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Ekpo, U, Ross, AB, Camargo-Valero, M et al. (1 more author) (2016) Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus in process water. Bioresource Technology, 214. pp. 637-644. ISSN 0960-8524

https://doi.org/10.1016/j.biortech.2016.05.012

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# Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus in process water.

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## ABSTRACT

This study investigates the influence of pH on extraction of nitrogen and phosphorus from swine manure following hydrothermal treatment. Conditions include thermal hydrolysis (TH) at 120°C and 170°C, and hydrothermal carbonisation (HTC) at 200°C and 250°C in either water alone or in the presence of 0.1M NaOH, $H_2SO_4$, $CH_3COOH$ or HCOOH. Phosphorus extraction is pH and temperature dependent and is enhanced under acidic conditions. The highest level of phosphorus is extracted using $H_2SO_4$ reaching 94% at 170°C. The phosphorus is largely retained in the residue for all other conditions. The extraction of nitrogen is not as significantly influenced by pH, although the maximum N extraction is achieved using $H_2SO_4$. A significant level of organic-N is extracted into the process waters following hydrothermal treatment. The results indicate that operating hydrothermal treatment in the presence of acidic additives has benefits in terms of improving the extraction of phosphorus and nitrogen.

Keywords: HTC, nutrient recovery, manure, pH, process water

# 1. Introduction

As a result of the extensive growth in concentrated animal feeding operations in the past decade, large amounts of manure are generated leaving farmers with the challenge of proper waste disposal (Szogi et al., 2015). Treatment facilities emit odorous and volatile compounds such as hydrogen sulphide ($H_2S$), ammonia ($NH_3$) and greenhouse gases ($CO_2$, $CH_4$, $N_2O$, etc.), and have resulted in public complaints from fugitive gas emissions and associated health problems. Therefore livestock producers are concerned about developing new methods and technologies to meet regulatory requirements and maintain good environmental standards. For instance, strategies for ammonia reduction includes renovation of barns, change in animal nutrition, regular cleaning of exhaust air from farm structures and proper manure treatment (Ndegwa et al., 2008).

Manures generally contain high levels of organic matter that is responsible for its characteristic odour, pathogens, hormones, pharmaceutic derived compounds and vital plant nutrients such as phosphorus and nitrogen. Animals retain about 50% of the nitrogen, phosphorus and sulphur in their diet (van Kempen et al., 2003). Nitrogen present in a typical soybean and corn diet is mainly excreted by pigs as uric acid in urine and organic-N in faeces (Hatfield et al., 1990). About 40 - 60% of the phosphorus intake is digested although undigested phosphorus from cereal grains or other complexes can be excreted as phytic acid (Hatfield et al., 1990).

Traditionally, manure management involves direct application on farmland as fertiliser. The nutrients leach during runoffs, contaminating both surface and ground water and causing eutrophication and hypoxia (Liang et al., 2014). As a result this has led to strict environmental legislations for farmers in the EU as well as other countries. The proportion of phosphorus and nitrogen in manure is unequal when compared with industrial fertilisers and hence, excessive application of manure on farmland to meet crop nutrient demand results in higher doses of nutrients beyond those effectively transferred to crops and pastureland, leading to nutrient saturated soils (Szogi et al., 2015). Storing excess manure is a huge challenge to farmers due to odour issues, the high solubility of phosphorus and high degradation rate releasing ammonia (Vadas and Powell, 2013).

Despite the keen interest in manure management over the past decades, development of sustainable management/treatment technologies on farm or nearby is still necessary to reduce these environmental concerns, improve agricultural benefits and reduce greenhouse gas emissions (Karakashev et al., 2008). Anaerobic digestion has been widely used to generate biogas for heat and power, which could be used locally in both small and large scale farms, for manure stabilization and odour control (Otero et al., 2011; Fernandez-lopez et al., 2015).

Manure is one of the major pathways of phosphorus loss and has gained research interests as a potential renewable source of recoverable nutrients (Azuara et al., 2013). Methods such as immobilization of phosphorus in manure by the addition of aluminium and calcium have been developed to precipitate phosphorus (Wagner et al., 2008). Phosphorus recovered in a concentrated usable form is essential to agriculture as it is a major ingredient in many industrial fertilisers, which are increasingly being produced from non-renewable phosphate rocks (Azuara et al., 2013; Szogi et al., 2015). Anaerobic treatment of pig manure and recovery of phosphorus via struvite precipitation from the digestate has been investigated (Karakashev et al., 2008). The 'quick wash' method with mineral and organic acids has been used to extract phosphorus from raw animal waste followed by recovery as calcium phosphate using lime and an organic polymer (Szogi et al., 2014). Pyrolysis of manure has also been identified as a potential route to recover phosphorus; however, pyrolysis requires drying after pressing, which introduces a major limitation with its associated energy cost (Azuara et al., 2013; Fernandez-lopez et al., 2015). Pyrolysis concentrates phosphorus in the char and this can be used as a soil additive or as a concentrated phosphorus source for further extraction and transformation. The former has been developed for treatment of sewage sludge (Bridle and Pritchard, 2004; Viana et al., 2015), however not all the phosphorus is bioavailable (Huang and Tang, 2015). Incineration of manure concentrates phosphorus in the resulting ash. Extraction of phosphorus from chicken manure incineration ash has proven successful in laboratory studies (Kaikake et al., 2009).

