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Phosphorus Reclamation through Hydrothermal Carbonization of Animal Manures

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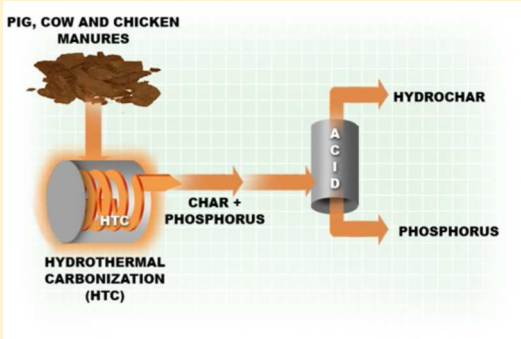
S *Supporting Information*

ABSTRACT: Projected shortages of global phosphate have prompted investigation of methods that could be employed to capture and recycle phosphate, rather than continue to allow the resource to be essentially irreversibly lost through dilution in surface waters. Hydrothermal carbonization of animal manures from large farms was investigated as a scenario for the reclamation of phosphate for agricultural use and mitigation of the negative environmental impact of phosphate pollution. Hydrothermal reaction conditions were identified for poultry, swine, and cattle manures that resulted in hydrochar yields of 50−60% for all three manures, and >90% of the total phosphorus present in these systems was contained in the hydrochars as precipitated phosphate salts. Phosphate recovery was achieved in yields of 80−90% by subsequent acid treatment of the hydrochars, addition of base to acid extracts to achieve a pH of 9, and filtration of principally calcium phosphate. Phosphate recovery was achieved in yields of 81−87% based on starting manures by subsequent acid treatment of the hydrochars, addition of base to acid extracts to achieve a pH of 9, and filtration of principally calcium phosphate. Swine and cattle manures produced hydrochars with combustion energy contents comparable to those of high-end sub-bituminous coals.



INTRODUCTION

The global human population is growing at a phenomenal rate, with the current population of 7 billion projected to increase an additional 2.3 billion by 2050.[1] Of the many accompanying and formidable problems that confront the world now and will in the future, one of the most serious may be the availability of phosphorus.[2−4] Although contrary opinions have been expressed on this issue,[5,6] phosphorus is an essential element for the growth and survival of both plants and animals, and the primary source of concentrated phosphorus is phosphate rock, which is a nonrenewable resource. Additionally, 84% of projected global reserves[6] of phosphate rock are located in just five countries, with one (Morocco) having 36% of the total reserves. Such disproportionate distribution of this natural resource could lead to significant fluctuation and instability in the price of phosphate rock, greatly affecting the cost of agriculture and food.[7] Regardless of whether a shortage of phosphorus impacts the world within this century or in the more distant future, it is important that appropriate reclamation processes be developed.

Prior to the mid-20th Century, cattle, hogs, and chickens in the United States were essentially all produced on small family farms, and phosphorus was recycled back onto the soil in fields by application of phosphorus-rich animal manures. That practice has changed considerably, with small family farms being displaced by large corporate-owned farms that specialize in the production of one domestic farm animal in very large numbers. Concentrated animal feeding operations (CAFOs) that produce massive amounts of manures have been created. In many instances, the literally thousands of animals present in one location create more manure than is useful for land application in adjacent and nearby fields. This creates a neutral or even negative value for the nutrient-rich material.

An additional environmental problem is also created by agricultural application of huge quantities of mined phosphate rock, i.e., 148 million metric tons globally per year.[4] It has been

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estimated[8] that only 30% of fertilizer and feed phosphorus is output into crops and animals. Phosphorus that is not incorporated is washed with rains into rivers, lakes, aquifers, and oceans, thereby undergoing dilution to a point that virtually precludes economical reclamation. Increased concentrations of phosphate (and nitrate) in surface waters stimulate the growth of microalgae causing "algal blooms". The microalgae die, and oxygen in the water is consumed by bacteria as they degrade the dead algae, leading to a hypoxic condition, fish kills, and "dead zones".[9] Having the ability to recover phosphates, fully or partially, will also facilitate meeting federal regulatory limits in discharged waters that are becoming more stringent for permissible phosphorus levels from CAFOs.

