3) plastics. Food containing bones was not used in this study because of experimental constraints. The food waste was subsequently mixed and homogenized with a food-grade blender (Ninja Master Prep, Euro-Pro Operating LLC). All packaging materials (e.g. paper, plastic, cardboard) were shredded using a titanium paper shredder (25 by 4 mm strips). All food and packaging wastes were frozen until use.

The moisture, carbon, nitrogen, phosphorus, potassium, calcium, and magnesium contents of the collected food waste and packaging materials were measured (Table 1). The moisture content of the separated components was measured using a gravimetric technique. A mass of each component was dried in a laboratory oven at 80 °C for at least 48 h, or until the dried sample mass remained constant. Following drying, the carbon and nitrogen contents of the samples was measured using an elemental analyzer (Perkin Elmer 2400). Phosphorus, potassium, calcium, and magnesium contents of these materials were measured on aqueous filtrates of acid digested materials by inductively coupled plasma (ICP) by the Agricultural Service Laboratory at Clemson University. This acid digestion process involved first ashing the samples in a muffle furnace and subsequently dissolving the ash in 6 N HCl.

2.2. Batch HTC experiments

All batch carbonization experiments were conducted following procedures previously described (Berge et al., 2011; Li et al., 2013; Lu et al., 2012). Briefly, 40 g of room temperature food waste and/or packaging materials were placed in 160-mL stainless steel tubular reactors (2.54 cm i.d., 25.4 cm long, MSC, Inc.) fitted with gas-sampling valves (Swagelock, Inc.). All reactors were subsequently sealed and heated in a laboratory oven to the desired temperature. Reactors were sacrificially sampled over a period of 24 h. All experiments were conducted in triplicate. Based on results from Li et al. (2013), the sample masses of food and/or packaging materials used in this study are sufficient for obtaining reproducible results.

Three sets of carbonization experiments were conducted: (1) experiments in which separated food was carbonized at three different temperatures (225, 250, and 275 °C), (2) experiments containing food and packaging materials to evaluate the influence of packaging on food waste carbonization at 250 °C, and (3)

Table 1
Collected food waste and packaging material properties.*

Waste component	Moisture content (% wet wt.)	C (% dry wt.)	N (% dry wt.)	P (% dry wt.)	K (% dry wt.)	Ca (% dry wt.)	Mg (% dry wt.)	Na (% dry wt)
Food Waste	63.79 (0.71)	50.90 (0.57)	3.18 (0.15)	0.42 (0.01)	0.52 (0.01)	0.21 (0.01)	0.05 (0.001)	1.11 (0.04)
Paper	24.52 (6.42)	46.80 (1.12)	0.21 (0.15)	0.02 (0.003)	0.05 (0.006)	0.55 (0.43)	0.03 (0.01)	0.18 (0.06)
Cardboard	12.79 (4.59)	41.43 (1.75)	0.09 (0.02)	0.01 (0.005)	0.05 (0.04)	1.68 (0.31)	0.04 (0.02)	0.11 (0.01)
Plastic	4.10 (2.03)	80.54 (5.42)	0.22 (0.29)	0.01 (0.004)	0.03 (0.01)	0.12 (0.08)	0.01 (0.004)	0.05 (0.03)

* All values represent average values of at least 5 samples. Values in parentheses represent the standard deviations.

experiments carbonizing packaging materials only at 250 °C. The first set of experiments was conducted to determine how reaction temperature and time influence nutrient fate. In these experiments, the food was carbonized at the as received solids content (36.2% dry solids). The second set of experiments was conducted to evaluate the influence of packaging materials on nutrient fate. In these experiments, a packaging concentration of approximately 20% (dry wt.) was evaluated. The third set of experiments, containing only packaging materials, was conducted to understand the nutrient fate when carbonizing packaging materials. These experiments were conducted at a packaging concentration of 20% (dry wt.); deionized water was added to achieve this solids concentration.

At each sampling time, reactors were removed from the oven and immediately submerged in a cold-water bath. Following cooling, the produced gas was collected either in a 1 or 3-L foil gas sampling bag. Gas composition of these samples was analyzed using GC-MS (Agilent 7890) with the method previously described by Li et al. (2013). Gas volumes were measured with a large volume syringe (S-1000, Hamilton Co.).

The process liquid and solid were separated via vacuum filtration through a 0.45 µm cellulose nitrate membrane filter (Whatman International Ltd.). The process water was analyzed for typical water quality parameters. Liquid conductivity and pH were measured using electrodes (Thermo Scientific Orion). Liquid chemical oxygen demand (COD) was measured using HACH reagents (HR + test kit, Loveland, CO). Liquid total organic carbon (TOC) was measured using a TOC analyzer (TOC-Vcsn, Shimadzu). Liquid-phase ammonia-nitrogen and total nitrogen were measured using HACH reagents for the salicylate and persulfate digestion methods, respectively (HACH test kits, Loveland, CO). Total phosphorus, potassium, calcium, sodium and magnesium were analyzed using ICP by the Agricultural Service Laboratory at Clemson University.

All collected solids were dried at 80 °C and moisture contents measured, following procedures previously described. The carbon and nitrogen content of the solids were analyzed using an elemental analyzer (Perkin Elmer 2400). Previously published literature report that solid-phase measurements of potassium, calcium, and magnesium can be complicated by the chemical recalcitrance and varied composition of the solid matrix in which they are integrated (Enders and Lehmann, 2012), with greater variability between measurement approaches (e.g., wet digestion, dry digestion) as carbonization conditions become more severe (e.g., higher temperatures and longer times). Results from solid-phase analyses using a dry digestion process in which aqueous filtrates of acid digested materials by ICP from this work confirm this phenomenon (data not shown). Therefore, solid-phase phosphorus, potassium, calcium, sodium, and magnesium were calculated as the difference between the mass of each found in the initial food waste samples and that measured in the liquid-phase, assuming 100% recovery of these elements.

2.3. Sequential nutrient extraction experiments

Experiments evaluating total leachable nitrogen and phosphorus mass from the hydrochar were conducted to determine potential nutrient release if using the hydrochar as a fertilizer or if extraction of nutrients from the hydrochar is desired. For each experiment, approximately 35-mL of an extractant was added to either 0.1 g or 0.2 g of dried hydrochar in plastic 35 mL centrifuge tubes. These solid to liquid ratios were chosen based on results from preliminary experiments conducted to determine ratios that maximized nitrogen and phosphorus removal in each extraction, while remaining above method detection limits, with the larger mass of solid used in the experiments evaluating the release of total nitrogen. The extractant used in the experiments to evaluate

the phosphorus leachability was Mehlich 3 (0.2 N CH₃COOH, 0.25 N NH₄NO₃, 0.013 N HNO₃, 0.015 N NH₄F, 0.001 M EDTA, Aqua Solutions), which has been commonly used to evaluate plant available phosphorus in different soil matrices (e.g., Wuenschel et al., 2015). When evaluating the leaching of the nitrogen species, 0.01 M CaCl₂ was used as an extractant (e.g., Mengel et al., 2000; Li et al., 2012).

