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A number of waste solutions from processes operating in Western Australia (anaerobic digester supernatants, facultative lagoon treated piggery and abattoir waste effluents) were characterised chemically and by automated titration to determine acid-base characteristics. The results indicate conditions for optimising the removal of N and P by precipitation (predominantly struvite) as well as the way forward in determining the full scope of N and P waste streams for which recycling by precipitation (either magnesium or calcium based salts) may be feasible.

INTRODUCTION

The solution chemistry of struvite (MgNH₄PO₄·6H₂O) precipitation from waste solutions is not well described, despite an increasing number of pilot and full scale precipitation plants being developed [1-4]. This solution chemistry is fundamental to the development of optimal performance of pilot plant and full scale struvite P recovery operations.

Idealistically, a molar ratio in solution of Mg: N: P of 1: 1: 1 is required for precipitation of MgNH₄PO₄·6H₂O.

The scope of waste streams or solutions for which P recovery by struvite precipitation might be reasonably achieved is quite wide. Raw animal wastes [5], poultry waste treated by anaerobic digestion [6-8], piggery waste treated by anaerobic digestion [8-10], liquid cattle manure [11] and municipal sewage [12-14] are some of the more common human and animal wastewater streams which may be associated with P recovery by struvite precipitation. This list is by no means comprehensive and there are numerous wastes not covered including pharmaceutical, chemical and food waste streams, biosolids (e.g. municipal organic waste) and landfill leachates [4,15]. It is apparent from the published component analyses of the above listed waste streams that present with the components of choice (COC) for struvite precipitation (NH₃-N, PO₄-P and occasionally Mg) are usually a number of components which react competitively with one or more of these COC (viz. Ca, CO₃-C and in some cases volatile fatty acids - VFAs). These competing components prevent the ideal 1:1:1 Mg:N:P condition being directly met without the loss of COC by counter reactions. Given this situation, the only realistic option is to adjust pH so that its value is conducive to struvite formation over other products and then introducing a good reactive form of excess magnesium, or some variation of this approach (e.g. alkaline sources of Mg), to allow precipitation of MgNH₄PO₄·6H₂O to a P or N limited solution state (usually P limited).

Similarly, if calcium phosphates (apatites) are the desired P recovery product, a solution pH conducive to these products needs to be achieved, followed by introduction of a reactive form of excess calcium or a variation of this approach.

Optimised process conditions for particular waste solutions are therefore obtained by determining the major chemical components of interest to the precipitation and the waste solution acid-base reactivity characteristics. This paper describes these measurements and our analysis for a number of waste solutions to optimise P recovery by struvite precipitation. Some of the analogous optimal calcium phosphate P recovery conditions are also briefly discussed.

MATERIALS AND METHODS

Samples for analysis were collected from a variety of waste treatment facilities in Western Australia (W.A.). These included a facultative lagoon network treating piggery effluent (Piggery Effluent Sample, PES; Mandurah, W.A; sampled from exit of final [fourth] pond), a facultative lagoon system treating abattoir wastewater (Abattoir Effluent Samples 1 and 2, AES-1, AES-2; Harvey, W.A; AES-1 sampled exit final [third] serial facultative pond, AES-2 sampled exit complete lagoon system [3 serial facultative and 1 parallel black water pond]) and municipal wastewater treatment facilities (Anaerobic Digestor Supernatant Sample A, ADDSA; Subiaco W.A; in-situ sample from 1 of 3 parallel anaerobic digestors [secondary treatment]; Anaerobic Digestor Supernatant Sample B, ADDSB;Woodman Point, W.A; in-situ sample of supernatant liquor from the anaerobic digestor [primary treatment]).

