PLANT NUTRIENTS AND BIOENERGY PRODUCTION VIA A NEW QUICK WASH PROCEDURE FOR LIVESTOCK MANURES

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Abstract

While livestock manures offer great potential to provide nutrients for cotton, most manures are unbalanced in nitrogen and phosphorous. Recovery of significant amounts of phosphorous (P) from manure provides a more environmentally safe application of the manure to land as well as the opportunity to transport excess P off the farm in a concentrated form. A treatment process called “quick wash” was developed for extraction and recovery of P from poultry litter and animal manure solids. The remaining washed manure solids can be used to produce energy via anaerobic digestion. Here, the methane potential from anaerobic digestion can be estimated by stoichiometric modeling. Alternatively, it can potentially be converted to energy via emerging thermochemical conversion technologies. Both traditional anaerobic digestion and thermochemical conversion technologies offer opportunities for energy production from the washed manures. The potential for methane production was not affected by the “quick wash” process. Under pyrolysis, the washed poultry litter had greater mass loss, indicating an improved feedstock for synthesis gas or pyro-oil production. When compared to the unwashed litter under aerobic combustion, the washed poultry litter was more energy dense (6600 vs. 6890 Btu/lb) and allowed for a more uniform release of heat.

Introduction

Traditionally, nutrients such as phosphorus (P) in animal manure have been recycled by applying manure to cropping systems to promote plant growth. However, P buildup to elevated levels in crop soils due to intense land application of animal manures has created environmental concerns such as recycling and disposal method. To solve accumulation and distribution problems of this nutrient, a substantial amount of manure P may need to be moved at least off the farm or longer distances beyond county limits (USDA-ERS, 2000). Thus, the ability to remove P from manure will be critical to livestock and poultry producers to accomplish manure utilization through land application without elevating soil P levels. In addition, the aspect of P reuse is becoming important for the fertilizer industry because the world P reserves are limited (Smil, 2000). For the U.S. as a whole, confined livestock produces 650 million kg of recoverable manure P annually, with 65% (420 million kg) in excess of on-farm needs (Kellogg et al., 2000). Recovery and reuse of P from manure could off-set the P obtained now from mining as much as 25% (Szogi et al., 2008a). Given that a major portion of the recoverable manure P (250 million kg) is supplied by poultry manure (Kellogg et al., 2000), new manure P management technologies are needed for environmentally sustainable poultry production (Sharpley et al., 2007).

Recently, efforts have focused on solving the problem of P in poultry operations through the development of a “quick wash” process (Szogi et al., 2008a, 2008b). The process was developed as an alternative to the following state-of-the-art technologies and programs: (1) improved manure application methods, such as immobilization of P with alum to prevent runoff (Moore, 2002; Sharpley et al., 2007); (2) energy generation by combustion (USDOE, 2000), gasification (Sheth and Turner, 2002), or anaerobic digestion (Kelleher et al., 2002); and (3) transport of waste or compost to agricultural lands with low levels of P (Kelleher et al., 2002). This “quick wash” processes animal manure using rapid extraction and subsequent recovery of P in solid form from solid manure prior to land application (Szögi et al., 2008b). The remaining solid residue (washed manure or litter) has a more balanced nitrogen:phosphorus (N:P) ratio that is more environmentally safe for land application and use by crops. The overall objective of this study was to describe the “quick wash” process as well as identify potential energetic differences of unwashed and “quick wash” poultry litter.

Methods

Process Configuration

Briefly, “quick wash” process consists of three consecutive steps: (1) P extraction, (2) P recovery, and (3) P recovery enhancement. In the first step, poultry litter is washed by mixing it with water and acid in a reactor vessel at pH lower than 5.0 (fig. 1a). The washed litter residue (fig 1b) is further settled and dewatered to prevent unnecessary carbon (C) and nitrogen (N) oxidation and digestion. This first step produces a liquid extract containing low suspended solids (<3 g L^{-1}) and extracted soluble P. The liquid extract is transferred to a second vessel where P is recovered (steps 2 and 3, fig. 1a; fig. 1c). Further details about the “quick wash” process are described by Szogi et al. (2008a).