After the hydrochar mass and extract volume were added to each centrifuge tube, the tubes were capped and mixed in a rotary mixer for 24 h. Subsequently, all tubes were then centrifuged at 3000 rpm for 30 min. Approximately 32 mL of supernatant was then removed from each vial and subsequently replaced with same volume of extractant. These vials were then placed in the rotary shaker for an additional 24-h. This process continued until three sequential extractions occurred, which, based on results from preliminary experiments, was sufficient to remove leachable nutrient mass to levels below detection limits. All collected supernatant was filtered through a 0.2-µm hydrophobic polytetrafluoroethylene (PTFE) filter prior to analysis. The phosphorus concentrations in the liquid samples were analyzed at the Agricultural Service Laboratory at Clemson University by ICP. The total nitrogen concentrations in the liquid-phase were measured using a Total Nitrogen Analyzer (Shimadzu, model TNM-L).

2.4. Solid and solution-state ³¹P-NMR

Solid-state ³¹P spectra were collected on a Bruker Avance III-HD 500 MHz spectrometer (202.49 MHz) using a 1.9 mm MAS probe. The spectra were collected at ambient temperature with sample rotation rate of 20 kHz. ¹H dipolar decoupling was performed with SPINAL64 modulation and 145 kHz field strength. Bloch decays were collected with a 25 ms acquisition time over a 590 ppm spectra width with a relaxation delay of 5 s. Chemical shifts are reported with respect to H₃PO₄, and referenced externally with NH₄·H₂PO₄ which was assigned a value of 0.72 ppm.

Solution-state ³¹P spectra were collected on a Bruker Avance III-HD 400 MHz spectrometer (162.03 MHz) using a 5 mm Bruker Prodigy cryo-probe. Sample temperature was regulated at 25 °C. A 200 ppm window centered at 0 ppm (with respect to H₃PO₃) was collected using 30 degree pulses and a 5 s relaxation delay. Inverse-gated ¹H broadband decoupling was used to minimized nuclear Overhauser enhancements. The neat liquids were spiked with 5% D₂O for field-frequency lock and required 256–1024 added transients.

3. Results and discussion

3.1. Carbon mass balances and hydrochar yield

Carbon recoveries in all experiments ranged from 90 to 113%. The observed time-dependent carbon distribution trends are similar to that reported by others (e.g., Knezevic et al., 2009, 2010; Li et al., 2013; Lu et al., 2012, 2013, 2014; Lu and Berge, 2014), during which the fraction of carbon found in the solid-phase decreases, while the fractions in gas-phase increase and fractions in the liquid increase and subsequently decrease. After carbonization reactions are complete, the fraction of carbon in the solid, liquid, and gas-phases stabilizes. Results also suggest that the reaction temperatures investigated in this work impart a small influence on carbon distribution following reaction completion; during early times, temperature plays a more significant role on carbon distribution. The fraction of carbon found in the liquid and solid-phases when carbonizing only food waste differs from that found when carbonizing mixed food and packaging wastes. A greater fraction of carbon is integrated within the solids when carbonizing in the

presence of packaging materials. Conversely, a slightly lower fraction of carbon is found in the liquid-phase when carbonizing in the presence of packaging materials (Fig. 1). Based on these carbon distribution data, carbonization reactions are complete after approximately 4 h, as evidenced by little changes in carbon distribution following this reaction time.

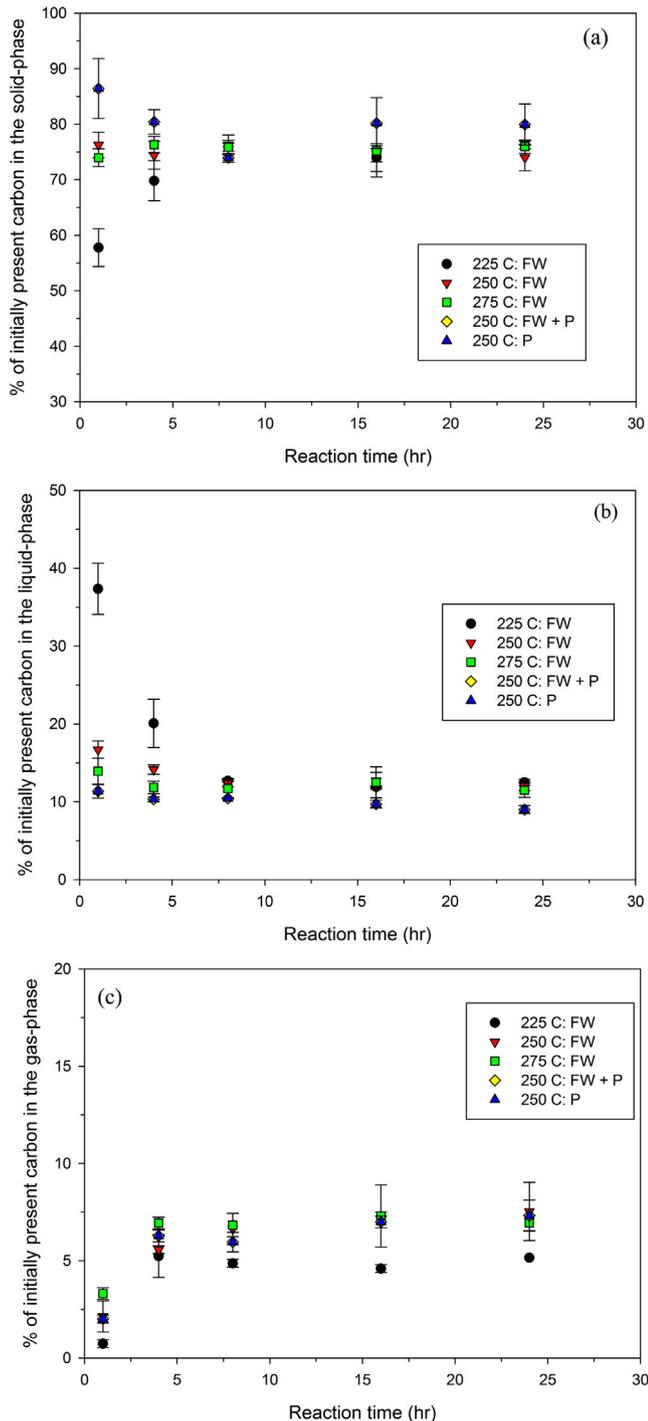


Fig. 1. Distribution of carbon following the carbonization of food waste and mixed food and packaging wastes in the: (a) solid-phase, (b) liquid-phase, and (c) gas-phase. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which only packaging was carbonized are represented by the abbreviation of P. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Trends associated with hydrochar yield are also consistent with that previously reported for a variety of feedstocks (e.g., Li et al., 2013; Lu et al., 2012; Lu and Berge, 2014). The solids recovered decrease with both reaction time and temperature (Fig. 2), resulting from the increased transfer of components of the feedstock to the liquid and gas-phases that occurs at higher reaction temperatures and/or longer reaction times. Hydrochar yields associated with experiments conducted with mixed food and packaging wastes are similar to those achieved when carbonizing at 225 °C. These data also suggest that transfer of inorganic compounds from the solid-phase to the liquid or gas-phases continue after organic carbon-based transformations are complete; at 275 °C, the solid yields do not appear to have stabilized until after 8 or 16 h.