Hydrothermal processing is an emerging but promising technology for treatment of wet wastes such as animal waste. It involves treating biomass in water at elevated temperature and pressure sufficient to keep the water in the liquid state or in a subcritical state (Peterson et al., 2008). It produces a solid residue within which phosphorus can be immobilised, making it less soluble compared to the untreated biomass. It also destroys pathogens, eliminates the characteristic odour and reduces soluble toxic metals initially present in the raw manure (Qian and Jiang, 2014). Processing at lower temperatures up to 170$^{o}$C generally results in hydrolysis of the carbohydrate fractions and extracts inorganics. Operating in this temperature zone is referred to as thermal hydrolysis (TH). Increasing the temperature and pressure further, results in the carbonisation of the residue, reducing its oxygen content and increasing its carbon content. The latter is termed hydrothermal carbonisation (HTC) and is under investigation to produce high energy density biofuels from wet wastes. Only limited studies have focussed on hydrothermal carbonisation of manure to produce bioenergy (He et al., 2000; Heilmann et al., 2014). Several studies have investigated the higher temperature processing of manure to produce bio-oils via hydrothermal liquefaction (Xiu et al., 2010; Vardon et al., 2011; Theegala and Midgett, 2012). Thermal hydrolysis on the other hand is less severe and does not result in carbonisation or liquefaction, it is sometimes used prior to anaerobic treatment of biomass wastes (Abelleira-Pereira et al., 2015). Other low temperature hydrothermal treatments such as hot water washing have been proposed to remove inorganics from biomass, thereby improving the combustion properties of biomass fuels (Saddawi et al., 2012). Other studies have focussed primarily on nutrient recovery from manures using hydrothermal carbonisation (Heilmann et al., 2014; Dai et al., 2015). Dai et al. proposed hydrothermal carbonisation as a method for manure management due to the immobilisation of the majority of the phosphorus in the hydrochar (Dai et al., 2015). Heilmann et al. indicated that up to 90% of the total phosphorus in the manures is concentrated in the hydrochar following hydrothermal carbonisation of pig manure; also, they proposed the acid extraction of the hydrochar followed by subsequent precipitation of the phosphorus by addition of alkali (Heilmann et al., 2014). Generally speaking, phosphorus is concentrated in the hydrochar, however this is feedstock dependent and it is largely associated with the inorganic content of the feedstock (Ekpo et al., 2016; Dai et al., 2015).

Lynam et al. investigated the influence of Ca salts and acetic acid on the hydrothermal treatment of lignocellulosic biomass (Lynam et al., 2011) and identified benefits from acetic acid treatment in terms of the calorific value of the resulting hydrochar. Reza et al. have investigated the influence of acid and alkali on the hydrothermal carbonisation of wheat straw (Reza et al., 2015). To the authors' knowledge, there are no reports on the hydrothermal processing of pig manure in the presence of acid and alkali additives and the potential recovery of nitrogen and phosphorus from the resulting process waters. This study investigates the influence of additives (e.g., acid and alkali) on the hydrothermal treatment of pig manure. The influence of pH on the extraction of nitrogen and phosphorus in process waters is presented following mild hydrothermal treatment (i.e., thermal hydrolysis-TH) and more severe treatment (i.e., hydrothermal carbonisation-HTC).

## 2. Materials and Methods

### 2.1 Materials

Swine manure used in this study was collected from the Spen Farm (Tadcaster, West Yorkshire, UK), which houses the Pig and Poultry Research Unit, University of Leeds. The manure was pre-dried in an oven at 60°C for several days after which it was ground into powder using an Agate Tema barrel before characterisation.

The ultimate analysis was performed using a CE Instruments Flash EA 1112 series elemental analyser to determine the weight percent (wt %) of carbon, hydrogen, nitrogen and sulphur (CHNS); oxygen content was determined by difference. Proximate analysis was performed using a Thermogravimetric Analyser (TGA) to determine moisture; volatile and fixed carbon; and ash content. Phosphorus content in the original manure and the subsequent products was performed by colorimetry following acid digestion in nitric acid using the ascorbic acid method. All measurements were made in duplicate and the mean value is reported.

### 2.2 Hydrothermal processing

Thermal hydrolysis (TH) and hydrothermal carbonisation (HTC) of swine manure samples were performed in an unstirred 500mL, high-pressure batch reactor (Parr, USA). In each experiment, the reactor was charged with a slurry containing 24g of dry swine manure powder (moisture content 5.3%) with either 220mL of de-ionised water or solutions of 0.1M

NaOH, 0.1M $H_2SO_4$ or 0.1M of the organic acid (i.e., $CH_3COOH$ and HCOOH). Hydrothermal processing for each slurry was performed at 120°C, 170°C, 200°C and 250°C for 1hour. The residence time was taken from the point the reactor reached the desired temperature. The heating rate was approximately 10°C $min^{-1}$ and the cooling rate was in a similar order. After processing, the reactor was allowed to cool to room temperature before separating the end products.

## 2.3 Product recovery and analysis

The solid residue and the aqueous product were separated by filtration using a pre-weighed Whatman glass microfiber filter paper (1.5 µm pore size) and rinsed with 80mL of de-ionised water and filtered again on the same filter paper. The aqueous product was collected in a volumetric flask and made up to 500mL with de-ionised water. Significant quantities of bio-crude were produced during the HTC at 200°C and 250°C. As a result, the reactor was rinsed with dichloromethane to extract the bio-crude, but the aqueous phase was not extracted in solvent and analysed as received. Yields and properties of the residues are not reported in this paper, as the main objective is to focus on the potential recovery of nitrogen and phosphorus species from process waters.

The pH of the concentrated aqueous product was measured before dilution. The concentration of total carbon (TC) and inorganic carbon (IC) in the recovered aqueous products was determined using a Schimadzu TOC-5000 analyser using the differential method. The total organic carbon (TOC) concentration in the aqueous product represents the difference between the TC and IC concentrations. Total phosphorus and reactive phosphorus concentration in each of the aqueous products recovered was determined by colorimetry using the ascorbic acid method. The analysis for total phosphorus requires a pre-digestion step using the persulphate digestion method before the colorimetric analysis. After digestion, the samples were made up to 100 mL using de-ionised water before analysis. The total nitrogen present in the aqueous product was determined by the Kjeldahl method. A known sample volume was digested with 10 mL concentrated sulphuric acid, in the presence of a copper based catalyst. After complete digestion (as indicated with a characteristic greenish colour), the samples were left to cool before distillation into 50 mL boric acid solution. The solution was then titrated with 10mM sulphuric acid to measure the released ammonia. In the case of ammoniacal nitrogen ($NH_4^+$-N) determination, known volumes of aqueous product samples were used directly in the distillation step, as no pre-digestion with acid is needed. Titration was performed as stated above.

