Nutrient solubilization and its availability following anaerobic digestion
Chirag M. Mehta and Damien J. Batstone

ABSTRACT

This study aims to investigate solubilization of elements (P, N, K, Ca and Mg) during anaerobic digestion (AD) of solid agriculture waste. It is important to maintain particularly phosphorous in the aqueous phase to be able to subsequently recover it in a concentrated form via crystallization. Batch AD was carried out at a mesophilic condition (37 °C) and pH 7.0 ± 0.2 on a variety of piggery and poultry solid waste streams. Less than 10% of the total P, Ca and Mg was in soluble form in the digestate. Most of the N and K remained soluble in the digestate. A bioavailability test (citric acid extraction) showed P, Ca and Mg in the digestate were totally available. Complete solubilization of P, Ca and Mg occurred below a threshold of pH 5.5. This indicates these nutrients were released during digestion, and then either bound to form inorganic compounds or adsorbed on solid surfaces in the digestate. These effects reduce the feasibility of post-digestion recovery of the nutrients via struvite crystallization. Strategies to improve nutrient solubilization and recovery during the AD include addition of complexing chemicals, operation at depressed pH, or otherwise modifying the operating conditions.

Key words | anaerobic digestion, digestate, nutrient binding, nutrient recovery

INTRODUCTION

Crystallization refers to the formation of solid crystals from a supersaturated solution. An early application of crystallization technology to water processing concerns the softening of drinking and process water (Caldwell & Lawrence 1953). The development of advanced crystallization technology as applied to wastewater treatment started in the 1970s, in response to more stringent phosphorus removal requirements combined with the desire to produce a more marketable end-product (Menar & Jenkins 1972). Crystallization processes can be retrofitted to most types of sewage treatment. In principle almost all heavy metals, metalloids and anions can be removed from all kinds of water types by crystallization as long as the solubility of the produced salt pellets is low and the metals or anions crystallize quickly into a stable crystal lattice. Metals are generally removed as hydroxide, carbonate or sulfide compounds and in some cases it has proved to be attractive to form metal phosphates. For example, phosphate can be removed as struvite (MgNH₄PO₄.6H₂O) while simultaneously reducing the wastewater nitrogen content. This has gained particular interest, as both struvite and calcium phosphates have been identified as marketable fertilizers (Gaterell et al. 2000). Several laboratory, pilot-scale and full-scale studies have been carried out to assess the potential of such methods in removing and recovering nutrients as a reusable product. The recovery of nutrients via crystallization is highly dependent on the availability of nutrients in soluble form (i.e., P as phosphates and N as ammonium) in solution.

The nutrient form in organic residues such as solid manure is highly variable and usually depends on its source, processing technique, method of storage, and the chemical form of the nutrients (Dou et al. 2001). Solid manure contains nitrogen and phosphorus mainly in organic form, whereas potassium is in inorganic form (Mikkelsen 2007). The processing of this solid waste via anaerobic digestion (AD) degrades the organics and releases nutrients (N and P) in digestate. The nutrient release from the organic matter depends on the extent of manure digestion (Gungor & Karthikeyan 2008). Often the digestate has abundant potential counter-ions, leading to precipitation of inorganic compounds (Wahal et al. 2010). These precipitates often end up in biosolids during sludge separation and
reduce their availability in the digestate. Recovery of mineral phosphates in a concentrated stream allows a wider range of options for eventual reuse than reuse of biosolids directly, due to their sterile and easily transportable nature. Hence it is crucial to solubilize these nutrients (P, N, Mg, K and Ca) for optimum recovery and removal of nutrients.

A nutrient recovery process from ash, derived from manure and municipal sludge, requires multiple stages to form a concentrated nutrient product (Biswas et al. 2009; Donatello et al. 2010). Any such recovery process would include an acid dissolution process as a first step to dissolve nutrients (P, Ca and Mg) from the ash. Several researchers carried out experimental work on the phosphorus release from the sewage sludge and animal waste ash (Stark et al. 2006; Biswas et al. 2009; Cohen 2009; Donatello et al. 2010). They found more than 85% of P is recovered from the ash using low-concentrated hydrochloric and sulfuric acids. Similar processes were applied to digestate from a dairy effluent to solubilize nutrients (Zhang et al. 2010). The dissolved species can then be recovered via crystallization. Optimization of the acid dissolution process for the nutrients solubilization in the digestate needs further research, particularly to identify whether the key nutrients are released, remain soluble or not, and if they bind, whether they bind via precipitation or other mechanisms (such as adsorption). Also further research is required on anaerobic processes to improve nutrient recovery post-digestion. In this work, we assess the level of phosphorus release and binding, and whether the mechanisms are likely to be precipitation-related, or otherwise.