The solids recovered from the carbonization of food waste and packaging materials separately were used to predict the mass of solids recovered when carbonizing food waste in the presence of packaging materials following procedures outlined by Li et al. (2013) and Lu and Berge (2014). Results from this analysis indicate that solid recoveries are relatively uninfluenced by the presence of packaging materials, with the ratio of the predicted to experimental values ranging from 0.90 to 0.98 (Fig. 3a).

3.2. Nutrient fate

3.2.1. Separated food waste

The influence of reaction time and temperature on nutrient fate resulting from food waste carbonization differs for each nutrient evaluated. Total recovered nitrogen (from the solid and liquid-phases) ranged from 89 to 130%, with the average total recovery reducing with reaction time. This result suggests that the presence of gas-phase nitrogen species is possible, with their concentrations slightly increasing with reaction time. Gas-phase nitrogen species were not measured in these experiments. Funke (2015) measured small concentrations of N₂O (volume fractions of up to 0.001) when carbonizing different digestates. Gas-phase ammonia-nitrogen presence is not expected in these studies because conditions are not conducive to ammonia-nitrogen partitioning to the gas-phase; gas samples are taken in cooled systems following carbonization and in which the pH of the process water is always <7. It should be noted, however, that at the high temperatures experienced during carbonization, gas-phase ammonia may be present.

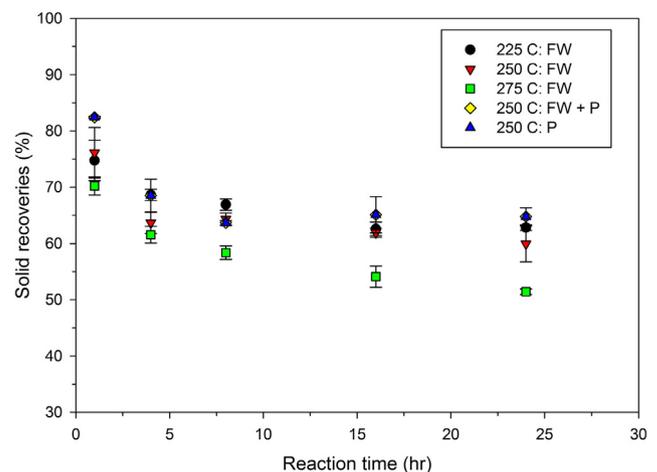


Fig. 2. Solids recoveries resulting from the carbonization of food waste and mixed food and packaging wastes at all reaction times evaluated. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which only packaging was carbonized are represented by the abbreviation of P. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

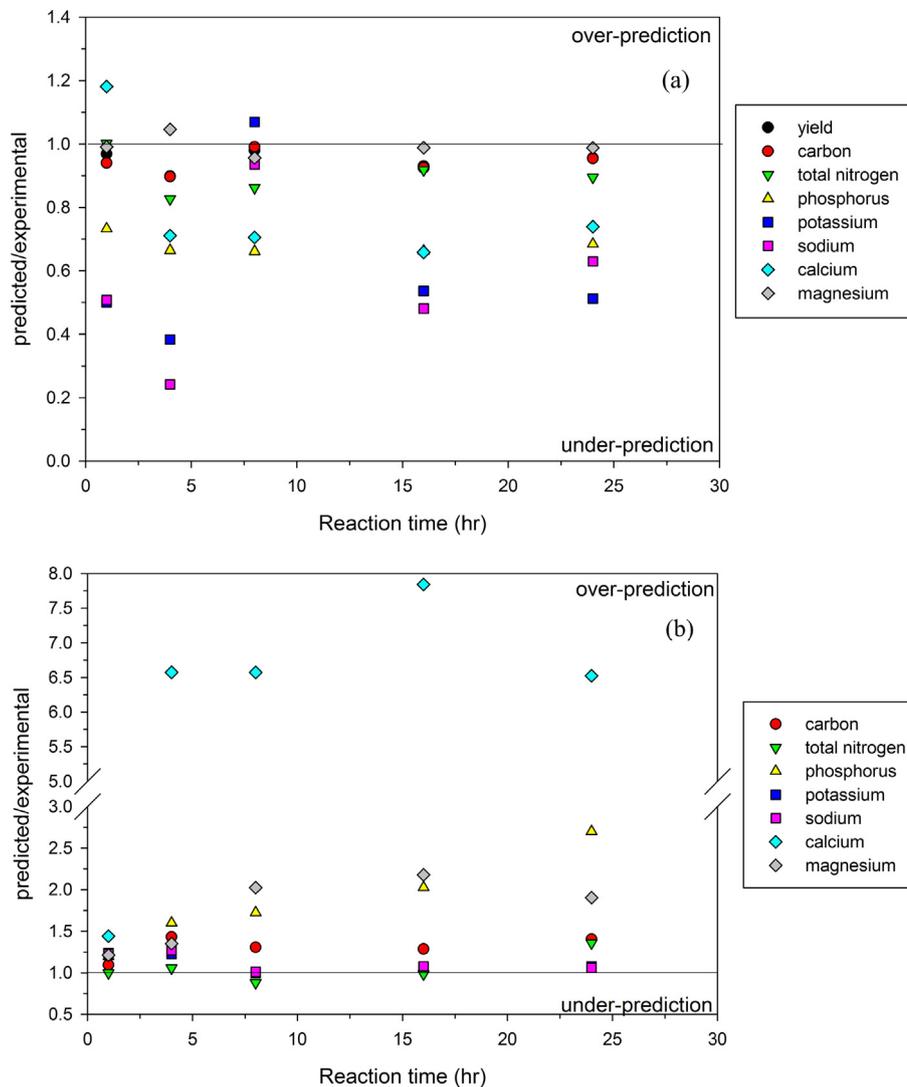


Fig. 3. Ratio of predicted (following procedures outlined by Li et al., (2013) and Lu and Berge (2014)) and actual parameters when carbonizing mixed food and packaging materials at 250 °C: (a) solid-phase and (b) liquid-phase.

If collecting such gas for heat recovery, measurement of real-time ammonia concentrations at the elevated temperatures is necessary.

Reaction temperature and time appear to impart only a small influence on nitrogen fate (Figs. 4 and 5). Changes due to reaction temperature and time are most significant at early reaction times. The majority of initially present nitrogen (>50%) remains integrated within the solid-phase at all reaction temperatures and times. Total nitrogen concentrations in the liquid-phase are also uninfluenced by reaction temperature and time. However, liquid-phase ammonia-nitrogen concentrations are impacted by reaction temperature and time, with ammonia concentrations increasing with higher reaction temperatures and longer times (Fig. 6), similar to those reported by Kruse et al. (2016). These results suggest that once the organic fraction of nitrogen is released to the liquid-phase, conversion to ammonia-nitrogen occurs. Conversion of organic-nitrogen to ammonia under high temperature and pressure environments has been previously reported (Sato et al., 2014).