## 3. Results and discussion

### 3.1 Characterisation of swine manure feedstock

Proximate analysis of the feedstock indicated that it contains relatively high ash content (12.7 wt %). The feedstock has a moisture content of 5.3 wt %, a volatile content of 61.1 wt % and a fixed carbon content of 21.6 wt %. The composition of pig manure varies with diet however the composition determined of this feedstock are typical of values identified by other workers (Tsai et al. 2012). The level of phosphorus in the manure was approximately 1.6 wt %, which is similar to the reported levels of 1.7 wt % in the swine manure processed by Heilmann et al. (2014). The ultimate analysis of the feedstock indicates a typical CHNSO content for swine manure (C: 46.4; H: 6.3; N: 3.0; S: 0.2 and O: 31.4 on a dry basis). Swine manure is known to contain high levels of protein and lipids, which explains the high levels of Nitrogen (N) and Phosphorus (P) and the relatively high gross calorific value. The composition of swine manure reported by Vardon et al., (2011) contains 70.6 wt% organic matter, 21 wt% crude protein and 18.5% crude lipids on a dry basis. The nitrogen levels in manure are typically high, reflecting the high levels of crude protein and range from 3-5 % (Heilmann et al., 2014). The nitrogen content in the current feedstock is slightly lower than that used by Hielman et al., (2014) (c.f. 3 wt % in this study to 4.9 wt %). Levels of carbon and oxygen in the feedstock are similar to those reported by Tsai et al., (2012) (c.f. 46.4 wt % C in this study to 42.2 wt % and 31.4 wt % O in this study to 36.4 wt %). The calorific value of the manure is 19.2 MJ $kg^{-1}$, which is similar to 19.3 MJ $kg^{-1}$ reported by Tsai et al. (2012). The HHV is towards the higher end of biomass fuels (15 - 20 MJ $kg^{-1}$) and is probably due to high levels of lipids in the feedstock. The manure is therefore regarded to be typical of the composition of swine manure.

## 3.2 pH and TOC of aqueous product

The use of the acidic reagents (e.g., formic acid, acetic acid and sulphuric acid) resulted in a reaction pH between 1.0 and 2.8. The use of the alkaline reagent sodium hydroxide had a pH of 12.8. The baseline condition using de-ionised water was neutral at pH 7.

The pH of the aqueous products was measured after the tested hydrothermal process and the results are shown in **Table 1**. The processing of the manure in water at each temperature consistently results in a reduction in the pH after extraction resulting in the final reaction mixture being acidic. This reduction increases as the temperature increases from 120°C to 250°C. This reduction in pH is due to the formation of organic acids that dissolve in the process water and is typical of hydrothermal carbonisation in water alone. Thermal hydrolysis breakdowns organic compounds and the resulting chemical species will interact with the corresponding aqueous conditions remaining after the extraction. The aqueous product from TH and HTC contain acetic acid and other organic acids as well as sugars and ammonium (Hoekman et al., 2011; Lynam et al., 2011). The resulting chemical species in solution will therefore be dictated by the resulting equilibriums within the process waters. When the manure is processed in the presence of NaOH, the pH similarly reduces as the temperature increases. At 120°C the pH is still basic but has reduced from 12.8 to 8.2. As the temperature increases, the pH gradually reduces and ranges between 5.5 and 6.0 after 200°C. This is again due to higher levels of organic acids being formed from the biomass as the temperature increases (Hoekman et al., 2011). The processing of the manure using the acidic reagents results in the opposite effect, the pH is increased for all acidic reagents. For the acidic reagents, the influence of temperature is less dramatic. The initial pH of the $H_2SO_4$ reaction is <1.0 and results in a final pH following hydrothermal treatment between 3.5 and 3.8. The presence of sulphuric acid can increase the extraction of cations and form soluble sulphates from K and Na and Mg. Sulphuric acid can also catalyse the conversion of organic acids by esterification and promote decomposition reactions involving hydration and decarbonylation. Each of these effects result in an increase in pH which, coupled with the presence of of ammoniacal nitrogen ($NH_4^+$-N) and soluble basic N-containing heterocycles such as pyrroles, explains the increase in pH. The initial pH of the formic acid and acetic acid were between 2.0 and 3.0 respectively, with the final pH increasing also to typically 4.2 to 4.9. Previous studies have shown that under hydrothermal conditions, some of the acetic and formic acids are consumed resulting in an increase in pH (Ross et al., 2010). This was also observed by Lynam et al. (2011) during HTC, who also suggested that it was indicative of the shift in concentration between the quantities of reactants and products that are in equilibrium. TOC in the aqueous products is indicative of the proportion of organic products that are water soluble. Generally, TOC in the process waters remains relatively constant at each temperature irrespective of the reagents used. The nature of the organic material generally includes organic acids, sugars and fatty acids, although the exact nature of this organic material is beyond the scope of this study.

### 3.3 Fate of phosphorus following hydrothermal treatment at different pH

**Figure 1** shows the relationship between the pH of the starting reagent and its effect on the extraction of total phosphorus from the raw feedstock into solution. Generally, the results show higher extraction of phosphorus is achieved under acidic conditions. **Table 1** shows the concentrations of reactive and total phosphorus present in the aqueous products after thermal hydrolysis at 120°C and 170°C, as well as during hydrothermal carbonisation at 200°C and 250°C. For each experiment, the level of reactive phosphorus (RP) was measured and compared to the total phosphorus (TP). The TP was determined following further digestion of the process water in $H_2SO_4$ to convert all phosphorus to $PO_4^{3-}$.