Samples were stored in ice for transportation to the laboratory and between separation procedures. Samples from all sites were centrifuged at 9000rpm for 15 minutes. In the case of the first anaerobic digestor sample (ADSSA), the supernatant from this separation was centrifuged at 9000rpm for a further 15 minutes. Centrifuged samples were then refrigerated (at 4°C) or kept in ice before gravity filtration through a Whatman® No.5 paper filter to remove particulate organic and other material. Filtered samples were stored at 4°C. Extracts from these samples were then prepared by a variety of means for a range of chemical analyses. The details of these extra preparations and the analytical methods used are given in table 1. Sample titrations were performed on a Radiometer® DTS800 Automatic Titrator, with glass membrane and calomel reference electrodes. The DTS800 was programmed with the necessary end-point pH and a delay time. The maximum volume setting was 40mL for all samples and the delay time set at 60s for 0.1M titrant experiments and 120s for 0.01M titrant experiments. The effect of the delay time is to automatically override an unstable pH reading following an addition of titrant, causing the DTS800 to register the most recent (stable) reading as an equilibrated measurement. The initial dose of titrant is relatively large, resulting in a concomitant rise in pH. Subsequent titrant doses become gradually smaller as the endpoint pH is approached, hence data at near-neutral pH is not as resolved (smooth) as in the upper and lower pH regions.
Table 1. Sample preparations and analytical methods used to measure field samples.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Sample preparation*</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (filterable)</td>
<td>acidification with conc. H₂SO₄ (to approximately 1% v/v), dilution</td>
<td>closed reflux, titrimetric [16]</td>
</tr>
<tr>
<td>COD (soluble)</td>
<td>filtration through Whatman GF/C type filter and 0.2μm membrane filter assembly, acidification with conc. H₂SO₄ (to approximately 1% v/v), dilution</td>
<td>closed reflux, titrimetric [16]</td>
</tr>
<tr>
<td>Alkalinity, CO₃⁻¹, HCO₃⁻¹</td>
<td>as described in text</td>
<td>calculation from acid-base titration [16]</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>filtration and acidification as per COD (soluble), dilution</td>
<td>phenate oxidation [16]</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>filtration and acidification as per COD (soluble), dilution</td>
<td>ascorbic acid reduction [16]</td>
</tr>
<tr>
<td>Volatile Fatty Acids (VFA)</td>
<td>filtration as per COD (soluble), addition of 15% v/v ortho-Phosphoric Acid to filtered solution</td>
<td>chromatographic separation (Varian® model 3700 GC with FID, Porapak® QS 80-100 mesh column packing, operating temperature 190°C) [16]</td>
</tr>
<tr>
<td>Mg, Ca, Na, Fe</td>
<td>filtration and acidification as per COD (soluble) and dilution</td>
<td>ICP-AES Analysis (Varian® Liberty model 2000)</td>
</tr>
<tr>
<td>Cl</td>
<td>filtration as per COD (soluble) and dilution</td>
<td>automated ferricyanide method [16]</td>
</tr>
<tr>
<td>Acid-base titration</td>
<td>as described in text</td>
<td>Automated titration with 0.1M, 0.01M standard solutions of HCl or NaOH (Radiometer® DTS800 automatic titrator with glass and calomel reference electrodes)</td>
</tr>
</tbody>
</table>

* other than as described in the text of the paper. All samples were frozen or refrigerated (at 4°C) prior to the time of analysis, where they reached room temperature by standing.

1 these quantities are calculated from the APHA Alkalinity Standard Method [16]

Titrations were in 2 separate series for each sample. The first series were titrations to pH 12 or 11, using 0.1M or 0.01M NaOH (ConVol® or Merck® analytical standard) respectively. The second series was titrations to pH 2 or 3 using 0.1M or 0.01M HCl (ConVol® or Merck® analytical standard) respectively. Each series was replicated 3 to 5 times for each wastewater solution sample type, excepting the anaerobic digestion samples (ADSSA and ADSSB) which were not titrated with 0.01M reagents. Waste solution samples were titrated as 10mL aliquots (A grade volumetric pipette) obtained from bulk solution brought to experimental temperature by standing. Temperature was maintained at 25±1°C by laboratory air conditioning. An acid resistant plastic stirrer operated at an approximate speed of 500 rpm during titrations. Titration data was logged by an IBM-PC type microcomputer.

RESULTS

Chemical Characteristics

Table 2 presents the chemical characteristics measured in the waste solutions studied. While it is clear that the AES samples have the lowest concentrations of all the soluble components measured (including nutrients), the relative proportions of soluble components (particularly nutrients) do not have obvious trends. While the NH₃-N to PO₄-P ratio of the PES to ADSSA samples are all approximately 5:1, the ADSSB sample has a proportion closer to 20:1 for this comparison. An explanation for this disparity between ADSSA and ADSSB lies in the digestor configurations, namely that after primary sludge digestion treatment, breakdown and solubilisation of the complex organic material in the sludge (into soluble nutrients and other entities) would not be as great as in the more extensive secondary treatment procedure.