Animal manures do posit promising future sources of phosphorus for recycling. Feces/urine outputs from CAFOs are collected in lagoons, deep pits, or other collection vessels and could conceivably be processed to recycle phosphate. Projections of quantities of phosphorus (as P_2O_5 equivalents) for various U.S. farm animals in CAFOs are listed in Table 1, and significant quantities of phosphate that could reduce pressure on limited phosphate rock reserves are potentially available from these manures.

Table 1. Phosphorus Contents in U.S. Farm Animal Manures[10]

animal type	animal size (lb)	P_2O_5 (lb/day)	no. of animals	annual P_2O_5 (lb)
poultry, layers	3	0.0008	345 million[11]	102 million
swine, grow to finish	50−300	0.060	40.9 million[12]	894 million
cow, lactating	1400	0.52	9.2 million[13]	1.745 billion

Phosphates have been recovered from animal manures that have been dried and incinerated to ash or pyrolyzed to biochars and processed to reclaim inorganic phosphates.[14] Hydrothermal carbonization (HTC), however, has received little if any attention as a reclamation operation with animal manures. Inherent with HTC is an advantage that energy is not required to dry biomass substrates. Water is required in HTC and involves a process in which biomass that is either dissolved or suspended in water is heated at temperatures from 180 to 250 °C in a confined system.[15] Two products are created: a solid hydrochar and an aqueous suspending solution containing soluble inorganic salts and organic compounds. HTC of municipal sewage wastes, often termed "thermal hydrolysis" in the waste processing industry, has been conducted sporadically over an extended period of time in Europe[16] and Canada.[17] Benefits of thermal hydrolysis conducted at temperatures of 130−175 °C are disinfection, odor improvement, greatly improved anaerobic digestion of the slurry product, and dewatering to as much as 80%.[18] More recently, overall energy input/output determinations that indicate that conducting HTC and drying the hydrochar are more energetically favorable than drying the sludge for incineration have been reported.[19] Separation of hydrochars and aqueous suspending media has generally not been conducted with sewage wastes because efficient filtration occurs only with product slurries generated at temperatures in excess of 190 °C.[20] Bioconvertibility, however, was shown to be negatively impacted with slurries created employing HTC temperatures in excess of 175 °C.[21] Therefore, anaerobic digestion has generally been conducted with lower HTC temperatures and on slurry products directly. It has been recognized that phosphorus is concentrated in sewage sludge hydrochars, even after digestion, and sewage hydrochars have been employed in agriculture and land reclamation.[16] The increased phosphorus content in hydrochar produced from swine manure compared to that in hydrochar produced from starting manure was also reported,[22] but no attempt to recover phosphate from the hydrochar was made.

European countries have assumed a leadership role in efforts to mitigate the potential scarcity of phosphorus,[23] and two processes have been developed[24] for its recovery from municipal sewage wastes. The BioCon process involves incineration of sewage sludge to obtain a phosphate-rich ash, followed by treatment of the ash with sulfuric acid to generate soluble phosphate. Phosphoric acid can ultimately be isolated by application of the following process sequence: (1) removal of metal cations by ion exchange, (2) acidification of the eluate, and (3) evaporation of water. The Cambi/Krepro process involves subjecting sewage sludge to mild (∼150 °C) HTC at low pH (∼1), which directly provides soluble phosphate in the aqueous product stream. The phosphate-depleted hydrochar can be separated by centrifugation and ferric chloride added to the aqueous centrate solution to produce insoluble ferric phosphate as a fertilizer product.

The principal objective of this investigation was to examine HTC of poultry, swine, and cattle manures, determine levels of phosphorus captured in the hydrochars under various reaction conditions, and examine methods of extracting phosphate from the hydrochars. Phosphates were recovered by acid treatment of hydrochars to solubilize multivalent metal phosphates, and calcium phosphate-rich solids were obtained by filtration after treatment with base to obtain an alkaline pH. Aqueous product streams obtained by filtration of the hydrochars were also characterized and their fertilizer efficacies assessed.