Following thermal hydrolysis at 120°C, the highest concentration of phosphorus (1,800 mg/L) was observed after processing in $H_2SO_4$ which represents 79% of the phosphorus present in the feedstock being extracted into solution (**Fig 1.**). The lowest concentration of phosphorus (290 mg/L) was observed after processing in NaOH and represents only 11% of TP. The latter indicates a significant immobilisation of the phosphorus in the residue using NaOH. Using water alone extracts 30% of the TP and the organic acids behave similar to water alone and extract between 26 - 27% of TP. The concentration of phosphorus in the water following treatment in organic acids- formic and acetic, was observed to be 510 mg/L and 550 mg/L respectively while it was 650 mg/L with de-ionised water suggesting that organic acids had limited impact on phosphorus extraction at this concentration.

Following thermal hydrolysis at 170°C, the extraction of phosphorus in water alone reduces to 13% while extraction of phosphorus using formic acid and acetic acid reduces to 21% and 22% respectively. Extraction in NaOH extracts 16% of the total phosphorus, a slight increase compared to the extraction at 120°C. Once again the extraction of phosphorus was highest with $H_2SO_4$ reaching the maximum extraction of 94% of TP and representing the highest concentration of phosphorus (2,200 mg/L) in the aqueous phase. A similar phosphorus concentration was observed using both organic acids; 390 mg/L from formic acid and 400 mg/L from acetic acid, while it was slightly lower using NaOH (320 mg/L) and de-ionised water (240 mg/L).

Extraction of phosphorus following treatment by hydrothermal carbonisation was generally lower compared to thermal hydrolysis. At 200°C, only 6% of the phosphorus was extracted in water alone resulting in a concentration of 110 mg/L. The extraction in $H_2SO_4$ was again the highest and represents 80% of TP however it is beginning to decrease compared to treatment at 170°C. The concentration of RP is 1,490 mg/L for HTC 200°C which was a 7 fold increase over the other reagents. The extraction in alkali reduced four-fold compared to thermal hydrolysis at 170°C and is only 90 mg/L. Extraction in organic acids also decreased to 9% for acetic acid and 13% for formic acid. The concentration was in a similar range with 170 mg/L and 210 mg/L for acetic acid and formic acid respectively. At 250°C, very little phosphorus is extracted in water alone, in alkali or organic acids (1-3%) and ranged from 10-40 mg/L. $H_2SO_4$ extracted the most phosphorus at about 1,050 mg/L. The extraction in $H_2SO_4$ reduced to 60% indicating that the higher the temperature, the more the phosphorus is associated with the hydrochar (Ekpo et al., 2016).This suggests significant immobilisation of phosphorus in the hydrochar in all but the mineral acid. This is consistent with other reports and is due to precipitation with cations such as Ca, mg and Fe.

The phosphorus speciation in the water includes both inorganic $PO_4^{3-}$ and organically bound phosphorus. The reactive phosphorus (RP) represents inorganic phosphorus and loosely-bound organic forms of phosphorus released during hydrolysis (Szogi et al., 2015). The organic-P fraction in the aqueous product was determined by difference between total and reactive phosphorus. The organic phosphorus in manure is dominated by phytate- like P, DNA-like or monoester-like P (Pagliari and Laboski, 2012). The soluble unreactive phosphorus is mainly organic forms of phosphorus containing condensed polyphosphates

(Szogi et al., 2015). Significant quantities of organic-P were observed in the aqueous products from thermal hydrolysis and HTC. This observation was similar to the study by Ekpo et al. (2016) in comparison with high-temperature hydrothermal processing (i.e., Hydrothermal Liquefaction - HTL and Supercritical Water Gasification - SCWG), which had much less organic-P.

The organic phosphorus following hydrolysis at 120°C accounts for 29% of the TP using NaOH, between 24 - 27% using formic and acetic acid respectively and 14% using de-ionised water. The lowest levels of organic phosphorus (about 6%) was observed using $H_2SO_4$. The higher levels of phosphate suggest the recovery would be easier following treatment in $H_2SO_4$. There was a decrease in the levels of organic phosphorus at 170$^o$C, particularly for processing in water alone. The highest levels are observed for the organic acids which account for between 20-24%. The organic fraction using $H_2SO_4$ at 120°C and 170°C was fairly similar, ranging between 6 to 8%. At 200$^o$C, most of the phosphorus present in solution was in the form of phosphate with the organic fraction representing between 0 to 3% for water and the acidic reagents. A significant quantity of organic phosphorus (12%) remained in the aqueous phase using NaOH. There was no organic phosphorus left in the aqueous product at 250$^o$C from de-ionised water, $H_2SO_4$, organic acids or NaOH.

In general, the extraction of phosphorus in water alone decreases with increasing temperature with the highest extraction being at the lower temperatures. This is in agreement with the results described by Szogi et al., who reported that 49% of the total phosphorus can be extracted from manure at ambient temperatures in water (Szogi et al., 2014). The ‘quick wash’ process described by Szogi et al. is operated at ambient temperature and extracts phosphorus from raw manure followed by recovery into a concentrated solid form (calcium phosphate) by the addition of lime and an organic polymer (Szogi et al., 2014). The extraction of phosphorus increases by adding mineral and organic acids and the type of acid was shown to influence phosphorus extraction. At equal molar concentrations, citric acid was shown to be more effective at extracting phosphorus than HCl, achieving 87% and 75% respectively (Szogi et al., 2014). The extraction of phosphorus at 170$^o$C in $H_2SO_4$ reaches 94% of the total and is therefore higher than the ’quick wash’ approach, however the use of $H_2SO_4$ could be more corrosive and promote oxidation of organic material. Levels of extraction are not matched using organic acids although this may possibly improve by increasing the acid strength.