Acid-Base Characteristics

Figure 1 shows the combined titration data for acid/base titration with 0.1M and 0.01M concentration reagents. The continuous nature of the titration profiles is achieved by "pairing" single acid and base run data for plotting. Continuity is not always attained due to ongoing calibration of the pH meter in either the acid or base range tending to create a slight discrepancy in the initial measured (near neutral) pH values of complementary acid and base range titration runs.

This is particularly pronounced in the more dilute titrant samples (figs. 1 ii, iv and vi). Another aspect of the titration data it is necessary to mention is the non-uniformity of pH interval and titrant addition in the profiles, explained earlier. The data show considerable accuracy, best evidenced by the lack of distinction between individual titration runs in the combined plots.
Table 2. Chemical characteristics of waste solutions studied in this paper.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Piggery Effluent Sample (PES)</th>
<th>Abattoir Effluent Sample 1 (AES-1)</th>
<th>Abattoir Effluent Sample 2 (AES-2)</th>
<th>Anaerobic Digestor Supernatant Sample A (ADSSA)</th>
<th>Anaerobic Digestor Supernatant Sample B (ADSSB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (filterable, mg L(^{-1}))</td>
<td>144 ± 14</td>
<td>72 ± 7</td>
<td>128 ± 13</td>
<td>983 ± 23</td>
<td>813 ± 19</td>
</tr>
<tr>
<td>COD (soluble, mg L(^{-1}))</td>
<td>146 ± 10</td>
<td>48 ± 5</td>
<td>106 ± 11</td>
<td>718 ± 16</td>
<td>514 ± 12</td>
</tr>
<tr>
<td>Total Alkalinity (as CaCO(_3), mg L(^{-1}))</td>
<td>680 ± 20</td>
<td>368 ± 2</td>
<td>335 ± 3</td>
<td>2520 ± 11</td>
<td>3252 ± 6</td>
</tr>
<tr>
<td>CO(_3) (as CaCO(_3), mg L(^{-1}))</td>
<td>53.9 ± 0.6</td>
<td>39.9 ± 0.2</td>
<td>45.9 ± 0.4</td>
<td>208.3 ± 0.8</td>
<td>341.5 ± 0.6</td>
</tr>
<tr>
<td>HCO(_3) (as CaCO(_3), mg L(^{-1}))</td>
<td>656 ± 8</td>
<td>348 ± 20</td>
<td>310 ± 25</td>
<td>2312 ± 9</td>
<td>2911 ± 5</td>
</tr>
<tr>
<td>NH(_3)-N (mg L(^{-1}))</td>
<td>138 ± 8</td>
<td>52 ± 2</td>
<td>59.4 ± 0.5</td>
<td>460 ± 10</td>
<td>517 ± 17</td>
</tr>
<tr>
<td>PO(_4)-P (mg L(^{-1}))</td>
<td>46.3 ± 0.2</td>
<td>17.9 ± 0.2</td>
<td>16.5 ± 0.2</td>
<td>128.3 ± 0.5</td>
<td>29.9 ± 0.3</td>
</tr>
<tr>
<td>VFA - Acetic acid (mg L(^{-1}))</td>
<td>-</td>
<td>7 ± 3</td>
<td>-</td>
<td>52 ± 3</td>
<td>27 ± 2</td>
</tr>
<tr>
<td>VFA - Propionic acid (mg L(^{-1}))</td>
<td>8 ± 1</td>
<td>7 ± 2</td>
<td>6 ± 1</td>
<td>33 ± 2</td>
<td>3.7 ± 1.7</td>
</tr>
<tr>
<td>VFA - n Butyric acid (mg L(^{-1}))</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.6 ± 1.4</td>
<td>6.6 ± 1.4</td>
</tr>
<tr>
<td>Mg (mg L(^{-1}))</td>
<td>55.3 ± 0.3</td>
<td>6.7 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>193.0 ± 0.6</td>
<td>177 ± 8</td>
</tr>
<tr>
<td>Ca (mg L(^{-1}))</td>
<td>79.0 ± 0.8</td>
<td>20.4 ± 1.0</td>
<td>24.1 ± 1.2</td>
<td>354.1 ± 0.4</td>
<td>184 ± 4</td>
</tr>
<tr>
<td>Na (mg L(^{-1}))</td>
<td>144 ± 2</td>
<td>122 ± 2</td>
<td>109 ± 2</td>
<td>1491 ± 2</td>
<td>1386 ± 25</td>
</tr>
<tr>
<td>Fe (mg L(^{-1}))</td>
<td>3.00 ± 0.05</td>
<td>4.1 ± 0.3</td>
<td>4.2 ± 0.3</td>
<td>5.60 ± 0.08</td>
<td>5.7 ± 0.4</td>
</tr>
<tr>
<td>Cl (mg L(^{-1}))</td>
<td>330 ± 18</td>
<td>64 ± 6</td>
<td>126 ± 5</td>
<td>2458 ± 66</td>
<td>2468 ± 21</td>
</tr>
</tbody>
</table>