### METHODS

**Batch anaerobic digestion**

AD was performed using a modified biochemical methane potential (BMP) test (Angelidaki et al. 2009). This method offers a high accuracy, 95% confidence in relative error < ± 10% on the principal parameters. Each BMP batch test was 100 ml in total consisting of inoculum (50 ml), organic matter (5 g sample was added as wet material), and deionized water for dilution. The samples were kept gas-tight in a 160 ml glass vial, with a pressure rating of approximately 6 bar. The pH of each batch was initially adjusted to 7.5 with either 1 M sodium hydroxide or 1 M hydrochloric acid, and oxygen in the headspace of the vials was purged with pressurized nitrogen prior to sealing. The tests were incubated at 38 °C to foster the biological degradation of the added solid waste and the resulting nutrient release.

The biological degradation of the waste material (organic matter) was tracked by measurements of the quantity of methane produced over time. The amount and composition (mainly methane and CO₂) of headspace gas were determined by a gas pressure measurement with a manometer and subsequent use of loop injection gas chromatography (Perkin Elmer, USA). The excess gas in the headspace was removed using a needle. The contents of each reactor vial were mixed by inversion prior to the collection of a gas sample. A leveling-off in the total amount of methane produced was interpreted as an approach to the maximum extent of nutrient release (due to a decline in the available biodegradable solid waste in the reacting batch). When the degradable material in the test batches was exhausted, the vials were opened and the reacted mixtures were analyzed for nutrients. Soluble components were determined on filtered samples (centrifuged and filtered at 0.2 μm) of the reacted mixtures. A list of samples (solid waste) used for the BMP test is given in Table 1. The methane yield from the sample-free blanks was subtracted from that of the batches containing sample and the corrected data were fitted with the relationship:

\[ Y_{CH_4} = Y_{CH_4, max} \cdot (1 - e^{-kt_{hyd}}) \]

(1)

where \( Y_{CH_4} \) is the methane produced per gm of volatile solids (VS) fed (ml CH₄/gVS), \( Y_{CH_4, max} \) is maximum methane potential per gm of VS fed (ml CH₄/gVS), \( k_{hyd} \) is the first order degradation rate constant (1/day) and \( t \) is the degradation period (days). \( Y_{CH_4, max} \) refers to the biodegradability of the sample. SigmaPlot® was used to estimate the parameters of Equation (1) using the secant method and errors were estimated as the 95% confidence interval.

**Analytical methods**

Water-soluble elements in the BMP feed solids were measured using 1:50 solids/water extract. For total elemental composition (P, K, Mg and Ca), the feed solids were solubilized using acid digestion followed by microwave digestion (MDS 2000, CEM, Matthews, NC, USA). The extracts were filtered using a 0.45 μm membrane filter. A flow injection analyzer (FIA, Lachat QuikChem8000, Lachat Instruments, Loveland, CO, USA) was used to measure P-PO₄ and N-NH₄ from the filtered extracts. For FIA, the pH of the filtrate
solution was then adjusted with HCl or NaOH so that the pH lies within the following ranges: pH 5.0–8.0 for phosphate analysis; pH 4.0–13.0 for ammonia analysis. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima 7300DV, Waltham, MA, USA) was used for total elemental concentration from the filtered extracts. Total solids (TS) and VS were measured according to Standard Methods (APHA 1998).

**Bioavailability test**

Citric acid (2%) was used to determine the bioavailability (plant availability) of phosphorus and metal salts from the digestate. This method was adopted from Veeken & Hamelers (1999). The sample was prepared by mixing 15 ml of digested effluent and 5 ml of 8% citric acid solution. The solutions were stirred for about 120 min at 23°C. The experimental setup included a 50 ml glass sample holder with a magnetic stirrer pin and a multiple stirrer plate. Leachate was separated from the solution using a centrifuge (4,000 rpm, 20 min) and a syringe filter (0.22 μm PES). The nutrient concentrations of the major dissolved elemental species were determined with FIA and ICP-OES techniques, as above.