### 3.4 Fate of nitrogen following hydrothermal treatment at different pH

**Table 1** shows the concentrations of ammonium and total nitrogen present in the aqueous products after thermal hydrolysis at 120°C and 170°C, as well as during hydrothermal carbonisation at 200°C and 250°C. Considering the nature of the N species present in the original sample, it is very unlikely that the swine manure samples used in this study contain any forms of oxidised nitrogen (nitrate or nitrite), due to the actual fate of metabolised nitrogen compounds, which will end up in the urine and faeces as organic nitrogen compounds and if any hydrolysis is happening (as it does rapidly with urea), the resulting end product from the transformation of organic nitrogen will be ammoniacal nitrogen. Generally the ammoniacal nitrogen ($NH_4^+$-N) increases with process temperature from 120°C to 250°C. As stated by Sun et al. (2013), reaction temperature plays a significant role in nitrogen solubilisation. Similarly in the study by Ekpo et al. (2016), $NH_4^+$-N significantly increased as the process severity increased from 170°C to 500°C. The level of extracted $NH_4^+$-N are affected by pH and is generally highest using $H_2SO_4$ and lowest using NaOH. The levels of $NH_4^+$-N for $H_2SO_4$ range from 430 mg/L at 120$^o$C up to a maximum of 850 mg/L at 170$^o$C. The influence of temperature on the levels of $NH_4^+$-N in water, NaOH and organic acids were significantly less than with $H_2SO_4$.

Generally, the highest levels of TN-N are extracted between 170 and 200$^o$C. For processing with $H_2SO_4$ the peak TN-N concentrations is at 170$^o$C and reaches over 2,000mg/L. The extraction of TN-N generally peaks at 170$^o$C and then reduces as the temperature increases. The difference between the TN-N and $NH_4^+$-N is attributed to the organic-N fraction in the aqueous product. Each of the aqueous products contains high levels of organic-N for all hydrothermal conditions. The levels of organic-N and $NH_3$-N are shown in **Figure 2**. Extraction of organic-N once again peaks between 170$^o$C and 200$^o$C and then reduces. The highest organic-N is observed at 200$^o$C in water and NaOH and the highest level of $NH_4^+$-N is observed at 170$^o$C using $H_2SO_4$. The organic-N typically represents between 60-70 % of the

N in the aqueous product. Even at 250°C, the organic-N is still 60% of the total-N. In comparison, Ekpo et al., (2016) indicated that higher temperature hydrothermal processing (HTL and SCWG) degraded organic-N significantly increasing the levels of $NH_4^+$-N (Ekpo et al., 2016).

**Figure 3** shows the percentage of total nitrogen extracted from the raw feedstock into the aqueous product for each of the different reagents. The percentage of N extracted increases up to 170°C and then remains relatively constant. The extraction of nitrogen was not significantly affected by pH at any given temperature. During thermal hydrolysis at 120°C, nitrogen extraction was between 25 - 29% for all additives. Although nitrogen extraction during thermal hydrolysis at 170°C was almost double compared with the extraction observed at 120°C, similar extraction levels were observed for all additives at this temperature ranging from 44 to 49%. During HTC 200°C, extraction was between 47 and 50% while during HTC 250°C, it was between 43 and 48%.

### 3.5 Mass balance of nitrogen and phosphorus following hydrothermal treatment

The results show that during thermal hydrolysis of swine manure at 120°C, about 61 to 65% of the total nitrogen present in the unprocessed feedstock remained in the hydrochar from de-ionised water and NaOH while the hydrochar from $H_2SO_4$, formic acid and acetic acid contained between 71 and 74% of the total nitrogen in the unprocessed feedstock. At 120°C and 170°C, no biocrude is produced and the resulting N and P is distributed between the hydrochar and the water phase. At 120°C, more phosphorus remained in the hydrochar (63 - 84%) than the aqueous phase for all additives (11 - 30%) except the $H_2SO_4$. For $H_2SO_4$, about 79% of the phosphorus was extracted into the aqueous product leaving about 11% in the hydrochar. At 170°C, nitrogen was almost equally distributed between the hydrochar and the aqueous phase for all additives as well as de-ionised water. Higher extraction of phosphorus (94%) was observed with $H_2SO_4$, with 6% in the hydrochar. Most of the phosphorus (77 - 92%) remained in the hydrochar using de-ionised water, NaOH and organic acids.

During HTC at 200°C, nitrogen was once again almost equally distributed between the hydrochar and the aqueous phase for all additives including de-ionised water. Small amounts of biocrude are produced at 200$^{o}$C (0.3 wt %) which contain levels of N ranging from 1-2 wt % and so this accounts for a small proportion of the initial N. No detectable P was observed in the biocrude. Almost 98% of the total phosphorus present remains in the hydrochar using water and NaOH, 86 - 87% using organic acids and 17% using $H_2SO_4$. The precipitation of phosphorus salts such as calcium phosphate, magnesium phosphate and magnesium ammonium phosphate (struvite) are known to immobilise P in the hydrochar and this precipitation is dependent upon the inorganic content of the feedstock (e.g. the levels of Mg, Ca and others) and pH. Analysis of the metal content in the hydrochars (not shown) indicates that treatment in $H_2SO_4$ reduces the levels of Ca, Mg and Fe in the hydrochar compared with the other reagents. The levels of Ca and Mg in the hydrochar are highest following processing in NaOH and water. The levels of Ca and Mg in the hydrochar typically increase with temperature for all reagents with the exception of $H_2SO_4$. The presence of Ca, Mg and Fe explain the higher levels of P immobilisation in the residues and hydrochar. During HTC at 250°C, nitrogen distribution between the hydrochar and the aqueous phase was similar with HTC at 200°C. At 250$^{o}$C, additional biocrude is observed ranging from 1-3 wt %. The typical N content in the biocrudes range from 1-2 wt% and phosphorus was not detected. The regents begin to have an impact on biocrude yields, with processing in NaOH producing the highest yield (3 wt %) and the processing in $H_2SO_4$, producing the lowest (1 wt %). The levels of N distributed in the oil are still however very low. Following HTC in NaOH and water, 91 - 97% of the total phosphorus present remained in the hydrochar, 98% using organic acids and 36% using $H_2SO_4$. The levels of phosphorus in the hydrochar following extraction in $H_2SO_4$, are correspondingly, significantly lower in the hydrochar following treatment in $H_2SO_4$ compared to the other regents. Generally, the levels of nitrogen increases with temperature but pH has little influence. The levels of phosphorus extraction is highest at the lower temperature and is facilitated by using mineral acids such as $H_2SO_4$.