■ EXPERIMENTAL PROCEDURES

Manures. All manures were "fresh" and not "litters" in the sense that they contained only feces and urine, with minimal additional water and no inert materials, e.g., bedding and straw. Furthermore, none of the manures were obtained from pit storage that had been subjected to microbial degradation. Poultry manure (chicken, layers; from Michael Foods, Inc., Gaylord, MN) and swine manure (finishing hogs; from the Brad Smith Farm, Terril, IA) were collected as the wastes fell into shallow gutters and were conveyed out of the building for collection. Dairy cattle manure (from Frederick Dairy, Inc., Waseca, MN) was collected from walkway scrapings beside the free stalls. All agricultural wastes were freeze-dried to a constant weight. The dry solids were homogenized using a blender, and the resultant dry wastes were stored at −16 °C prior to being added to distilled water to achieve the desired moisture content for experiments.

Hydrothermal Reactions. All hydrothermal reactions were conducted in a 450 or 1000 mL stirred, stainless steel reactor (Parr Instruments, Moline, IL) with heat provided by a heating mantle. The time to reach temperature ranged from 35 to 45 min, and reaction times specified were in addition to the heating periods. Observed reaction pressures were essentially those of water alone at the respective temperatures, and gaseous products were not analyzed. Cooling was expedited by use of a fan. Cooled mixtures were then filtered, and "initial filtrates" were isolated before the hydrochar filtercakes were washed with distilled water. Hydrochars were washed well with

distilled water and freeze-dried to a constant weight before being submitted for analysis.

Analysis of Manures and Hydrochars. C, H, N, S, and ash contents were determined by combustion analysis at Galbraith Laboratories, Inc. (Knoxville, TN). Phosphorus and other metal contents were determined on digested manures, digested hydrochars, and aqueous filtrates by inductively coupled plasma (ICP) (Department of Geology, University of Minnesota). A complete description of the previously unreported digestion procedure is provided as Supporting Information. Higher heating values (HHV) were calculated[25] using elemental analysis and ash content values. Fatty acid analyses were conducted using a literature hydrolysis method[26] and gas chromatography at Covance Laboratories (Madison, WI).

Scanning Electron Microscopy (SEM) Imaging and Energy Dispersive Spectroscopy (EDS). SEM images were obtained using a JEOL 6500 instrument at the University of Minnesota Surface Characterization Laboratory. Hydrochars were dried at 105 °C and stored under vacuum until they were analyzed. In addition to collected images, EDS was conducted on the observed surface-precipitated salts to assess their chemical composition (Thermo-Noran Vantage system). There was no surface coating applied for this imaging

Acid Extraction of Hydrochars. To retrieve as much phosphate from the hydrochars as possible, a stoichiometric excess of hydrochloric acid was employed. Typically, 10 g samples of hydrochars were treated with 220 mL of 4 M HCl using an orbital shaker for 30 min. Suspensions were filtered, and both "acid filtrates" and extracted hydrochars (washed with distilled water to neutral pH) were analyzed by ICP.

Phosphate Isolation. The procedure involved addition of 5 M NaOH to well-stirred acid extract solutions to achieve a pH of ~9.0, with 0.1 N NaOH and 0.1 N HCl utilized to achieve a final pH of 9 ± 0.05. The solids created were filtered, washed with water, dried, and analyzed by ICP.

Statistics. Standard deviations for outputs for hydrochars were determined from triplicate experiments of center point reaction conditions and from triplicate elemental analyses of the starting animal manures.

■ RESULTS AND DISCUSSION

Design of Experiments (DOEs). The generally accepted initial step in the reaction mechanism of HTC with insoluble biomass substrates involves hydrolysis of polysaccharides[27] present in the system, with starch and hemicellulose being engaged much more readily than cellulose.[28] Cellulose is a crystalline biopolymer, generally requiring high reaction temperatures to be hydrated forming glucose, which undergoes subsequent hydrochar-forming reactions. Employing a flow reactor arrangement, Bobletter et al.[29] determined that temperatures in excess of 260 °C and reaction periods of ~0.5 h were required to induce the production of glucose (43% yield) from microcrystalline cellulose. Consequently, in our previous reports of HTC with microalgae[30] and fermentation residues,[31] consideration of the amount of cellulose present in those substrates was an important factor in determining reaction conditions for conversion into hydrochars having significantly increased carbon and combustion energy contents. With single-cell microalgae, which contain little or no cellulose, hydrochars having 65−72% carbon contents and corresponding HHV levels as high as 31.58 MJ/kg were obtained at 200 °C in ≤2 h. A moderate amount (16%) of cellulose was tolerated, however, in distillers grains, and hydrochars having HHV levels of >28 MJ/kg were obtained by employing the same reaction conditions.