**Nutrient solubilization**

Nutrient solubilization at different pH was assessed by adding hydrochloric acid (8%) to municipal sewage wastewater treatment plant digestate (MWT), collected in Brisbane. The experimental setup included a 100 ml glass sample holder with a pH probe and a pH data logger. The digestate was stirred at 200 rpm using a magnetic stirrer pin. A known amount of the HCl (8%) was added to the 80 ml digestate every 120 min. Samples were collected before the addition of HCl and solubilized nutrients were measured with FIA and ICP-OES techniques, as above.

**Modeling using PhreeqC**

Aqueous equilibrium simulations were performed with the software package PhreeqC using literature solubility products (Parkhurst & Appelo 1999). The solution temperature for each simulation was set at 23°C and the pH was varied over the range investigated in the experiments (1.8–7.6). Chlorine ion concentration was allowed to vary to balance the charge of the solution (i.e., pH effectively adjusted by HCl). At each equilibrium condition (specific pH), equilibrium concentrations of the ionic species of P, Ca and Mg and precipitations of the inorganic compounds were modeled.

**RESULTS AND DISCUSSION**

The solid waste moisture content, VS content and elemental composition are shown in Table 1. Moisture contents were highly variable due to generation methods; stockpile litter contained typically less moisture compared to fresh litter. The total nitrogen content varied in the range 1.5–5.4 wt % on dry basis, and 6–36% of the N is water soluble (NH4). The total phosphorus varies in the range 0.43–2.6 wt % on a dry basis and contained water-soluble P (PO4) in the range 10–49%. Comparatively, the water-soluble content of P was higher than for N for the measured samples.

Figure 1 shows experimental data for the digestion of different solid wastes tested in this work. The amount of

| Characteristics of the solid waste tested. Variation in the sample is shown by standard deviation for three subsamples |
|------------------|------------------|------------------|------------------|------------------|------------------|
| Moisture (%)     | VS (wt %)        | aTN (wt %)       | aNH4-N (wt %)    | aCa (wt %)       | aK (wt %)        |
| Poultry chicken manure | 71 ± 1.2         | 21 ± 0.64        | 5.3              | 1.1              | 7.0              |
| Meat chicken processing waste | 88 ± 0.39        | 11 ± 0.38        | 5.4              | 1.1              | 1.3              |
| Meat chicken waste | 31 ± 0.63        | 60 ± 0.63        | 2.4              | 0.87             | 2.1              |
| Piggery stockpile litter | 9.9 ± 0.82       | 49 ± 0.38        | 2.9              | 0.16             | 2.5              |
| Piggery screw-press waste | 68 ± 0.27        | 27 ± 1.34        | 2.2              | 0.62             | 0.43             |
| Piggery stockpile screened manure | 80 ± 0.53        | 18 ± 0.89        | 2.9              | 0.56             | 0.38             |
| Piggery separated solid | 64 ± 0.67        | 32 ± 0.43        | 1.5              | 0.19             | 0.44             |
| aDry basis. Errors were not measured. |
| VS: volatile solids; TN: total nitrogen; TP: total phosphorus. |
methane produced by batches in triplicate was highly reproducible, as indicated in Figure 1 by the uncertainty estimates. The measured data were fitted by the first order model (Equation (1)). The methane potential curves in Figure 1 are typically observed for the BMP assay (Angeldaki et al. 2009). Such a first order curve with exponential rise suggests maximum methane yield and negates any inhibitory or toxic effects during the test.

Table 2 lists the biodegradability ($Y_{\text{CH}_4, \text{max}}$) and the rate constant ($k_{\text{hyd}}$) of solid waste streams tested under anaerobic conditions. Overall, the degradability of chicken waste streams (meat and poultry) were higher than for piggery samples. The difference in degradability could be related to the bedding material and storage conditions. The degradability of the piggery samples was largely insensitive to the extent of treatment and storage. The maximum methane produced per gram of VS added from organic solid residue was highest in meat chicken processing waste followed by poultry chicken manure, piggery processed samples and meat chicken farm waste.

The compositions of phosphorus, nitrogen, calcium, magnesium and potassium in digestate, digestate filtrate and filtrate from the bioavailability test are shown in Figures 2–4. The nutrient concentrations in Figures 2–4 are the nutrient concentrations in the solid waste subtracted from the blanks, which contained only an inoculum. Water-soluble P and N are also shown in Figures 2 and 4 respectively. The digestate filtrate contained 5–10% of the total P available in the digestate (Figure 2). In similar work, Wahal et al. (2010) reported that nearly 95% of P present in digested dairy waste was insoluble and bound to Ca as precipitates. In this work the total water-soluble P fraction decreased during AD; this behavior was also observed during digestion of dairy manure (Gungor & Karthikeyan

---

**Figure 1** | Cumulative methane produced over time for the digestion of solid waste as listed in legend. The lines are first order model fits (Equation (1)). Errors were estimated as the 95% confidence on the mean for three samples (two-tailed 95 percentile T-test with two degrees of freedom).