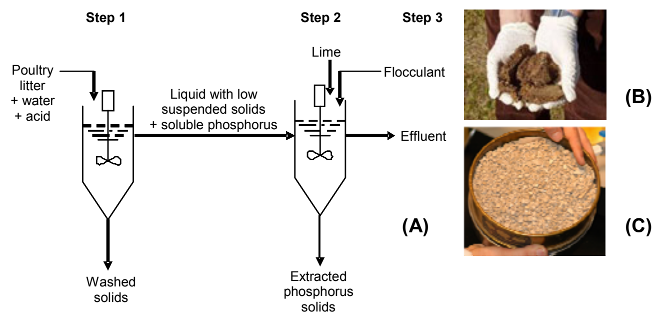

Figure 1. Quick wash process schematic (A): (Step 1) P extraction, (Step 2) P recovery, and (Step 3) P recovery enhancement; Washed poultry litter (B); and Concentrated recovered phosphorous after the “quick wash” process (C).

Phosphorous Extraction Experiments

Three different phosphorous extraction experiments were performed that investigated the following: (1) the potential ability of various organic and inorganic acids along with a control of distilled water to extract P (step 1 at lab-scale) from poultry litter using the “quick wash” process; (2) lab-scale demonstration of the removal and recovery of P from the liquid extract steps (steps 2 and 3) generated by the litter washing in step 1; and (3) development and testing of a field prototype system. Methods and testing procedure for these experiments are detailed in Szogi et al. (2008). For the first experiment, aqueous solutions of acetic, citric, and hydrochloric acids were tested at seven concentration levels — 0, 2.5, 5, 10, 20, 40, and 80 mmoles L^{-1}. For the second experiment, P precipitation was tested with hydrated lime [$Ca(OH)_2$] with or without anionic polyacrylamide (PAM) organic flocculant (no lime addition was also tested as a control). For the field prototype experiment, approximately 15.2 kg of poultry litter was subjected to the “quick wash” process using 10% w/w citric acid. This prototype unit was operated four times to constitute four “quick wash” runs. For all experiments, solids were analyzed for total P (TP) and total Kjeldahl N (TKN). These constituents were also analyzed in the liquid supernatant. Treatment efficiency of the various treatments and field prototype unit was established by comparison of P extraction relative to initial P content in untreated poultry litter.

Poultry Litter Characteristics

The bedding material that constituted the base of the broiler litter in all experiments was wood chips. Broiler litter was collected from a 27,400-bird broiler house in Sumter County, South Carolina. At the time of sampling, the litter was being used by the fifth consecutive flock (6.5 flocks per year). Two composite litter samples were taken in two 12 m transects covering the width of the house. Composite samples were placed in 20 L plastic sealed containers and stored in the freezer until preparation for laboratory experiments. Prior to laboratory experiments, litter samples were ground and passed through a 5.8-mm sieve. The broiler litter contained 17.1% (±0.2%) moisture, 19.2 (±0.2) g kg^{-1} TP, and 35.1 (±0.6) g kg^{-1} total Nitrogen.

Analytical Methods

Analyses of supernatant liquid were performed as detailed by Szogi et al. (2008a) according to *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998). Elemental analysis of recovered washed litter and P-rich solids for total C and N was done by dry combustion (Leco Corp., St. Joseph, Mich.); Ca, Mg, K, Na, and P were analyzed by inductively coupled plasma (ICP) from nitric acid plus H_2O_2 digested extract (Peters et al., 2003).

Thermal Analysis

From the unwashed and washed poultry litter sample, triplicate samples were sent to Hazen Research, Inc. in Golden, CO, for analyses. Gross energy content or higher heating value (HHV) was determined following ASTM Standard D5865 (ASTM, 2006). Proximate and ultimate analyses were performed following ASTM D 3172 and 3176 standards, respectively (ASTM, 2006). Proximate analysis yields a biomass sample's moisture, ash, volatile matter, and fixed carbon contents. The ultimate analysis for a biomass sample measures the carbon, hydrogen, nitrogen, sulfur, and ash. The oxygen content was determined by difference.