The majority of initially present potassium (>75%) and sodium (>75%) reside in the liquid-phase following carbonization of food waste, with specific reaction conditions imparting little influence on this distribution (Fig. 5) after 4 h. Potassium and sodium have

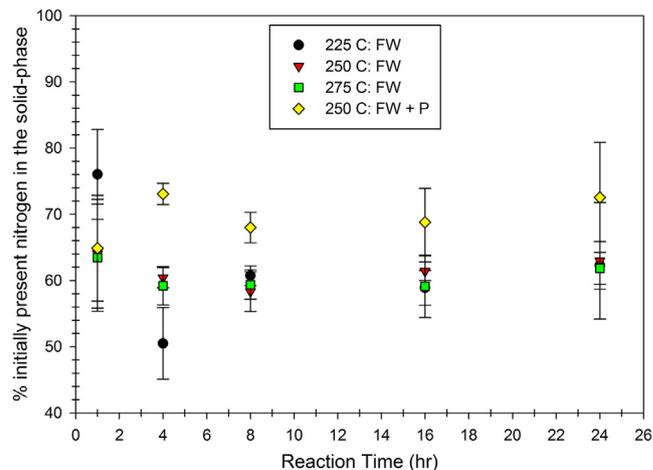


Fig. 4. Fraction of total nitrogen in the solid-phase. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

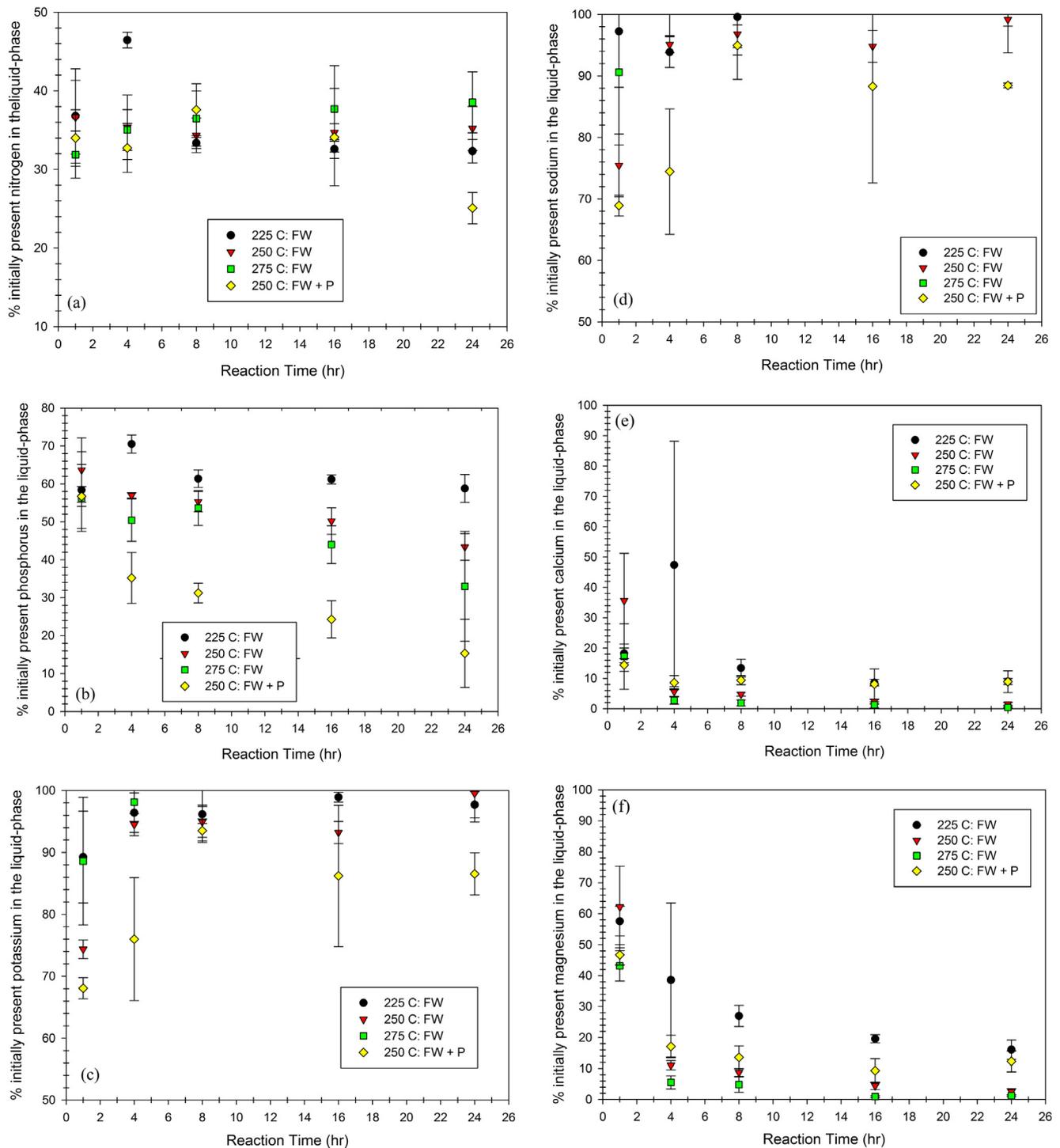


Fig. 5. Fraction of nutrients in the liquid-phase: (a) total nitrogen, (b) phosphorus, (c) potassium, (d) sodium, (e) calcium, and (f) magnesium. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

large water solubilities, so this result is expected. This is also consistent with many previously published reports (e.g., Funke, 2015; Funke et al., 2013).

Phosphorus fate does depend on reaction time and temperature. Phosphorus integration within the liquid-phase decreases with reaction temperature and time (Fig. 5b). This decreasing trend of phosphorus in the liquid-phase corresponds to increases in the fraction of initially present phosphorus integrated within the

solid-phase as the reaction time and temperature increase (note that the trend associated with the solid-phase is a result of a calculation). These trends may result from precipitation with cations present in the process water (e.g., calcium, magnesium, aluminum, iron) and/or integration within the solids via sorption. The pH of the process water following carbonization increases with reaction time, but is always less than 6.6, with higher pH values resulting when carbonizing at higher reaction temperatures. This increase

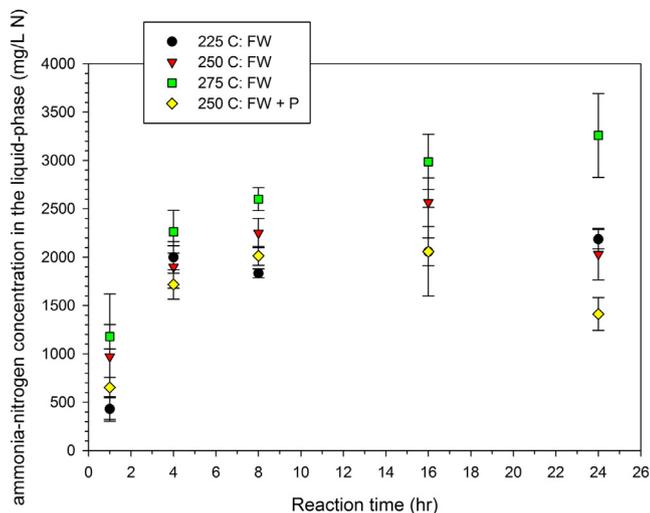


Fig. 6. Ammonia-nitrogen concentrations in the liquid-phase for all reaction temperatures, times, and feedstocks evaluated. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

in pH correlates with the increasing trend of phosphorus integration within the solids, suggesting this integration may result from precipitation-induced phenomena. Phosphate sorption to any deposited and active iron and/or aluminum sites is also possible, which has been observed in soils and clays (e.g., Giesler et al., 2005; Takaya et al., 2016; Violante and Pigna, 2002).