**Table 2** | Biodegradability and rate constant of the sample tested for the BMP test. Errors are 95% confidence interval

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{\text{hyd}}$ (1/day)</th>
<th>$Y_{\text{CH}_4, \text{max}}$ (ml/gVS fed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poultry chicken manure</td>
<td>0.24 ± 0.02</td>
<td>361 ± 7</td>
</tr>
<tr>
<td>Piggery separated solid</td>
<td>0.07 ± 0.02</td>
<td>176 ± 12</td>
</tr>
<tr>
<td>Piggery stockpile screened manure</td>
<td>0.09 ± 0.02</td>
<td>157 ± 12</td>
</tr>
<tr>
<td>Piggery screw-press waste</td>
<td>0.14 ± 0.02</td>
<td>224 ± 10</td>
</tr>
<tr>
<td>Piggery stockpile litter</td>
<td>0.16 ± 0.02</td>
<td>103 ± 4</td>
</tr>
<tr>
<td>Meat chicken waste from farm</td>
<td>0.10 ± 0.02</td>
<td>164 ± 5</td>
</tr>
<tr>
<td>Meat chicken processing waste</td>
<td>0.23 ± 0.04</td>
<td>429 ± 17</td>
</tr>
</tbody>
</table>
P was fully released to the soluble phase with addition of 2% citric acid (Figure 2). Similar results were observed for Ca and Mg (Figure 3). N and K were released in the digestate and remained soluble in the filtrate (Figure 4). Results were consistent for different solid waste streams tested in this work. The addition of 2% citric acid also dropped the digestate pH from 7.6–7.8 to 3.4–3.6. The release of nutrients could also be related to the drop in the solution pH.
During AD, P and other key nutrients (N, Mg, K and Ca) associated with the organic matter are released into the digestate. The release of ionic species of P and Mg during AD is related to polyphosphate hydrolysis and organic matter degradation, whereas Ca release is due to organic matter degradation (Marti et al. 2012). Partitioning of P, K, Mg, and Ca to the solid phase has been related to the formation of inorganic compounds or adsorption of these species on solid surfaces (Parson et al. 2001; Marti et al. 2008). Interestingly, the data in Figures 2–4 indicate that substantially all minerals are bioavailable and hence mineral bound. Therefore, the fractions bound in the non-degradable fraction are very low. In general, in particular, P, Ca and Mg are released from organic matter during AD but remain bound (or precipitate) as inorganic compounds, which are re-dissolved at low pH.

The impact of pH on the nutrient release was assessed by adding HCl (8%) to the digestate. The pH of the untreated digestate was 7.6. Addition of HCl released ionic species of P, Ca and Mg and reduced pH of the digestate (Figure 5(a)). The HCl (8%) was added every 120 min to the well-stirred beaker; it gave sufficient time to dissolve any inorganic precipitates in the digestate. No significant release of P and Ca was observed at a pH of 5.5. Below pH 5.5, the soluble concentration P, Ca and Mg increased with a rise in acid concentration (Figure 5(a)). The release of nutrients leveled at pH 4.5, with no significant release of nutrients with further addition of HCl. The release of

Figure 4 | Nitrogen and potassium composition in digestate, soluble fraction in digestate and soluble fraction of digestate after bioavailability test. The water-soluble fraction of N is shown in (a).

Figure 5 | (a) Effect of pH, reduced by addition of HCl, on releases of P, Ca and Mg from the digestate. Curves generated by PhreeqC. Solid symbol is measured values at each pH and open symbol is total concentration of the element in digestate. (b) Precipitates at different pH identified by PhreeqC.
Mg above pH 5.5 can be related to dissolution of struvite (MgNH₄PO₄·6H₂O) and newberyite (MgHPO₄·3H₂O) as indicated in Figure 5(b). Dissolution of brushite (Ca(HPO₄)·2H₂O) and hydroxyapatite (Ca₃(PO₄)₂(OH)·H₂O) was related to the release of P and Ca in the digestate. The dissolution trend suggests P was mainly bound to Ca in the digestate (Figure 5(a)).