## 4. Conclusion

Phosphorus extraction is pH and temperature dependent whereas nitrogen extraction is more significantly affected by temperature rather than pH. Extracted phosphorus reduces with increasing process temperature. Acidic conditions favour higher phosphorus extraction particularly with the addition of a mineral acid ($H_2SO_4$) and presents an opportunity for nutrient recovery. Although the extraction of nitrogen is not as significantly influenced by pH, the maximum N extraction is achieved using $H_2SO_4$. A significant level of organic-N is extracted into the process waters following hydrothermal treatment.

## Acknowledgements

The authors would like to thank the Niger Delta Development Commission (NDDC), Nigeria for the financial support of Miss Ugochinyere Ekpo and the European Commission for financial support through the 'Biorefine' project via the ERDF Interreg IVb NWE region programme.

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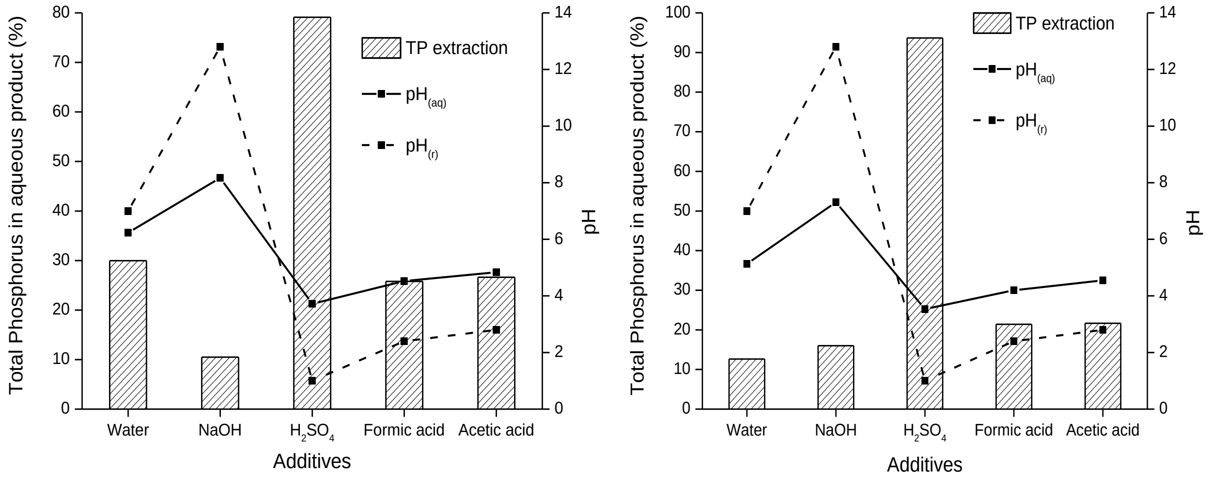
**a) Hydrolysis 120°C** **b) Hydrolysis 170°C**