**DISCUSSION**

**Interpretation of Chemical and Acid-Base Characteristics**

In terms of representing field waste solutions, the samples analysed are modified primarily by the centrifuge and filtration procedures applied to remove gross particulates and heterogeneous organic material which would degrade the quality of the glass electrode and its signal. In any event, the purified samples contained the components of greatest relevance to this study - soluble organics, nutrients and metals. The differing sample preparations mean the soluble chemical component data is not strictly the concentration of components present in the titrated samples - the measurements would actually be underestimates because of the centrifuging and filtering. Many of the samples were observed to develop cloudiness or precipitate when titrated in the basic pH range. In particular, PES samples were observed to develop cloudiness and precipitation was observed in ADSSA and ADSSB samples at high pH. This is clearly saturation with respect to one or more metal salts (calcium or magnesium) in the titrating solutions. Part of this turbidity could also represent colloidal phenomena or organic hydrolysis. From the data of table 2, it is obvious one of the salts forming in these solutions is struvite. This also means that solution mass balance is not maintained at higher pH, meaning further data interpretations or calculations (related to component concentrations) could be compromised in this high pH region. From the titration data of figure 1, it can be clearly seen that the concentration of a waste directly affects the molar quantity of acid or base required to reach the lower or upper pH bounds respectively. Hence the abattoir effluent samples (AES-1 and AES-2) require the least acid or base and the anaerobic digestor supernatant samples (ADSSA and ADSSB) require the most acid or base to reach the prescribed pH limit. This fact is corroborated by the alkalinity data (table 2), which is directly derived from the titration profiles (fig. 1). This relationship is quantified to a greater extent in table 3, which details the reagent base consumption of each sample to reach pH values of 9 and 10. This pH range is particularly important, in that it is the region from which optimal struvite precipitation is obtained [17]. It can be seen that in comparison to the facultative pond samples (PES and AES), the anaerobic digestor samples (ADSSA and ADSSB) require almost an order of magnitude more OH\(^{-}\) to reach pH 9. This comparison is preserved to reach pH 10. The ratio of OH\(^{-}\) required to reach the optimal pH range for struvite precipitation would not however be reflected in the expected (P limited) struvite production from the various samples. In the case of PES, if a pH of 9 was maintained to achieve a 90% reduction of P as struvite precipitate (taken as an arbitrary condition), 1.34 millimoles per litre (mM) of struvite would be produced for the consumption of approximately 2.5 mM OH\(^{-}\) (cf. tables 2 and 3). The ADDSA sample would yield 3.72 mM struvite for 12.6 mM OH\(^{-}\), ADDSB 0.87 mM struvite for 20.6mM OH\(^{-}\) and the AES samples would yield approximately 0.5 mM struvite for 1.5 mM OH\(^{-}\), under the same criteria. Clearly the most efficient production of struvite from the field samples considered would be from PES.
Figure 1. Titration data plots showing combined data for titrations to pH 2/12 with 0.1M HCl/NaOH or pH 3/11 with 0.01M HCl/NaOH (i) PES titrated with 0.1M HCl/NaOH (ii) PES titrated with 0.01M HCl/NaOH (iii) AES-1 titrated with 0.1M HCl/NaOH (iv) AES-1 titrated with 0.01M HCl/NaOH (v) AES-2 titrated with 0.1M HCl/NaOH (vi) AES-2 titrated with 0.01M HCl/NaOH (vii) ADSSA titrated with 0.1M HCl/NaOH (viii) ADSSB titrated with 0.1M HCl/NaOH.
Table 3 Reagent OH⁻ requirements for each sample to reach pH 9 and 10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagent OH⁻ consumption to reach pH value (mol OH⁻ L⁻¹ of solution)</th>
<th>pH 9</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES (with 0.1M NaOH)</td>
<td></td>
<td>3.6 x 10⁻³</td>
<td>1.18 x 10⁻²</td>
</tr>
<tr>
<td>PES (with 0.01M NaOH)</td>
<td></td>
<td>2.2 x 10⁻³</td>
<td>1.03 x 10⁻²</td>
</tr>
<tr>
<td>AES-1 (with 0.1M NaOH)</td>
<td></td>
<td>2.2 x 10⁻³</td>
<td>5.5 x 10⁻³</td>
</tr>
<tr>
<td>AES-1 (with 0.01M NaOH)</td>
<td></td>
<td>1.4 x 10⁻³</td>
<td>5.5 x 10⁻³</td>
</tr>
<tr>
<td>AES-2 (with 0.1M NaOH)</td>
<td></td>
<td>1.8 x 10⁻³</td>
<td>5.1 x 10⁻³</td>
</tr>
<tr>
<td>AES-2 (with 0.01M NaOH)</td>
<td></td>
<td>1.3 x 10⁻³</td>
<td>4.4 x 10⁻³</td>
</tr>
<tr>
<td>ADSSA (with 0.1M NaOH)</td>
<td></td>
<td>1.26 x 10⁻²</td>
<td>4.65 x 10⁻²</td>
</tr>
<tr>
<td>ADSSB (with 0.1M NaOH)</td>
<td></td>
<td>2.06 x 10⁻²</td>
<td>6.57 x 10⁻²</td>
</tr>
</tbody>
</table>