In this investigation, as well, cellulose levels were expected to be important, and reported[32] levels of dry matter (protein, hemicellulose, cellulose, and lignin), as well as ash contents, and elemental compositions determined in this investigation of laying chicken, finishing swine, and dairy manures are listed in Table 2.

Table 2. Dry Matter, Fatty Acid, Ash Content, and Elemental Compositions of Manures[a]

	poultry	swine	cow
% protein	31.6	22	18.1
% hemicellulose	20.2	20.4	12.2
% cellulose	12.0	13.3	27.4
% lignin	2.3	5.4	13.0
% fatty acids	2.1	9.1	8.7
% ash	15.9	15.1	12.0
% C	41.28	42.24	41.57
% H	6.65	5.93	5.93
% N	5.03	4.88	3.94
% S	0.95	0.88	0.41
% P	1.86 (0.05)	1.66 (0.15)	0.71 (0.04)
% Al	0.68 (0.08)	0.05 (0.02)	0.09 (0.03)
% Ca	3.21 (0.85)	1.80 (0.16)	1.64 (0.12)
% Fe	0.79 (0.04)	0.27 (0.13)	0.07 (0.02)
% Mg	0.41 (0.01)	1.04 (0.09)	0.80 (0.04)

[a]Mean values for phosphorus and metals are reported from triplicate analyses of three separate digestions. Standard deviations are reported in parentheses.

The experimental design consisted of a full factorial of three independent variables of temperature, time, and percent dry solids, with the center point in triplicate. The dependent variables were hydrochar % yield, % C, % H, % N, and % P. Design of experiment (DOE) reaction conditions employed with poultry and swine manures included 200, 225, and 250 °C; 1, 2, and 3 h; and 5, 10, and 15% solids. Because of its higher cellulose and lignin contents, it was anticipated that more severe reaction conditions would likely be required for dairy cattle manures, and the following conditions were employed: 240, 250, and 260 °C; 1, 2, and 3 h; and 5, 10, and 15% solids. Because of the relatively low fatty acid contents, i.e., <10%, of all the animal manures, isolation of fatty acids in the manner reported in our earlier investigation with microalgae[33] was not conducted. Complete output data and linear regression coefficients obtained in the various DOEs are listed in Tables S1−S6 of the Supporting Information.

Analysis of Variance. The two-level full factorial design with three independent variables and replicated center points is an orthogonal design. As such, covariance between the independent variables is eliminated, and the significance of the independent variables as they affect the various dependent variables can be assessed through an analysis of variance (ANOVA) by utilizing the statistical F test.

Poultry Manure. For poultry, the % yield of hydrochar was strongly (99% significance level) dependent on temperature (negatively) and solids (positively). There was also some nonlinearity in the response surface as indicated by an interaction term between temperature and solids (90% significance level). The response surface for % C in the

hydrochar also appears to be nonlinear in that there is no linear dependence on time, temperature, or solids but a strong interaction term (positive) between temperature and solids (99% significance level). The % phosphorus in the hydrochar was statistically unaffected by any of the independent variables with a range of 89−100% incorporation in the hydrochar under all conditions used in the experiments. This would indicate that the variable range employed was well beyond that required for almost total incorporation of phosphorus to occur.

The % H decreased with all inputs of time, temperature, and solids as expected with dehydration reactions, which are the principal reactions occurring under HTC conditions.[28] The increase in % C, however, was very small, increasing only 1−3% compared to that of starting manure. A similar result was reported[34] for pyrolysis of poultry manure at 350−600 °C. Corresponding biochars had % C values that either remained essentially unchanged or increased only 4% compared to those of starting manure.

Swine Manure. The % yield was strongly impacted (99% level) by solids (positive) and temperature (negative). The % C values increased with reaction temperature and % solids but decreased with reaction time at statistically significant levels (99%). In addition, there were significant interaction terms indicating some nonlinearity of the response surface. The % P values in hydrochars displayed a strong positive dependence on temperature (99% level) but decreased with an increase in % solids (90% level). Overall, center point reaction conditions of 225 °C, 2 h, and 10% solids provided a nearly optimized hydrochar for phosphorus reclamation. One other important observation with the swine manure that was not made with poultry manure was that the hydrochar % C values increased significantly, with recorded values of 52−59% (from 42% in the starting material).