**b) HTC 200°C** **a) HTC 250°C**

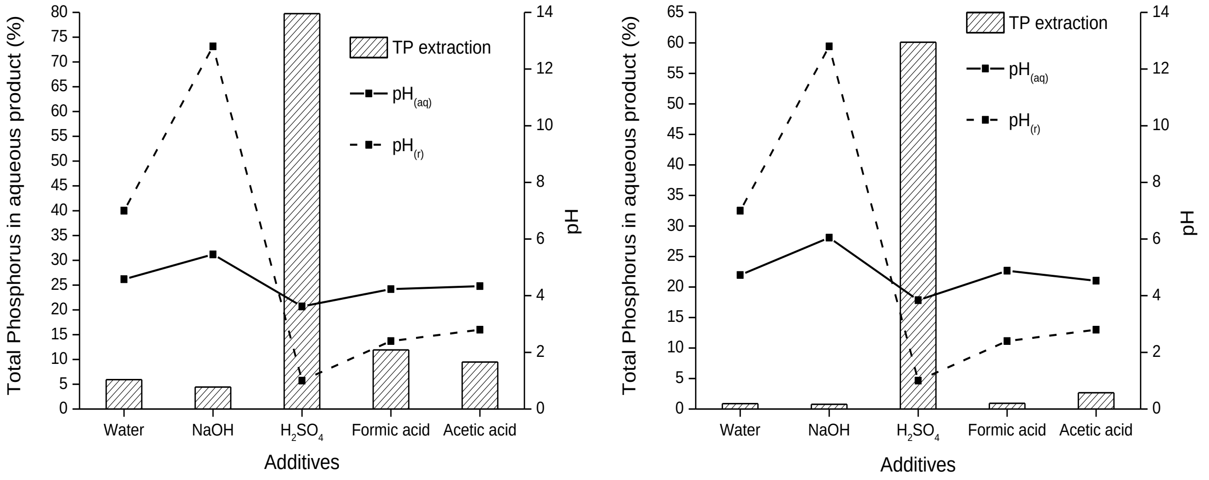
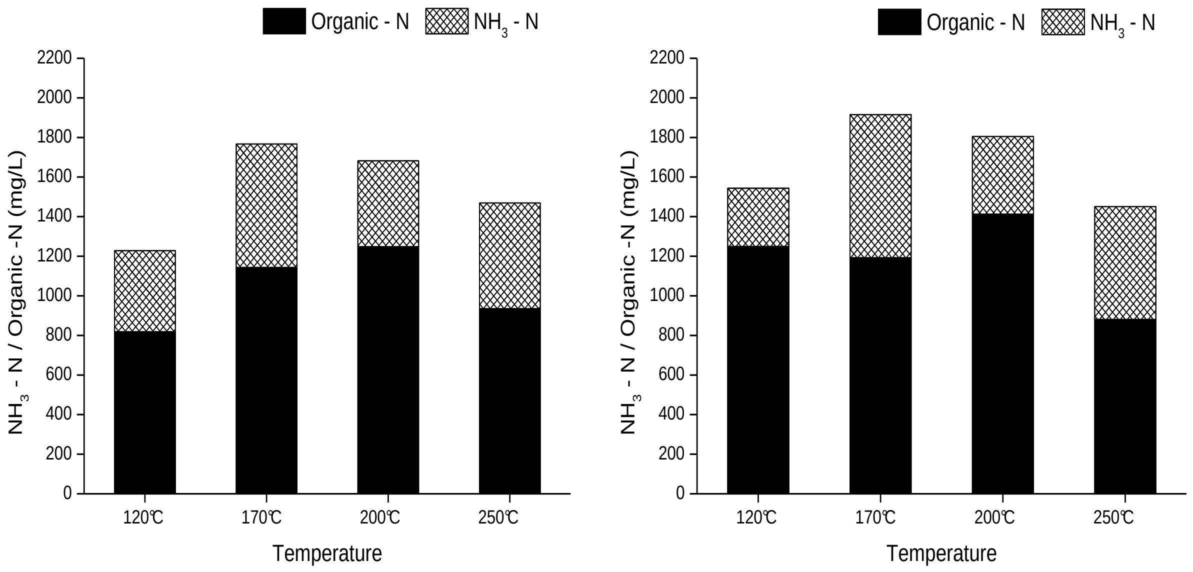


Figure 1: Effect of pH on the extraction of total phosphorus into the aqueous product

**a) Water** **b) NaOH**



**c) $H_2SO_4$** **d) Acetic**

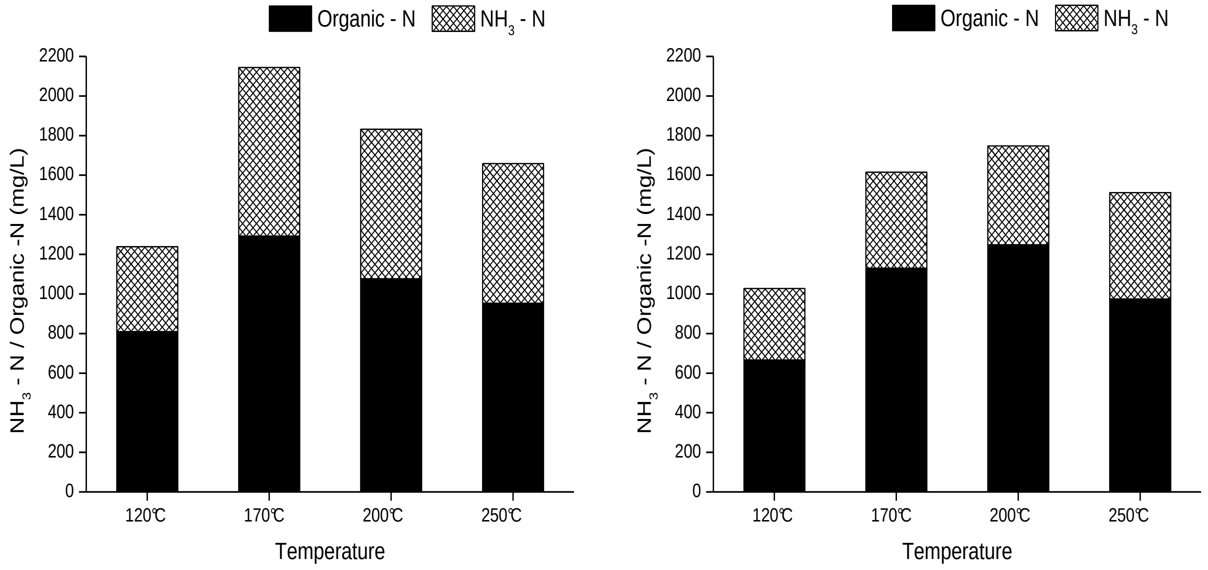
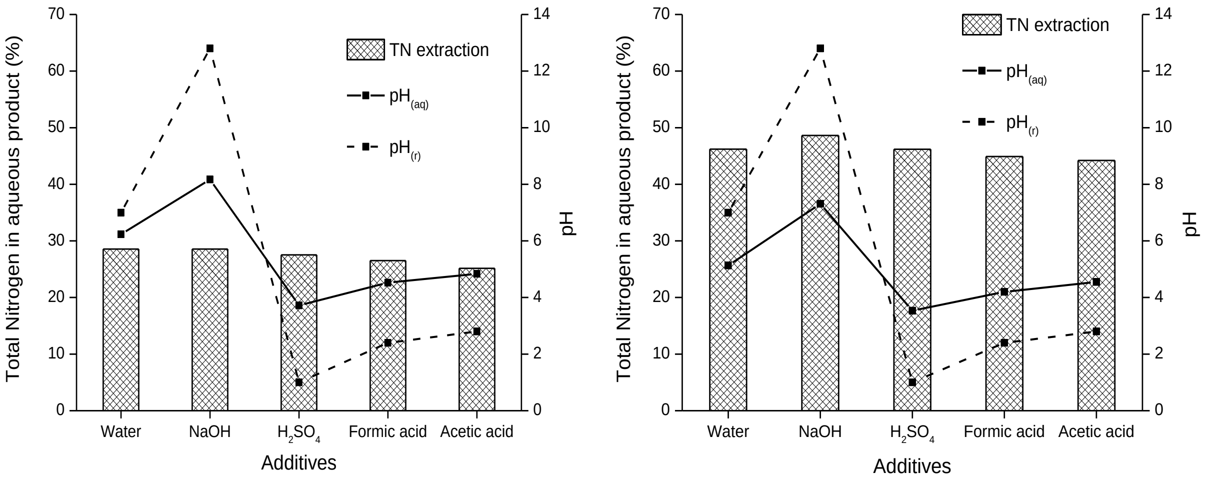


