ABSTRACT

The 'uncontrolled' formation of struvite (MgNH$_4$PO$_4$.6H$_2$O) is one of the major challenges facing most wastewater treatment plants (WWTPs). It is particularly prevalent around post-anaerobic digestion (AD) processes (treating sewage sludge) where NH$_3$, PO$_4$ and pH levels can be quite high. Common struvite-related problems include the clogging of pipes, pump and dewatering equipment downstream of the AD; resulting in poor performance, increased maintenance and energy costs. This study aimed at utilising the combined effect of varying pH and Mg$^{2+}$ doses in digesters to pre-precipitate PO$_4$ and NH$_4$-N (as struvite) thereby reducing their availability in post-AD processes. Bench-scale AD-reactors were fed with pre-pasteurised sewage sludge with varying Mg-doses and pH, to control struvite formation by reducing PO$_4$ and NH$_4$-N availability in post-AD processes for 'uncontrolled' struvite formation. Post-AD Mg$^{2+}$-dosing tests (with pH variation) were also conducted to compare removal rates as a function of the location of Mg-addition. More than 40% PO$_4$ and NH$_4$-N-removal efficiencies were observed in post-AD tests. Methane production was also seen to increase with increasing Mg$^{2+}$.

Keywords

Ammonium, Anaerobic Digestion, Magnesium, Phosphate, Struvite

Introduction

The high cost of treating nutrient-rich wastewaters (especially digested sludge supernatants); coupled with the stringent regulations limiting nitrogen (N) and phosphorus (P) discharge into aquatic environments have stimulated research in the development of anaerobic digestion processes capable of producing reduced P and N levels in the effluent (Capdevielle et al. 2013). About 60 - 70% of sewage sludge in the UK is treated by mesophilic anaerobic digestion (AD). Most of these AD processes produce liquors (following sludge dewatering) with elevated pH and high soluble P and N concentrations. These conditions favour the precipitation of struvite in digested sludge processing equipment, further resulting in significant financial (increased maintenance costs) and operational problems (e.g. pipeline blockages, fouling of pumps, interrupted plant operations) (Neethling and Benisch 2004; Barat et al. 2005; Marti et al. 2008). The situation is even worsened by the accumulation of P in systems (with little or no P-removal technology in place) resulting from the recycling of liquors (following digested sludge dewatering) back to the head of the WWTP for treatment. Struvite (MgNH$_4$PO$_4$.6H$_2$O) is a white orthorhombic crystal that forms when magnesium, ammonium and phosphorus react in equimolar amounts as presented in the following chemical reaction:

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4.6\text{H}_2\text{O} (s) \]

Struvite component ions commonly get resolublized during the AD process making them available for struvite formation (Mamais 1994; Parsons and Smith 2008; Marchi et al. 2015). Struvite formation and subsequent precipitation occurs when the concentrations of soluble magnesium, ammonium and phosphate exceed supersaturation levels. As the supersaturation ratio (i.e. the ratio between the product of the component ions and the solubility product (Ksp))
increases, the potential for struvite formation also increases (Doyle and Parsons 2002). Other factors which have been observed to influence struvite formation in water resource recovery systems include; pH, mixing rate, temperature, and the concentrations of other ions (e.g. Ca\(^{2+}\)) (Bhuiyan et al. 2007). The potential for struvite formation has been found to increase with increasing pH (between 6 and 10); commonly in areas where pH increases in response to carbon dioxide stripping or pressure drop (Tansel et al. 2014). Such is the case with anaerobically digested sludge with pH commonly between 7.2 and 8.5. The solubility constant (pKsp) of struvite was also observed to increase with increasing pH, thereby increasing the potential for struvite precipitation at higher pH (with the highest struvite precipitation observed at pH 9.5) (Doyle and Parsons 2002; Sharp et al. 2013). Struvite has been observed to be a slow release fertilizer (Demirer et al. 2010).

In order to control struvite-related problems it is important to understand the underlying factors responsible for its formation. Parsons et al. (2007) proposed pH to be a very important factor in struvite control. Some studies also suggested the use of metal salts (e.g. ferric chloride, magnesium chloride, magnesium hydroxide, magnesium oxide, alum etc.) to control the formation of struvite (Bergmans et al. 2014). Most technologies developed to recover P (as struvite) in WWTPs have generally been applied to the aqueous phase (i.e. dewatering liquors from sludge lines). Although, recent studies (Bergmans et al. 2014; Geerts et al. 2015; Marchi et al. 2015) have shown improved dewaterability of digested sludge as one of the benefits of P-recovery in the sludge phase, a lot still needs to be done to cost-effectively minimise available P and N levels in processes downstream of anaerobic digesters (ADs).