Dairy Cattle Manure. The % yield strongly increased with increasing % solids (97.5% level) but also showed some nonlinearity in the interaction between temperature and solids. The % C was strongly dependent (99% level) on time (negative), temperature (negative), and solids (positive). Some nonlinearity was shown by the time−temperature interaction. The hydrochar % P was strongly dependent on solids (positive, 99% level), with a weaker (90% level) positive dependence on temperature. With dairy cattle manure, the best conditions for obtaining high % yields and % P levels in hydrochars probably included 15% solids, 1 h, and 260 °C. Although comparable levels of hydrochar yield and % P values were observed at 5% solids, 1 h, and 240 °C, the % C value of the hydrochar obtained at the higher temperature was significantly greater. As with the swine material, the % C values for dairy manure were relatively high, ranging from 52 to 59% (from 41% in the starting dairy).

Comparison of the Animal Manures as HTC Substrates. While output values of % H and % N may be important for secondary applications of hydrochars, for the purposes of this investigation and recovery of phosphate, % yield, % P, and % C of hydrochars were the most important outputs. Of all the outputs, % yield was the most sensitive and affected by reaction conditions while % P was the least sensitive, and a rationale for this result is discussed in Mechanism of Phosphorus Capture in Hydrochars. As in our previous investigations of HTC with microalgae[30] and distillers grains,[31] % yield was strongly influenced with all three manures by concentration and increased significantly at higher % solids. Increased % C levels in hydrochars were also consistent with carbon remaining relatively inert and unchanged as hydrogen and oxygen were stripped away during the dehydrative carbonization process. HHV levels of swine and cattle hydrochars ranged from 27.07 and 25.82 MJ kg^{-1}, compared to 19.31−26.75 MJ kg^{-1} for sub-bituminous coals.[35] Especially with cattle manure and the massive quantities of manure created in large dairy operations,[10] utility of the hydrochars as carbon-neutral fuels could be especially attractive. After combustion and further concentration of phosphorus in the ash, reclamation could still be conducted in the manner described in this investigation.

Mechanism of Phosphorus Capture in Hydrochars. In previous investigations with microalgae[33] and grains of distillers,[31] phosphorus in reactant biomasses was found almost exclusively in the form of soluble phosphates in the aqueous solution filtrate products. However, the opposite was true with manure substrates examined in this investigation, with the majority of phosphorus being contained within the solid hydrochars. Our working hypothesis was that the presence of multivalent metal cations such as aluminum, calcium, magnesium, and iron could lead to formation of insoluble phosphates that are present in colloidal form or electrostatically attached to proteins present in the manures and become entrapped on or within growing hydrochars. Solubility product constants for corresponding phosphate salts of these metals are extremely low, i.e., ranging from 10^{-16} to 10^{-33},[36] and support this concept. Reported in Table 2 are metal contents of the aforementioned metal cations in the animal manures. Total concentrations of these metal ions were 5.09% in poultry, 3.16% in swine, and 2.60% in cattle. By contrast, concentrations of these multivalent metal ions in microalgae[37] and distillers grains[38] were <0.5% and were therefore insufficient for the formation of significant quantities of insoluble phosphates that could be incorporated in hydrochars. The fact that hydrochar % P was the least sensitive output across all manures was probably a result of its mechanism of incorporation in the hydrochars. Insoluble multivalent metal phosphates were likely only slightly affected by HTC reaction conditions, and the mechanism of binding in which insoluble metal phosphate salts were trapped within or precipitated onto growing hydrochars was common to all manures. The total multivalent metal ion content of the starting manures and their relative stoichiometry with respect to phosphorus also provided an explanation of differences among the manures of the overall percent yield of phosphorus captured. With cattle having the highest metal:phosphorus ratio (2.60:0.71 = 3.66), essentially all the phosphorus in the system was trapped and contained in hydrochars across the whole reaction space examined. Poultry manure (5.09/1.86 = 2.73) gave more intermediate levels, and swine (3.16/1.66 = 1.90) exhibited some of the lowest values observed. Additional confirmation of high concentrations of insoluble metal phosphates present in the hydrochars was obtained by comparison of ash contents (from center point conditions in the DOE Tables S1, S3, and S5 of the Supporting Information) of hydrochars with the ash contents of starting manures. The ash content of hydrochars would be expected to increase significantly because of the presence of additional masses of multivalent metal phosphate salts, and the corresponding increases in the ash contents of hydrochars compared to those of starting manures were as follows: 69% with poultry, 60% with swine, and 85% with cattle.