Based on results from solid-phase ^{31}P -NMR (Fig. 7a contains some representative spectra), fractions of initially present phosphoesters (e.g., lipids) in the food waste are hydrolyzed to phosphates as food wastes are carbonized. Following 24-h of carbonization, some phosphoesters remain integrated within the solids at all evaluated reaction temperatures, suggesting either sequestration and/or incomplete conversion of the initially present phosphorus-containing material. Based on comparisons between the normalized aggregate areas (area/number of scans) of the phosphoester regions present in the ^{31}P -NMR spectra, reaction time, temperature, and presence of packaging materials play a role in phosphoester hydrolysis (Fig. 7b). The phosphoester content of the solids generated at the different reaction temperatures when carbonizing only food wastes is smallest after carbonizing for 24 h and decreases with increasing reaction temperature. The presence of phosphate in the solids is observed at all reactions times when carbonizing food wastes at 250 °C, but only at late (24 h) and early times (1 h) when carbonizing at 225 and 275 °C, respectively, consistent with the relative degree of hydrolysis occurring at each temperature. The presence or absence of phosphate in solids may be indicative of either kinetic effects associated with phosphoester hydrolysis, phosphate dissolution in the liquid-phase, interaction with metal complexes, and/or instrument detection limits. Phosphate-metal precipitates may be formed, which are difficult to distinguish using standard ^{31}P -NMR. These results differ from those reported for the carbonization of sewage sludges. Huang and Tang (2015) report that all initially present phosphoesters are hydrolyzed when carbonizing sewage sludges. However, initially present phosphoesters in the sludges are significantly lower than those found in food waste. Liquid-phase ^{31}P -NMR results from select process waters indicate that >99% the phosphorus present in the process water is in the form of phosphate (data not shown).

The majority of initially present calcium (>50%) also remains integrated within the solid-phase at the majority of the reaction

times and temperatures (Fig. 5). After 4 h, reaction temperatures and time appear to impart a slight influence on calcium fate. Integration of calcium within the solid-phase increases with reaction temperature. After a reaction period of 4 h, calcium integration within the solid-phase stabilizes. Similarly, with the exception of carbonizing for 1 h, the majority of magnesium remains integrated within the solid-phase (Fig. 5). The degree of this integration increases with reaction temperature and time, with trends stabilizing after 16 h for all reaction temperatures.

3.2.2. Influence of packaging material presence

The nutrient masses resulting from the carbonization of food waste and packaging materials separately in both the solid and liquid-phases can be used to predict the distribution of each nutrient in the mixed food waste and packaging experiments. Results from this analysis, coupled with experimental results (Fig. 5), indicate that the presence of packaging materials does influence the fate of most of the nutrients evaluated.

All solid-phase nutrients, with the exception of magnesium, are under-predicted (Fig. 3a), suggesting the presence of packaging materials promotes either nutrient precipitation, nutrient chemical incorporation within the solid matrix during carbonization, and/or nutrient sorption to the solids, leading to their greater retention in the solid-phase. It is not possible to determine which (or if all) of these processes cause greater nutrient retention in the solid-phase. Although the total nitrogen content of the solid-phase is under-predicted, the ratios of predicted to experimental values (1.0 to 0.83) suggest such predictions are reasonable.

The composition of packaging materials (e.g., paper, plastics, and cardboard) may promote enhanced nutrient precipitation. The cardboard and paper components of the packaging materials used in this work contain approximately 8 and 3 times more calcium than that found in the food waste (Table 1). In addition, packaging materials typically contain significantly greater levels of iron, aluminum, and chromium than food wastes, all potentially contributing to possible enhanced precipitation and/or sorption. The pH of the process water following carbonization of mixed food and packaging materials is always less than 4.7, suggesting precipitation in these experiments may be limited. Enhanced sorption of phosphate to active aluminum or iron sites on the hydrochar may also occur (e.g., Giesler et al., 2005; Takaya et al., 2016; Violante and Pigna, 2002).

Based on comparisons between the normalized aggregate areas of the phosphoester regions present in the ^{31}P -NMR spectra, the presence of packaging materials decreases (or slows down) phosphoester hydrolysis (Fig. 7b). In addition, when carbonizing food and packaging materials, no phosphates are observed in the solids, only phosphoesters. The presence or absence of phosphate in solids may be indicative of either kinetic effects associated with phosphoester hydrolysis, phosphate dissolution in the liquid-phase, interaction with metal complexes, and/or instrument detection limits.

Greater integration of potassium and sodium in the solids is not likely due to precipitation because of their high water solubilities. Instead, it is more likely greater retention of these nutrients is due to either sorption and/or incorporation within the solid matrix during carbonization. Incorporation of greater calcium in the solid-phase may result from either sorption or precipitation.

3.3. Nutrient availability

Because the majority of the nitrogen and phosphorus found in the food waste remains integrated within the solids following carbonization, a series of leaching experiments were conducted to determine availability of nutrients in the hydrochar when applied to soil as an amendment. Nitrogen and phosphorus present in the