Thermal analyses of the unwashed and washed poultry litter subsamples were conducted in triplicate using a Mettler-Toledo TGA/SDTA851e apparatus where the mass loss (thermogravimetry, TG) and temperature changes (differential thermal analysis, DTA) were recorded simultaneously. This unit operated under a three-point calibration using Indium, Aluminum, and Gold. All samples were placed in an Al_2O_5 70-□l crucible with a lid and either pyrolyzed under UHP N_2 or combusted using zero-grade air (composition 21.5% O_2, 78.5% N_2; total hydrocarbons < 1ppm) at a flow rate of 60 ml min^{-1} within a temperature range from 40 to 800°C at a constant heating rate of 10°C min^{-1}. All DTA curves accounted for instrumental effects using Version 9.10 of STARe software (Mettler Toledo International Inc., Columbus, OH).

Results

Phosphorous Extraction Experiments

During extraction, a significant portion of total P in poultry litter was released from the litter solids. Total P extraction rates increased with decreasing pH of both mineral and organic acids extracting solutions (i.e., increasing acid concentrations) (fig. 2). In contrast, the distilled water wash (control) extracted only 20% (results not shown). In addition to the concentration of acid, the type of acid made a difference. Citric acid was more efficient at extracting P than HCl or acetic acid at similar molar applications (2.5 to 40 mmol L^{-1}). High extraction efficiencies (>70%) were also possible with HCl and acetic acid (>50%), but the required molar rates were doubled (80 mmol L^{-1}).

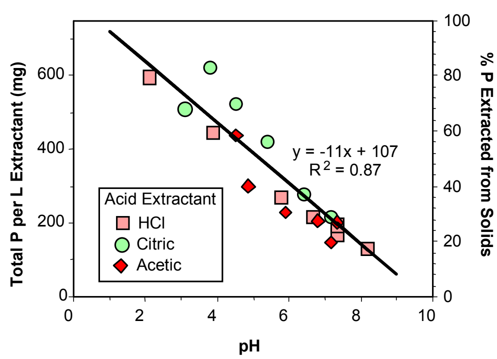

Figure 2. Effect of pH on TP extracted from broiler litter.

Even though P extraction increased with increased citric acid treatment, N was extracted much less efficiently than P (Szogi et al., 2008a). For instance, about 81% of initial total P in the litter was extracted at pH 3.8 (40 mM citric acid), but only 27% of N was extracted (data not shown). Thus, the extraction of P from litter with addition of acid produced a washed litter residue with an N:P ratio as high as 9.8 (fig. 3). This was about 5-fold higher than the N:P ratio of the untreated litter (N:P = 2.1). Furthermore, this 9.8 N:P ratio was within the range required for balanced fertilization of crops for both N and P with an acceptable N:P ratio for cotton being obtained at a pH of 4.4 (Edwards and Daniel, 1992).

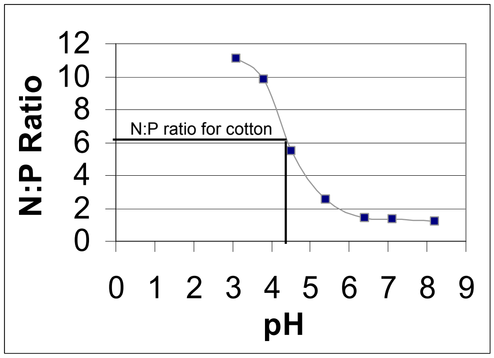

Figure 3. Effect of citric acid treatment on the N:P ratio in solid residue left after washing poultry litter.

A 20-mmol L^{-1} citric acid extract solution was selected for step 1 (fig. 1a). This first step produced a liquid extract containing a high TP concentration of about 600 mg L^{-1} at pH 4.7 (fig. 4) and a low TSS concentration (2.1 g L^{-1}) after liquid-solid separation by decantation. In step 2 (fig. 1a), TP was removed from solution by precipitating soluble P compounds under alkaline conditions. Addition of hydrated lime decreased TP exponentially with decreasing pH ($y = 16211 \exp(-0.6428x)$, $R^2 = 0.939$; fig. 4). Subsequent addition of a flocculant improved the percentage of TP removed at pH higher than 8.0. A small amount of an organic flocculant was added at a rate of 7 mg L^{-1} (active ingredient) to all treatments to enhance thickening and TP content in the precipitated product (step 3). Results in figure 4 show an increase of the amount of P extracted and higher TP content of the precipitate by addition of Ca $(OH)_2$ followed by flocculant enhancement. The highest P extraction rate (72.5%) and content in the precipitate (18.8% P_2O_5) were obtained when pH reached a value of 10.0.