This study investigated the feasibility of recovering P (as struvite) in Anaerobic Digesters (ADs) through the addition of Mg\(^{2+}\) (as MgCl\(_2\)) and pH adjustment. The study also provided analysis on the effect of Mg\(^{2+}\) addition and pH adjustment on the performance of the ADs (in terms of methane production and volatile solids (VS) removal). Experiments involving Mg\(^{2+}\) addition and pH adjustment in post-AD sludge (i.e. digested sludge) were also conducted to compare P- and N-removal rates with that of the P-recovery experiments in the ADs. It was observed that both methods reduced the available soluble P and N levels in the dewatering liquor which could not only minimise the potential for scaling resulting from ‘uncontrolled’ struvite precipitation in downstream sludge lines, but could also potentially reduce any associated energy costs involved in treating these liquors via activated sludge treatment processes (as is currently being done when the liquors get recycled to the ‘head’ of most WWTPs for treatment).

**Materials and Methods**

A WWTP in northeast England, which had significant struvite scaling problems, was chosen as case study and a mass balance for P and N around key units on the site was established. Bench experiments were then conducted to evaluate the efficiency of PO\(_4\) removal in sludge and the subsequent reduction in available P in digested sludge supernatant following Mg\(^{2+}\) addition and pH adjustment in sludge (both pre- and post-AD). Magnesium Chloride (MgCl\(_2\)) was used as Mg\(^{2+}\) source due to its high solubility in water (Parsons et al. 2007).

**Bench-Scale AD Tests**

Eight 1L flat-bottomed cylindrical glass culture vessels were used to set-up bench-scale AD reactors (ADs). The ADs were seeded with digested sludge (DS) samples from the chosen STWs. These ADs were then fed daily with pre-pasteurised sewage sludge (See its constituents on Table 1 below) collected from the chosen WWTP. The pH of the ADs was adjusted on a daily basis and the various Mg\(^{2+}\) doses were added alongside the feed. The ADs were operated at temperatures between 38-40°C and solid retention time (SRT) of 18days so as to simulate the operating conditions of the full-scale ADs at the WWTP under study. Mixing in the ADs was provided by magnetic stirrers. The ADs were first operated for 42 days to investigate the effect of varying pH and Mg-doses on PO\(_4\), NH\(_4\)-N and VS removal rates. The effect on methane production by the ADs was also analysed. These ADs were operated in duplicate under four different conditions (i.e. pH 7 with no additional Mg\(^{2+}\); pH 7 with 50 mg/L added Mg\(^{2+}\); pH 8 with
no additional Mg^{2+}; pH 8 with 50 mg/L added Mg^{2+}). The pH 7 and 8 regimes were chosen because previous studies had shown that pH values outside this range often reduced the dewaterability of digested sludge (Bergmans et. al. 2014).

The ADs were then further operated for a further 60 days. All 8 ADs were adjusted to pH 8 (which was closest to the operating pH conditions (pH ~7.8) of the full-scale ADs at the aforementioned WWTP). They were operated in duplicates at four different Mg^{2+} doses (0, 50, 100 and 150 Mg^{2+}mg/L to give a Mg:PO_{4} ratio in the sludge of 0.01, 0.4, 0.7 and 1.1 respectively). This range was chosen based on observations from previous studies that revealed that stable struvite crystals are formed at Mg:PO_{4} ratio ≤ 1.2 (Rahaman et al. 2014). Samples of the feed and effluent from the ADs were analysed three times weekly for pH, volatile solids (VS), COD, NH_{4}-N and PO_{4}. The NH_{4}-N and COD concentrations were measured using Merck Spectroquant test kits (www.analytical-test-kits.com) supplied by VWR; while the VS and PO_{4} levels were determined by standard methods (APHA 1995). Gas sampling bags (2L, ALTEF) were connected to each bench AD and the daily biogas volume was measured. Methane (CH_{4}) concentration in the biogas was measured using a Carlo Erba Gas Chromatograph coupled to a flame ionisation detector (FID). The VS removal rate and the cumulative CH_{4} volume were used to assess the effect of varying pH and Mg doses on the performance of the ADs.