Lastly, the fact that phosphorus was present in the hydrochars in the form of metal phosphates was directly

supported by the SEM and EDS analyses (Figures S1−S3 and Table S7 of the Supporting Information) of the three animal hydrochars. The EDS data (Table S7 of the Supporting Information) indicated that both $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ were predominant and present with Ca:Mg atom ratios of 55:45 for poultry, 6:94 for swine, and 53:47 for cattle.

Recovery of Phosphate. In Table 3, the elemental analyses of completely digested starting hydrochars are reported, and corresponding Ca:Mg atom ratios for the unextracted hydrochars were as follows: 77:23 for poultry, 64:36 for swine, and 54:46 for cattle. Just why the digested values differ substantially from the EDS values, especially for swine hydrochar, is presently unknown. The fact that the EDS method is conducted with solid, heterogeneous materials and the depth of penetration is limited may offer some explanation. However, the ICP analyses that were conducted with digested and soluble analytes likely provide a more accurate total analysis of the hydrochars.

Table 3. Metal Analyses of Hydrochars (HC) before and after Acid Extraction[a]

manure	Ca	Mg	Fe	Al	P
poultry hydrochar	3.96	0.74	1.62	1.42	3.29
extracted hydrochar	0.30	0.19	0.34	0.96	0.34
swine hydrochar	5.35	1.83	0.50	0.19	3.91
extracted hydrochar	0.43	0.30	0.63	0.18	0.42
cattle hydrochar	3.55	1.86	0.28	0.30	1.86
extracted hydrochar	0.02	2.18	0.15	0.38	0.03

[a]Extracted hydrochar values are weight percent amounts of each element and were corrected for mass loss during the extraction process.

Acid extraction was conducted with hydrochars obtained from center point reaction conditions. Hydrochars were treated with a stoichiometric excess of hydrochloric acid and filtered, and the extracted hydrochars were washed with distilled water until they were neutral. Hydrochar mass losses caused by acid extraction were as follows: 26% for poultry, 23% for swine, and 18% for cattle. Metal contents of both initial hydrochars and acid-washed hydrochars are listed in Table 3. From the very low residual levels of calcium and phosphorus in extracted hydrochars (8 and 10% for poultry, 8 and 10% for swine, and 1 and 2% for cattle), it was apparent that significant loss of both calcium and phosphorus was occurring, thereby supporting the hypothesis that calcium phosphate was the principal component of the precipitated salts.

Additional experiments designed to potentially obtain a higher yield of phosphate by production of struvite [$Mg(NH_4)(PO_4)$] were also examined. Addition of stoichiometric quantities (based on phosphate) of magnesium and ammonium chlorides, followed by increasing the pH, did not result in increased yields of phosphate-containing solids.

Addition of base to the acid extract to achieve a pH of 9 caused precipitation of brown solids. Precipitated solids were filtered, washed well with water, and characterized by ICP. Metal analyses, P_2O_5 equivalents, and reclamation yields are listed in Table 4.

Metal:phosphorus ratios for possible phosphate salts are 1.93 for $Ca_3(PO_4)_2$, 2.15 for hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, 1.16 for $Mg_3(PO_4)_2$, 1.76 for $FePO_4$, and 0.87 for $AlPO_4$. Along with the aforementioned calcium and phosphorus depletion values for hydrochars with acid treatment, another indication that the precipitated solid was chiefly calcium phosphate was indicated by the relative proximities of the measured calcium:phosphorus ratios to that of calcium phosphate, especially so for the precipitated salt obtained from cattle hydrochar. Compared to those of poultry and swine manures, the lower P_2O_5 equivalent for cattle manure can be attributed to the lower percentage of phosphorus in cattle manure. As with phosphate rock, which is a mixture of calcium phosphate and apatites, calcium phosphate is too insoluble in water to be employed directly as a fertilizer. Subsequent treatment with acid, however, can result in more soluble forms termed superphosphates[39] that are very effective fertilizing compounds.