Figure 2: Forms of nitrogen present in the aqueous products

**a) Hydrolysis 120°C**

**b) Hydrolysis 170°C**



**c) HTC 200°C**

**c) HTC 250°C**

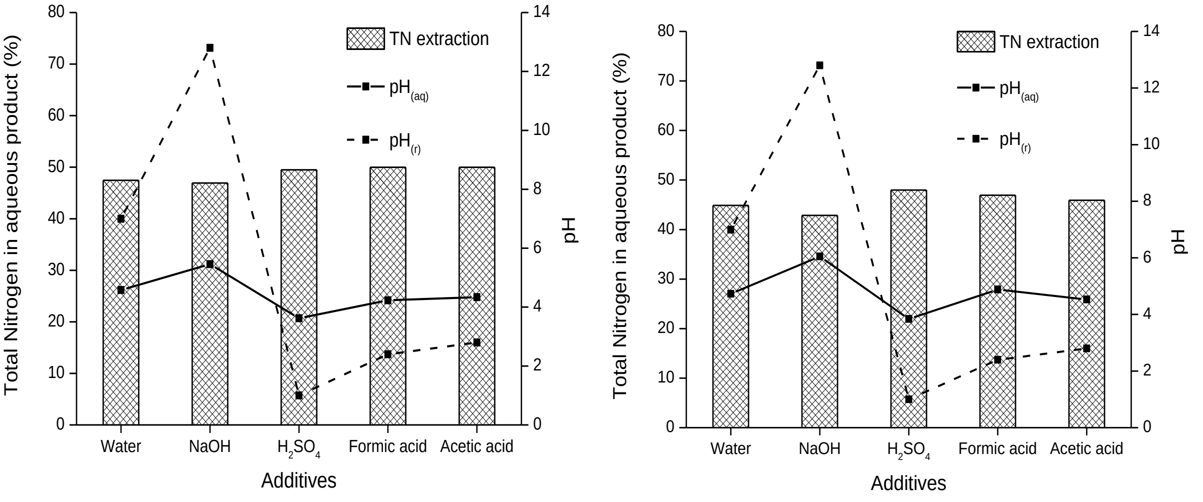


Figure 3: Effect of pH on the extraction of total nitrogen into the aqueous product

Table 1: pH, total organic carbon (TOC), nitrogen and phosphorus in the aqueous products

| | | Concentration (mg/L) | | | | |
|---|---|---|---|---|---|---|
| **Hydrothermal Process** | **pH** | **TOC** | **$NH_4^+$ -N** | **TKN** | **$PO_4^{3-}$** | **TP** |
| **120°C** | | | | | | |
| water | 6.2 | 8,900 | 410 | 1,230 | 560 | 650 |
| 0.1M NaOH | 8.2 | 13,270 | 290 | 1,540 | 200 | 290 |
| 0.1M $H_2SO_4$ | 3.7 | 10,410 | 430 | 1,240 | 1,690 | 1,800 |
| 0.1M Formic acid | 4.5 | 9,200 | 380 | 1,030 | 380 | 510 |
| 0.1M Acetic acid | 4.8 | 10,370 | 360 | 1,030 | 400 | 550 |
| **170°C** | | | | | | |
| water | 5.1 | 17,760 | 620 | 1,770 | 220 | 240 |
| 0.1M NaOH | 7.3 | 18,520 | 720 | 1,920 | 270 | 320 |
| 0.1M $H_2SO_4$ | 3.5 | 17,810 | 850 | 2,140 | 2,020 | 2,200 |
| 0.1M Formic acid | 4.2 | 16,750 | 500 | 1,620 | 370 | 390 |
| 0.1M Acetic acid | 4.5 | 18,680 | 490 | 1,620 | 390 | 400 |
| **200°C** | | | | | | |
| water | 4.6 | 14,520 | 430 | 1,680 | 100 | 110 |
| 0.1M NaOH | 5.5 | 16,820 | 390 | 1,810 | 80 | 90 |
| 0.1M $H_2SO_4$ | 3.6 | 12,850 | 760 | 1,830 | 1,470 | 1,490 |
| 0.1M Formic acid | 4.2 | 15,110 | 570 | 1,750 | 210 | 210 |
| 0.1M Acetic acid | 4.3 | 16,970 | 500 | 1,750 | 170 | 170 |
| **250°C** | | | | | | |
| water | 4.7 | 14,260 | 530 | 1,470 | 10 | 10 |
| 0.1M NaOH | 6.0 | 16,230 | 570 | 1,450 | 10 | 10 |
| 0.1M $H_2SO_4$ | 3.8 | 12,090 | 710 | 1,660 | 1,050 | 1,050 |
| 0.1M Formic acid | 4.9 | 14,680 | 540 | 1,550 | 20 | 20 |
| 0.1M Acetic acid | 4.5 | 16,880 | 540 | 1,510 | 40 | 40 |

TOC – Total Organic Carbon
TP – Total Phosphorus
$PO_4^{3-}$ – Phosphate
TKN – Total Kjeldahl Nitrogen
$NH_4^+$-N – Ammoniacal Nitrogen