**Table 1:** Constituents of Pre-pasteurised sludge used to feed the bench – scale ADs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>NH_{4}-N</td>
<td>2110</td>
<td>mg/L</td>
</tr>
<tr>
<td>PO_{4}</td>
<td>661</td>
<td>mg/L</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>41</td>
<td>mg/L</td>
</tr>
<tr>
<td>Total Solids (TS)</td>
<td>213899</td>
<td>mg/L</td>
</tr>
<tr>
<td>Volatile Solids (VS)</td>
<td>128339</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

**Bench-scale Post-AD Mg^{2+} dosing Experiments**

These were Jar test experiments performed on digested sludge to assess the removal rates of NH_{4}-N and PO_{4} as a direct consequence of dosing Mg^{2+} and adjusting the pH in post-AD sludge. This was a comparison test to ascertain which condition (pre-AD Mg^{2+} dosing or post-AD Mg^{2+} dosing) provided the most effective scenario for controlling struvite precipitation. Twelve 500ml beakers (each containing 200ml of DS collected from the STWs mentioned above) were adjusted in duplicate to the following pH values 6.5, 7.0, 7.5, 8.0, 8.5 and 9.0. This was to investigate the effect of pH on NH_{4}-N and PO_{4} concentrations in solution.

The next set of experiments involved adjusting the pH of the DS in the beakers to pH 8 and adding the following Mg^{2+} doses 0, 50, 100 and 150 Mg^{2+}mg/L. In each Jar test experiment, there was mixing for 10mins at 100rpm, followed by a settling period of 3hours. The NH_{4}-N and PO_{4} concentrations in the supernatant were then determined as described above.

**Results and Discussion**

**P and N mass balances**

Figure 1 shows the PO_{4} and NH_{4}-N mass balance around few key treatment units on the WWTP under study. Due to the seasonal variations in the data (e.g. flow, PO_{4} and NH_{4}-N) obtained from the site, the figures presented on Figure 1, represent average values over the period of May 2013 – May 2015. The mass balance showed that without the incorporation of N and P recovery measures, there was a potential build-up of P and N (as PO_{4} and NH_{4}-N) in the
WWTP, with approximately over 90% of influent PO_4 being recycled throughout the system. It was difficult to determine the actual amount of PO_4 and NH_4-N load that arrives the WWTP via the influent that gets recycled to the head of the WWTP via the digested sludge centrate due to the fact that the ADs at the WWTP treat both sludge produced on site and imported sludge (from other WWTPs in northeast England). Figure 1 also revealed the PO_4 and NH_4-N load in sludge rose on average by a factor of ~8 (from 529kg/day to 4.6tons/day) and ~4 (252kg/d to 849kg/day) respectively after AD. This coincides with previous studies which revealed that struvite component ions commonly get resolubilized during the AD process making them available for struvite formation (Mamais 1994; Parsons and Smith, 2008; Marchi et al. 2015). The 2% and 23% drop in the PO_4 and NH_4-N load (respectively) in digested sludge centrate, suggests possible their possible precipitation/recovery (as struvite) in the dewatered cake.

**Figure 1:** Basic P and N mass balance around the WWTP under study.

**Comparison between P and N recovery in AD and post-AD sludge**

Jar test experiments revealed a correlation between the pH, and the NH_4-N (R² = 0.88) and PO_4 (R² = 0.9) levels in digested sludge (see Figure 2). It was observed that the concentration of NH_4-N and PO_4 the aqueous phase of digested sludge decreased with increasing pH (with up to ~12% and ~21% removal of NH_4-N and PO_4, respectively, observed at pH 9). This be could linked to their possible precipitation as struvite (whose solubility decreases with increasing pH (typically between 7.5 and 10)). This is typically so because at high pH the ionic product of struvite constituent ions often exceeds the solubility constant (Ksp) for struvite (Neething and Benisch, 2004; Bergmans et al. 2014).

The post-AD Mg addition experiments showed even stronger correlation between added Mg²⁺ doses, and the NH_4-N (R² = 0.89) and PO_4 (R² = 0.95) levels in digested sludge (see Figure 3). Higher NH_4-N and PO_4 removal efficiencies with increasing Mg²⁺ concentration and pH were observed. Removal efficiencies of up to 45% and 88.6% for NH_4-N and PO_4, respectively, were observed when 150mg/L Mg²⁺ was added into digested sludge (giving a Mg:PO_4 ratio of 1.2 in the sludge) and its pH adjusted to 8 and (see Figure 4). This is consistent with the revelations of Bergmans et al. (2014) which showed that, as the molar Mg:PO_4 ratio approaches one, more N- and P- can be recovered as stable solid minerals (e.g. struvite). This is further explained in Barat et al. (2005) which showed that increasing the available Mg²⁺ concentration in solution, increases the competitiveness over Ca²⁺ ions during ionic exchange reactions to form phosphate compounds.