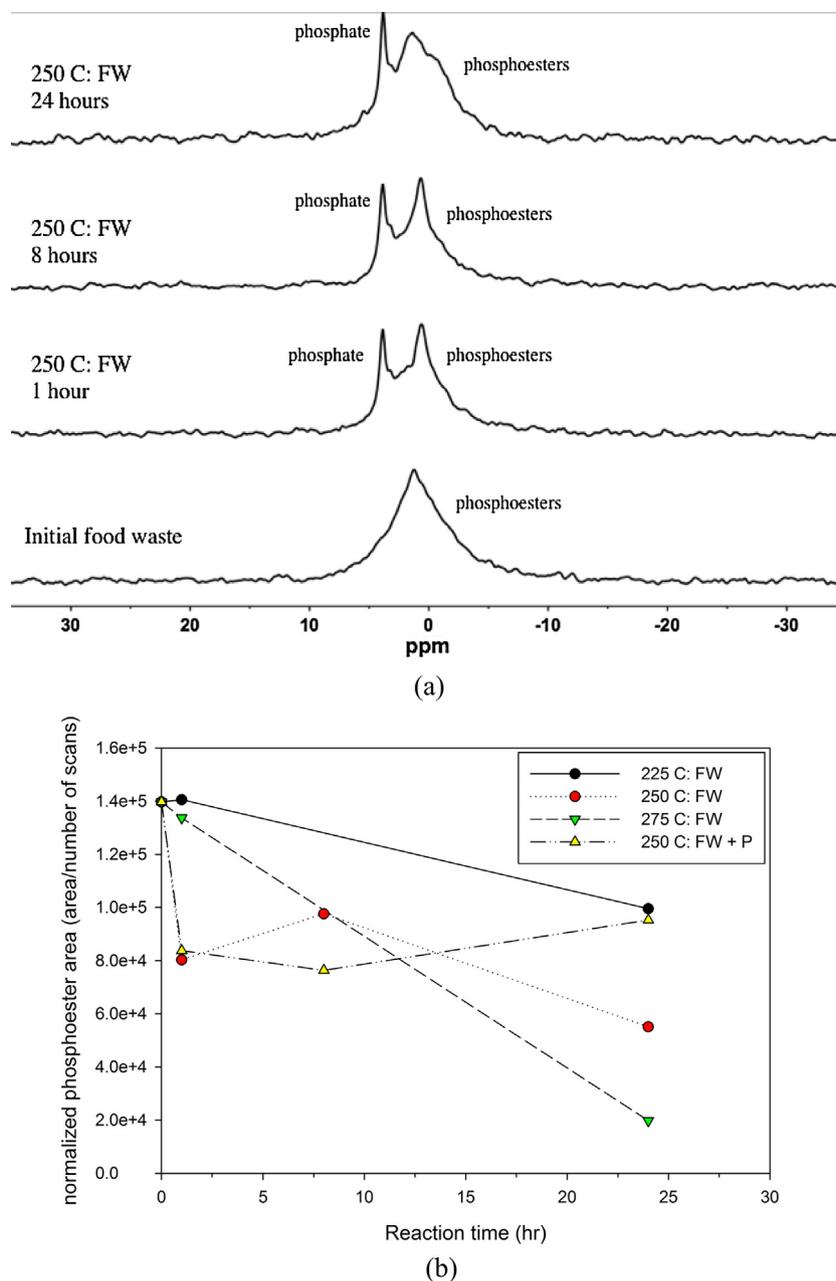


Fig. 7. ^{31}P -NMR results from hydrochar generated during the carbonization of food and mixed food and packaging wastes: (a) representative ^{31}P -NMR spectra for food waste and hydrochars generated when carbonizing at 250 °C and (b) normalized phosphoester areas detected in the hydrochars generated at select reaction times and temperatures (note that the lines are provided for visual guidance). Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

dried solids result from either: (1) processes occurring during hydrothermal carbonization (e.g., chemically integrated with the solids and/or sorbed on the solid matrix) or (2) are a result of deposition of nutrients present in the bound process water during solids drying. It is assumed that nutrients deposited during solids drying and those sorbed on the solids matrix are more loosely bound than those integrated within the solids matrix via chemical reactions.

Results from experiments associated with the leaching of total nitrogen from hydrochars generated from food waste with and without packaging material suggest that the majority of leached nitrogen is from the nitrogen deposited on/within the hydrochar matrix during the evaporation of bound process water (Fig. 8). At each reaction condition, the mass of nitrogen deposited on the

hydrochar from liquid evaporation (based on the mass of nitrogen in the liquid that is evaporated during oven drying) is always greater than the mass of released total nitrogen (Fig. 8), except for the mildest carbonization condition (e.g., 225 °C and 1 h). These results suggest that, at least in the short term, most nitrogen is either tightly bound within the solid matrix or is present in an insoluble form and is unlikely to be released in the liquid-phase. It should also be noted that carbonization at more mild conditions (e.g., lower reaction times and shorter reaction temperatures) may reduce the fraction of tightly bound nitrogen or formation of high molecular weight insoluble nitrogen, as suggested by the result at 225 °C and 1 h; more experiments at such conditions are needed to substantiate this hypothesis. It is possible that additional nitrogen

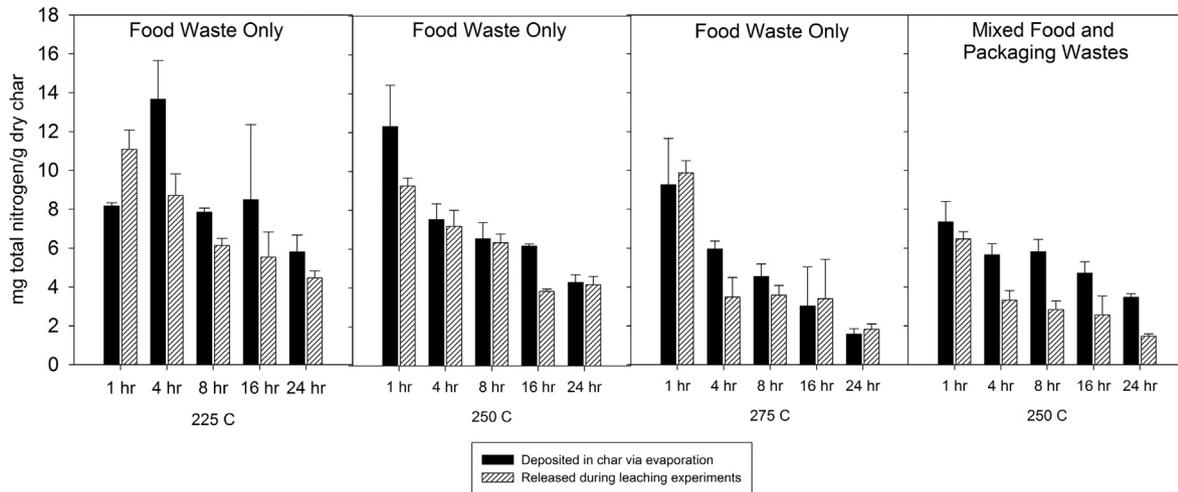


Fig. 8. Comparison between the total nitrogen deposited in the hydrochar from process water evaporation and the total nitrogen released from the sequential extraction experiments. Error bars represent the standard deviation of the conducted experiments.

will be released from the solids if hydrochar degradation occurs. These results also suggest that it may be more beneficial to recover nitrogen from the process water.

Results associated with the release of solid-phase phosphorus are different. Almost all of the phosphorus present in the solids at reaction temperatures of 225 and 250 °C is released (Fig. 9). At a reaction temperature of 275 °C, smaller fractions of the total phosphorus present in the solids are released as reaction times increase, likely due to increased solids recalcitrance (e.g., Enders and Lehman, 2012). These results suggest that recovery of phosphorus from the solids is feasible, and when considering strategies for using hydrochar as a fertilizer, reaction temperatures should remain below 275 °C.

3.4. Potential environmental implications

A potential environmental benefit associated with using HTC to treat/manage food wastes is the ability to recover and use the nutrients embedded within these wastes. Accomplishing this nutrient recycling has the potential to reduce the need for acquiring virgin nutrients required to produce chemical fertilizers, ultimately reducing the stresses on current nutrient supplies and reducing the energy required with this acquisition. Recycling of

nutrients from products resulting from HTC may occur separately or simultaneously from the liquid and solid-phases.