Aqueous Product Streams (initial filtrates). The % solid values of corresponding initial filtrates from center point DOEs, elemental analysis, NPK information, pH, and conductivity determinations are listed in Table 5.

As expected with removal of phosphorus by inclusion in the hydrochars, initial filtrates were predominantly nitrogen-rich solutions. Fatty acids created from hydrolysis of triacylglycerides present were likely responsible for the observed slightly acidic pH values. The relatively high carbon contents of the initial filtrates also suggested that these solutions should be suitable substrates for anaerobic digestion, as was the case with our earlier research with filtrates from stillage products.[40]

This investigation described a method of reclamation of phosphorus in the form of inorganic phosphate from domestic animal manures that is especially suitable for large corporate farms. Phosphorus that is initially concentrated in manures can be further concentrated in hydrochars prepared by heating aqueous slurries of the manures, generally without addition of more water or any catalysts, at temperatures generally less than 250 °C in a confined reactor. Reaction periods for batch reactions of generally ≤2 h were sufficient, and reaction pressures were typically those of the vapor pressure of water alone. Hydrochars thus created contained >90% of the phosphorus as phosphate salts of calcium, magnesium, aluminum, and iron. Phosphate recovery was achieved in >80% yield by the following sequence: addition of acid, filtration, increasing the pH of the filtrate to alkaline levels, and filtration of precipitated material that was principally calcium phosphate. Extracted hydrochars from swine and cattle manures, especially, had relatively high combustion energy contents and promising utility as carbon-neutral fuels.

Table 4. Metal Analyses and Fertilizer Potentials of Solids Isolated at pH 9 from Acid Extracts[a]

animal filtrate	Ca	Mg	Fe	Al	P	equivalents[b] of P_2O_5	phosphorus[c] reclamation yield (%)
poultry	16.49 (1.47)	1.77 (0.16)	4.84 (0.43)	2.64 (0.24)	13.46	0.03	89
swine	19.17 (1.32)	4.72 (0.32)	2.27 (0.16)	0.24 (0.02)	14.53	0.031	81
cattle	27.41 (1.91)	1.55 (0.11)	0.35 (0.02)	0.10 (0.01)	14.36	0.01	84

[a]Metal ion contents in weight percent. Values in parentheses are metal:phosphorus ratios. [b]Calculated value in pounds based on 1.00 pound of starting dry manure mass. [c]The % yield values based on phosphorus contents of starting manures.

Table 5. Properties of the DOE Center Point Filtrates

manure	% solids	pH	% C[a]	% N[a]	P (ppm)	K (ppm)	NPK[b] ratio	conductivity (mmhos/cm)
poultry filtrate	3.2	7.0	46.08	12.5	90	239	5682:1:26	13.1
swine filtrate	3.8	6.6	40.74	6.6	51	1995	7362:1:38	12.6
cattle filtrate	3.0	5.2	43.22	5.2	5	2020	54881:1:383	19.2

[a]Values are weight percent determined by elemental analysis of freeze-dried filtrate samples. [b]The NPK ratio is the N:P(P_2O_5):K(K_2O) ratio on a dry weight basis.

It is recognized, however, that for this technology to receive significant attention in the near term, recovery of phosphate and utility of extracted hydrochars as carbon-neutral fuels may be insufficient for commercial development. Conversion of extracted hydrochars by chemical or thermal methods into higher-value coproducts that have potential use in water purification, energy storage as lithium ion battery electrodes and carbon fuels cells, and materials for carbon dioxide sequestration sorbents may be required.[41] One thing is certain, however; phosphorus shortages will not be abated by plucking a solution out of the air in the manner that global depletion of fixed nitrogen was solved in the early 20th Century by converting nitrogen gas into ammonia using the Haber–Bosch process.[42]

■ ASSOCIATED CONTENT

Supporting Information

Procedure for digestion of starting manures and hydrochars, design of experimental tables for animal manures, linear regression coefficients for outputs, a table containing the EDS results, and figures of SEM analyses and EDS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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