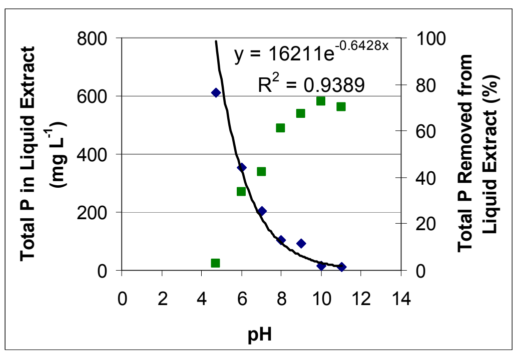

Figure 4. Total P remaining in liquid effluent and percentage recovered from liquid extract following lime and flocculant addition after the "quick wash" process (steps 2 and 3).

On average, the prototype unit performance recovered 9.8 g TP kg^{-1} litter or 68%. This recovered precipitate from the prototype unit contained relatively large amounts of P, C, N, and Ca, and small amounts of Mg, K, and Na (table 1). These results confirm laboratory data that the "quick wash" approach can extract and recover P from poultry litter in a concentrated product that has the potential of being reused as fertilizer.

Table 1. Selected mean element composition in percent of the weight of the solid precipitate recovered from poultry litter using the "quick wash" process (g/100 g). [a]

Phosphorous	P_2O_5[b]	C	N	Ca	Mg	K	Na
5.9	13.5	23.8	2.4	13.4	1.0	1.1	0.3

[a] Percent composition expressed as oven dry values
[b] Phosphorous grade expressed as P_2O_5 = % P x 2.29

<u>Thermal Analysis</u>
The washed and unwashed poultry litters on a dry basis (db) were rich in volatile material and, consequently, carbon content was high (table 2). Significant contributions of oxygen and ash to feedstocks can lower the heating value.

When comparing the two litters, the washed litter had lower N, S, and ash content. Therefore, the "quick wash" process generated a more energy dense feedstock with an improved higher heating value (6600 vs. 6890 Btu/lb).

Table 2. Proximate and ultimate analyses of unwashed and washed poultry litter (*n*=3; VM= volatile matter; FC= fixed carbon).

	Higher Heating Value	Proximate Analysis			Ultimate Analysis				
		VM	FC	Ash	C	H	N	S	O*
	Btu/lb	%db	%db	%db	%db	%db	%db	%db	%db
Unwashed	6600	61.1	16.6	22.3	38.9	4.56	3.03	0.47	30.7
Washed	6890	65.9	13.9	20.2	40.9	4.64	1.95	0.24	32.1

Anaerobic Digestion

One potential application of the washed poultry litter is anaerobic digestion to generate a microbial biogas that typically contains 30 to 45% CO_2 and 55 to 70% CH_4. This generated methane can be used as a replacement for natural gas or used in engine-generators for on-farm electricity production (Kelleher et al., 2002). Anaerobic digestion has the following stoichiometric degradation (Buswell and Neave, 1930) represented for unwashed and washed poultry litter, respectively:

$$CH_{2.22}N_{0.067}O_{0.994}S_{0.005(s)} + 0.407H_2O_{(l)} \rightarrow 0.503CH_{4(g)} + 0.497CO_{2(g)} + 0.005H_2S_{(g)} + 0.067NH_{3(aq)} \quad (1)$$

$$CH_{2.16}N_{0.041}O_{0.988}S_{0.002(s)} + 0.399H_2O_{(l)} \rightarrow 0.508CH_{4(g)} + 0.492CO_{2(g)} + 0.002H_2S_{(g)} + 0.041NH_{3(aq)} \quad (2)$$

With anaerobic digestion, minor amounts of H_2S and NH_3 appear, and approximately half the carbon is converted into CH_4 and CO_2. Theoretical methane production was slightly improved with the "quick wash" technique. Additionally, lower ammonium concentrations were predicted that may reduce the potential for ammonium inhibition and allow more efficient digestion.