3.4.1. Nutrient recovery from the solid-phase

Using the experimental data obtained from this work (e.g., solid yields and leaching of solid-bound nutrients), estimates of potential nutrient recovery from currently landfilled food wastes were performed. Table 2 contains the information used to estimate the amount of fertilizer that can be replaced by recycling nutrients following the carbonization of food wastes. These calculations were performed for a range of food waste masses diverted from landfills (10–100% diversion). Fig. 10 shows the average percentages of nitrogen and phosphorus fertilizers that can be replaced with nutrients available from the hydrochar. Table 3 presents the HTC conditions yielding the maximum hydrochar nutrient recovery, as well as the percentage of fertilizer used in the US in 2011 that can be replaced with the hydrochar generated from food waste carbonization. These results indicate that the generated hydrochar can replace only a small fraction of the currently used nitrogen and phosphorus-based fertilizers (0.61% and 2.06%, respectively). Although these fractions are not large, substitution of these fertilizers with the recovered nutrients from food wastes would alleviate the dwindling phosphorus supply. In addition, mostly non-

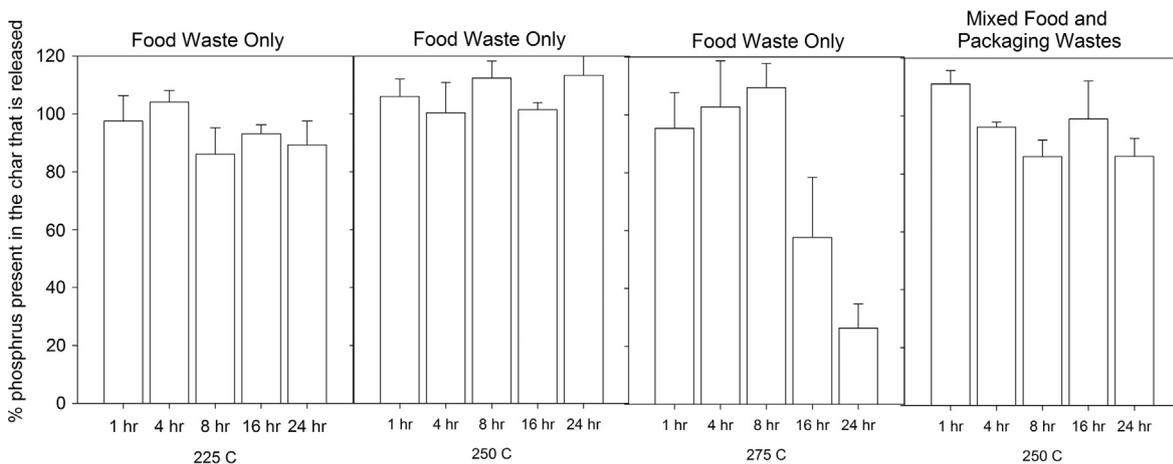


Fig. 9. Percentages of phosphorus released during the sequential extraction experiments. Error bars represent the standard deviation of the conducted experiments.

Table 2

Data used to estimate the amount of fertilizer that can be replaced by recycling nutrients following the carbonization of food wastes.

Parameter	Value	Source
Landfilled Food Waste	26.7 million tonnes	USEPA (2016)
Food Waste Moisture Content	70% (wet wt.)	Tchobanoglous (1993)
Amount of phosphorus (as P ₂ O ₅)-based fertilizer used in 2011 in the US	3.92 million tonnes	USDA (2013)
Amount of nitrogen (as N)-based fertilizer used in 2011 in the US	11.65 million tonnes	USDA (2013)
Amount of potassium (as K ₂ O)-based fertilizer used in 2011 in the US	4.16 million tonnes	USDA (2013)
Energy required to manufacture phosphorus-based (as PO ₄ ³⁻) fertilizer	7700 kJ/kg	Gellings and Parmenter (2004)
Energy required to manufacture nitrogen-based fertilizer	69530 kJ/kg	Gellings and Parmenter (2004)

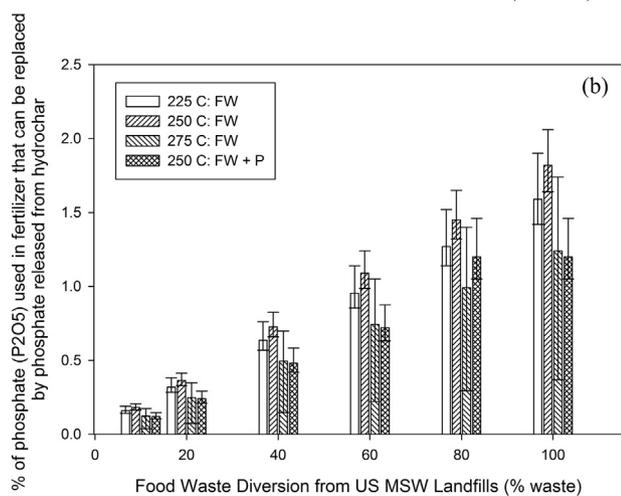
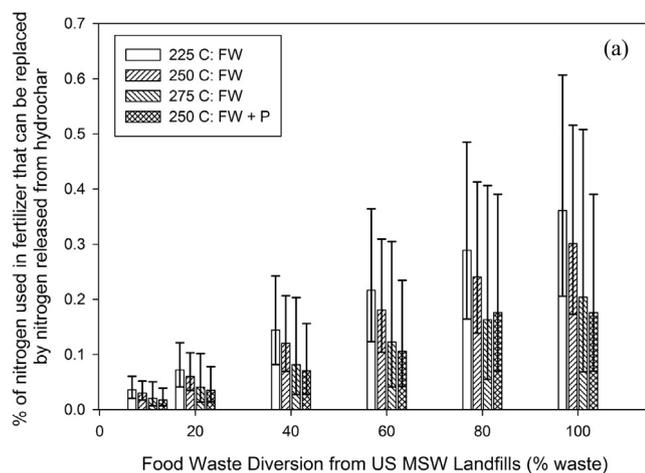


Fig. 10. Percentage of nitrogen and phosphate fertilizers that can be replaced by nutrients released from the hydrochar: (a) nitrogen and (b) phosphate. Each bar represents the average value associated with all reaction times evaluated. Error bars represent the range (max and min) of the data at each condition. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Table 3Reaction conditions resulting in the maximum average nutrient recovery from the solid-phase.^a

Nutrient	Reaction Temperature (°C)	Reaction Time (hr)	Recoverable Nutrient Mass (mg/g dry hydrochar)	% Replacement of fertilizer used in 2011
Total Nitrogen	225	1	11.1	0.61
Phosphorus (as P ₂ O ₅)	250	1	13.8	2.06

^a Assuming 100% diversion of food wastes from landfills in the US.

Table 4Average energy savings associated with replacing virgin fertilizer with hydrochar-based fertilizer (kJ).^a

Carbonization conditions		Nitrogen fertilizer		Phosphate fertilizer	
Feedstock	Temperature	min	max	min	max
FW	225	1.66E+12	4.91E+12	5.74E+11	7.68E+11
FW	250	1.40E+12	4.18E+12	6.64E+11	8.33E+11
FW	275	5.54E+11	4.11E+12	1.49E+11	7.04E+11
FW + P	250	5.65E+11	3.16E+12	4.24E+11	5.88E+11

^a Assuming 100% diversion of food wastes from landfills in the US.

renewable energy used for synthesizing chemical fertilizers will be reduced. Table 4 presents the energy savings resulting from replacing chemical fertilizers with recycled nutrients from the hydrochar (note that this value does not include any energy-related needs/savings associated with the HTC process). It should also be noted that the hydrochar contains appreciable levels of secondary nutrients, particularly calcium and magnesium. Leaching experiments were not conducted to evaluate the availability of these nutrients, but it is likely that some of them may be slowly released in soils, providing an extra benefit.