At pH 1.8, the amount of Ca and Mg released was below the total concentration where complete release of P was observed (Figure 5(a)). The equilibrium concentration of P, Ca, and Mg at different pH was modeled using PhreeqC and fitted to the experimental data (Figure 5(a)). The model fitted well with P concentration and low concentration Ca and Mg for the different pH conditions. Ca and Mg were over-predicted by the model below pH 5.0. This could be related to the presence of organically or inorganically bound Ca and Mg in digestate and not detected by the model. Different authors (Schuiling & Andrade 1999; Wilsenach et al. 2007) have observed that potassium struvite (KMgPO₄·6H₂O) could precipitate instead of struvite in the case of low ammonium concentrations. However, in this study due to high concentration of ammonium no potassium chemical fixation was observed in the digestate or predicted by the model. The precipitation of aluminum and iron phosphates was not considered in this work due to the negligible soluble iron and aluminum concentrations in the streams. In any case, our work below indicates that particularly calcium binding dominates in minimizing soluble phosphorous levels.

Strategies to avoid nutrient precipitation during anaerobic digestion

Based on the results in this paper, even if there are significant amounts of Ca or Mg present, the soluble phosphorous concentrations usually are too low for economic recovery. This is particularly so for animal manures and litters. There are a number of options to optimize the anaerobic system and promote recovery of the nutrients:

(a) **Additives.** Ethylenediaminetetraacetic acid (EDTA) is a chelating agent for calcium with a high stability constant. Zhang et al. (2010) managed to release 91% of the phosphorus in their digestate effluent by adding EDTA up to 70 mmol/l concentration. Other calcium chelating agents are nitrilotriacetic acid (NTA), citrate, tartrate and diethylene tri-amino pentaacetic acid. As compared to EDTA, NTA is easily biodegradable and is almost completely removed during wastewater treatment. Acid (e.g., HCl) and recycled CO₂ could also be used as additives. These are more likely to have negative impacts on digester operation (e.g., depressed pH).

(b) **Two-stage AD process.** AD for solid waste can be operated in two stages. The first stage includes hydrolysis/acidification and liquefaction of the solid waste and the second stage includes methanogenesis. It has been shown that the acidic conditions in the first stage favor solubilization and mobilization of nutrients from the solid biomass to the leachate, making them more accessible for removal (Lehtomaki & Björnsson 2006). Solid wastes suitable for two-stage digestion include materials with high TS content, such as energy crops or solid manure.

(c) **Membrane processes.** Anaerobic membrane bioreactors (AMBR) have short hydraulic retention times while maintaining high solids retention time to obtain high biomass. As a consequence, the solid retained in the reactor can eventually be hydrolyzed to release nutrients to the solution over the retention time period. Dissolved nutrients can be continuously removed from the membrane permeate through appropriate nutrient recovery techniques. Ion-exchange columns have recovered 95–98% P-PO₄ and N-NO₃ from the permeate (Johir et al. 2011). Grundestam & Hellström (2007) produced a concentrated nutrient-rich stream from the AMBR permeate using reverse osmosis membrane with 91% recovery of N and about 99% of P from domestic wastewater. Continuous removal of the nutrient from permeate would reduce in-reactor precipitation and improve economy of the process through side-stream recovery of valuable fertilizer product.

**CONCLUSIONS**

In this work, we found that the soluble phase of the digestate from animal solid waste contained less than 10% of the total P, Ca and Mg added as solid waste. However, these elements were acid-soluble, indicating that they were mainly precipitates rather than organically bound. Precipitates were probably a mixture of calcium and magnesium precipitates (struvite, hydroxyapatite, brushite and newberyite). Modeling with PhreeqC predicted well the release of phosphorous at low pH but not the calcium and magnesium, possibly indicating that at low pH calcium and magnesium are binding with other organic ligands.
ACKNOWLEDGEMENTS

The Grains Research and Development Corporation (GRDC) funded this research under the project UQ00046: Fertilizer from Waste Phase 1 and Phase 2. Dr Chirag Mehta is a GRDC research fellow. We would like to thank Dr Beatrice Keller-Lehmann (AWMC, UQ), Mr David Appleton (Land and Food Sciences, UQ) and Ms Susan Cook (AWMC, UQ) for analyses. Dr Stephan Tait helped with the PhreeqC software.

REFERENCES


Stark, K., Plaza, E. & Hultman, B. 2006 Phosphorus release from ash, dried sludge and sludge residue from supercritical water oxidation by acid or base. Chemosphere 62, 827–832.


First received 5 June 2012; accepted in revised form 25 September 2012