Thermal Degradation

Regardless of test condition, unwashed and washed poultry litter demonstrated a slight decrease in weight within the temperature range of 40 – 200°C (Fig. 5) and was primarily attributed to the loss of residual water as well as light volatile compounds (Whitely et al., 2006). For combustion of the poultry litter, the mass losses as well as the degradation profiles were similar for the unwashed and washed litters. For pyrolysis, a greater mass loss was observed for the washed solids. This mass loss coincided with the measured volatile matter (table 2). However, the degradation profiles varied slightly for the unwashed and washed poultry litter with the washed poultry litter demonstrating a second peak of a significant rate of mass loss close to 350°C. As such, the "quick wash" process produced a litter by-product with more volatile matter amenable to pyro-oil production.

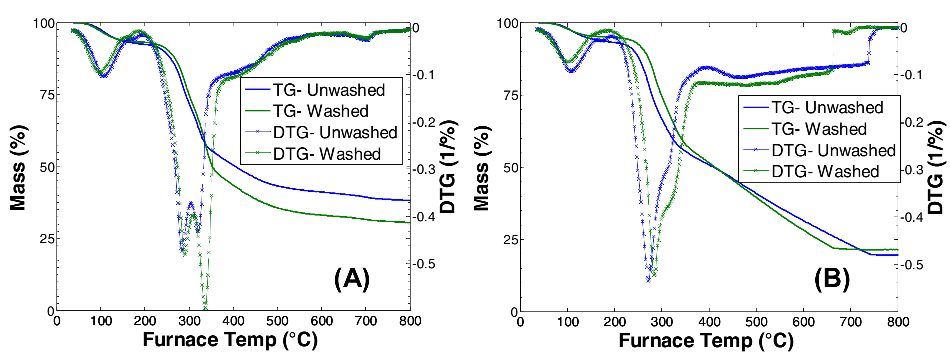

Figure 5. Pyrolytic (A) and burning (B) mass loss profiles of unwashed and washed poultry litter (60 ml min^{-1} N_2; 10°C min^{-1}).

Despite the combustion degradation profiles being similar, the differential thermal analysis (DTA) or heat flow profile varied in peak broadness and intensity (fig. 6). Once enough energy was absorbed to remove water, the rapid weight loss and ultimately combustion of these components quickly resulted in broad thermopositive peaks. The DTA profile suggests that combustion of washed litter would produce an even release of heat. However, for the unwashed litter, temperature fluctuations would occur between 350 and 500°C.

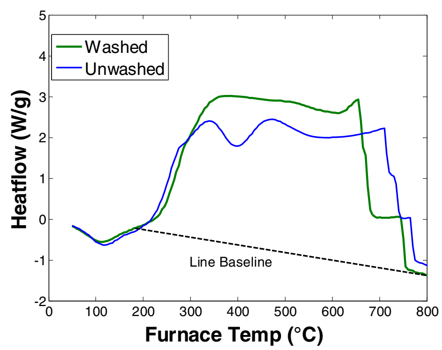

Figure 6. Heat flow profile for burning of unwashed and washed poultry litter (60 ml min^{-1} N_2; 10°C min^{-1}).

Conclusion

A treatment process called "quick wash" was developed for the extraction and recovery of P from poultry litter and animal manure solids. This "quick wash" process with an organic acid extraction slurry with a pH <5.0 was able to extract more than 65% of initial TP. The extracted P was precipitated by the addition of lime and organic poly-electrolyte flocculent to produce a concentrated P product that can be moved more easily off-farm and reused as a fertilizer. The washed litter residual solid had a balanced N:P ratio suitable for land application of crops including cotton. In addition, this washed litter residual could be converted into energy via anaerobic digestion or combustion. The theoretical potential for methane production was not affected by the "quick wash" process; however, methane production may improve since washed litter yielded lower ammonium concentrations. Under pyrolysis, the washed poultry litter had greater mass loss indicating an improved feedstock for synthesis gas or pyro-oil production. When compared to the unwashed litter under aerobic combustion, the washed poultry litter was more energy dense (6600 vs. 6890 Btu/lb) and allowed for a more uniform release of heat.

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