3.4.2. Nutrient recovery from the liquid-phase

Recovery of nutrients from the process water may also be possible. Table 5 presents the HTC process conditions in which the maximum nutrient recovery in the liquid is achieved, as well as the percentage of fertilizer used in the US in 2011 that can be replaced by recycling these nutrients from food waste. The information in this table is based on the data in Table 2 and assuming 100% of food wastes landfilled are carbonized. It is important to note that these calculations assume that only nutrients found in the process water drained via gravity will be applied as a fertilizer. Additional nutrient recovery from the liquid will be possible if liquid recovery via mechanical processes occurs. Du et al. (2012) report that diluted process water can serve as an effective fertilizer for cultivating microalga *Chlorella vulgaris*, suggesting that this assumption may be valid. Conversely, Bargmann et al. (2013) report components present in HTC process water adversely influence plant growth/germination. However, no studies specifically evaluating the ability of the process water from food wastes and mixed food and packaging wastes to serve as an effective fertilizer

Table 5
Maximum average nutrient recovery from the liquid-phase.*

Nutrient	Reaction temperature (°C)	Reaction time (h)	Recoverable Nutrient Mass (mg/g wet food waste)	% Replacement of fertilizer used in 2011
Total Nitrogen (as N)	275	16	2.9	0.66
Phosphorus (as P ₂ O ₅)	275	8	1.05	0.71
Potassium (as K ₂ O)	275	24	2.06	1.32

* Assuming 100% diversion of food wastes from landfills in the US.

Table 6
Optimal operating conditions for maximum average combined nutrient recovery from the solid and liquid-phases.*

Nutrient	Reaction temperature (°C)	Reaction time (h)	% Replacement of fertilizer used in 2011
Total Nitrogen (as N)	225	1	0.96
Phosphorus (as P ₂ O ₅)	250	24	2.30

* Assuming 100% diversion of food wastes from landfills in the US.

have been reported in the literature. Additional studies are necessary to confirm that the other organic compounds present in the liquid do not cause any inhibitory effect on plant growth or present any environmental concerns. If using the process water as a fertilizer, secondary nutrients will also be added to the soil. The nutrient mass per mass of wet food waste of each of these nutrients is provided in Fig. 11.

3.4.3. Combined nutrient recovery from the liquid and solid-phases

The carbonization process conditions associated with optimal nitrogen and phosphorus recovery from the solid and liquid-phases are different (Tables 3 and 5). The optimal HTC process conditions for the maximum possible recovery of the nutrients from both hydrochar and its process water are shown in Table 6. Using these data, it is estimated that up to 0.96% and 2.30% of nitrogen and phosphorus-based fertilizers in the US (accounting for recovery from both hydrochar and the process water), respectively, can be replaced by the nutrients integrated within hydrochar and process water generated from the carbonization of currently landfilled food wastes.

4. Conclusions

Results from this work indicate that at all evaluated reaction times and temperatures, the majority of nitrogen, calcium, and magnesium remain integrated within the solid-phase, while the majority of potassium and sodium reside in the liquid-phase. The fate of phosphorus is dependent on reaction times and temperatures, with solid-phase integration increasing with higher reaction temperature and longer time. Results from the leaching experiments suggest that, at least in the short term, nitrogen within the solid matrix is unlikely to be released because it is either tightly bound within the solids matrix or in an insoluble form, while almost all of the phosphorus present in the solids generated when carbonizing at 225 and 250 °C is released. At a reaction temperature of 275 °C, smaller fractions of the solid-phase total phosphorus are released as reaction times increase, likely due to increased solids incorporation. Using these data, it is estimated that up to 0.96% and 2.30% of nitrogen and phosphorus-based fertilizers (accounting for recovery in the liquid and solid-phases), respectively, in the US can be replaced by nutrients integrated within hydrochar and liquid-phases generated from the carbonization of currently landfilled food wastes.

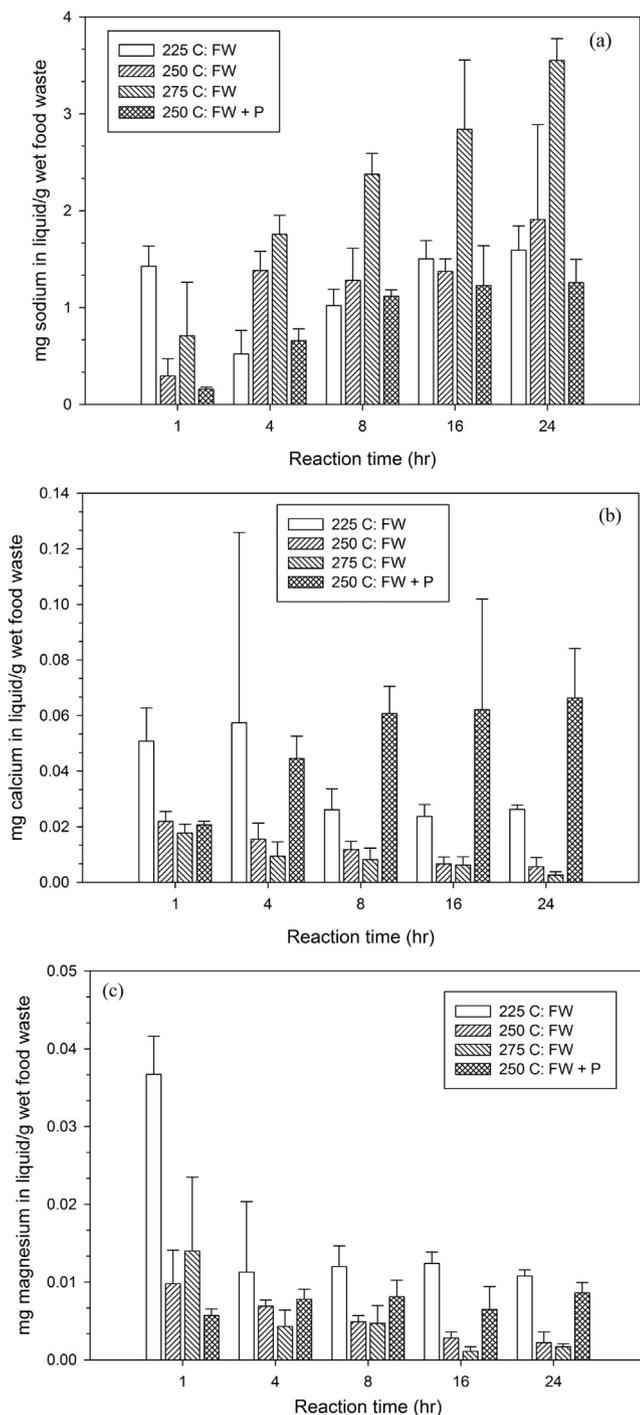


Fig. 11. Time and temperature dependent availability of secondary nutrients in the liquid: (a) sodium, (b) calcium, and (c) magnesium. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

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