The Bench AD experiments also showed increasing NH_4-N and PO_4 removal efficiencies with increasing pH and Mg²⁺ dose. The NH_4-N removal efficiency rose from 2.2% (when the pH of
the AD was adjusted to 7 with no added Mg\textsuperscript{2+}) to 19.7\% (when 150mg/l Mg\textsuperscript{2+} was added and the pH adjusted to 8); while PO\textsubscript{4} removal efficiency rose from 5.8\% (when the pH of the AD was adjusted to 7 with no added Mg\textsuperscript{2+}) to 61.3\% (when 150mg/l Mg\textsuperscript{2+} was added and the pH adjusted to 8) (see Figure 5). The relatively higher NH\textsubscript{4}-N and PO\textsubscript{4} removal efficiencies in post-AD Mg\textsuperscript{2+} dosing experiments compared to that of the Bench ADs could have been as a result of the relatively higher chance for CO\textsubscript{2} stripping (resulting in a further increase in pH and the potential for struvite precipitation) in the former (which was done in open beakers) compared to the completely sealed ADs. Also, the ADs were continuously stirred with very minimal allowance for the settling (hence less effective removal of NH\textsubscript{4}-N and PO\textsubscript{4} by precipitation) compared to the Jar test scenario where there was adequate settling time for effective removal. This is consistent with the revelations of Wang et al. (2006) and Ariyanto et al. (2014) which state that mixing speed significantly influence crystal growth. Furthermore, the jar test experiments were conducted at room temperature which falls within the temperature range (15 – 35 °C) for effective struvite precipitation and the determination of struvite solubility constants (Ksp) (Hanhoun et al. 2011), whereas the ADs were operated at 38 – 40 °C (which could potentially disintegrate the struvite crystals) (Marchi et al. 2015).

![Graph showing the effect of varying pH on NH\textsubscript{4}-N and PO\textsubscript{4} in digested sludge from the WWTP under study](chart.png)

Figure 2: The effect of varying pH on NH\textsubscript{4}-N and PO\textsubscript{4} in digested sludge from the WWTP under study
**Figure 3:** The effect of varying Mg doses and pH on NH$_4$-N and PO$_4$ in digested sludge

**Figure 4:** The effect of varying post-AD Mg dosing rates on NH$_4$-N and PO$_4$ removal efficiencies at pH 8
**Benefits Analysis**

As shown in Figures 4 and 5, the ‘controlled’ precipitation of NH$_4$-N and PO$_4$ as struvite strongly diminishes the available NH$_4$-N and PO$_4$ concentrations. Theoretically, this should slow down the speed of struvite scaling in downstream operations; thereby leading for significant economic savings arising from less pump, centrifuge and pipeline maintenance.

The Bench AD experiments revealed improved AD performance with increasing Mg$^{2+}$ dose between pH 7 to 8. The VS removal was observed to increase from 32.7% in digested sludge from ADs operated at pH 7 with no additional Mg$^{2+}$ to 52.2% in digested sludge from ADs operated at pH 8 with 150mg/L additional Mg$^{2+}$. There was a corresponding increase in daily methane production with increasing Mg$^{2+}$ dose between pH 7 to 8; with up to 8.3% methane production observed in ADs operated at pH 8 with 150mg/L additional Mg$^{2+}$. This increase is methane production could be linked to the falling free ammonia levels in the ADs (implying less toxicity on methanogens) with increasing Mg$^{2+}$ dose. The additional methane production could also lead to significant economic savings by offsetting some of the energy costs (e.g. for aeration of to provide mixing during struvite recovery experiments) and/or the purchase of chemicals (e.g. MgCl$_2$ and alkali/acid (for pH adjustment)) for the struvite experiments on site.

**Conclusion**

The study confirmed that pH is very important in struvite control. It was observed that slightly raising the pH (to 8) was beneficial to: NH$_4$-N and PO$_4$ reduction, and biogas production. Magnesium addition to sludge (during or post-AD) presumably increases struvite formation in the
sludge, therefore potentially reducing the uncontrolled formation of the mineral within wastewater treatment plant due to high P and N present in sludge dewatering liquors.

The major challenges ahead, include; an appropriate method for the effective separation of struvite crystals from sludge and measures to effectively minimise the precipitation of heavy metals alongside P and N in the sludge. These challenges will form part of the investigation in the next phase of the project.

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References