This comparison is somewhat superficial, as it does not consider the relative proportions of Mg and Ca, counter reactions in the wastewater (e.g. with carbonates) or the need for reagent supply for reaction, all of which are major factors in practically achieving the conditions discussed above. We can deduce from the above analyses and calculations that it will be desirable to treat the wastewater to reduce its acidity before attempting to neutralise with an alkaline substance. Treatment of the anaerobic digestor supernatant by aeration will accomplish the acidity reduction biologically.

In a similar way to that outlined above for struvite, calcium phosphate salts are optimally precipitated at pH 7.5-8.0 [18,19]. The interference of the carbonate system on the precipitation of apatites is considerable, given the relative solubilities (Ksp values) of calcium carbonates are many orders of magnitude lower than that of apatites [20,22,23] and both predominate in this pH range. In contrast, struvite is kinetically and thermodynamically favoured over other products at pH 9-10 [17].

Another point to be addressed regarding table 3 is the molar consumption of OH⁻ per L of solution for the same field samples titrated with different concentrations of titrant. In principle, there should not be any discrepancy in this quantity. However, the concentration of titrant does affect the type of reaction occurring. Minor, indirect or slow acid and base reactions will not be completed in the time between titrant additions if relatively large amounts of acid or base are delivered. This can result in erroneous estimates of the true molar OH⁻ consumption of a titrating sample in reaching a specific pH. For example, insufficient time may be available for back-reactions with the excess of OH⁻, despite a reasonably stable pH reading which triggers the addition of a further dose of titrant. Dilution effects may also be evident, although these are accounted for in the data calculations.

**Estimating Species Concentrations from Titration Inflection Points**

The plots of figure 2 each display a number of inflections or changes of slope. These regions can be more precisely identified by considering the first derivative to each titration curve (hereafter described simply as the derivative). Estimates of the derivative to a titration curve are obtained by successive approximation. The primary derivative is obtained by calculating the point-to-point slope within the titration data set. The mathematical relationships used to calculate the primary derivative and successive approximations to the derivative are detailed in the Appendix.

In the case of the PES titration curve (figure 1i), 3 clear inflections can be determined through a combined use of the primary and successive approximations to the derivative. These are to be found at pH 4.6, 6.5 and 7.8.

Using the theory of acid-base equilibria [24], these inflections can each be related to a particular component equilibrium in the titrated solution. After assigning an inflection to a component equilibrium, it is possible to estimate the total solution concentration of that component. A procedure is outlined in the Appendix.

Using the method in the Appendix, the total concentration of species A, A_T is 2χ and is determined by equation i.

\[
A_T = 2\chi = \frac{2(10^{-\text{pH}} + 1)\Delta T/(10^{-\text{pH}} + 1)}{10^{-\text{pH}} + 1} \quad (i)
\]

Using the molar concentration derived from equation i, mg L⁻¹ (ppm) concentrations can be calculated for the particular species involved. Table 4 lists the inflections, assigned equilibria and calculated concentrations of the respective component species for PES using equation i. The measured component concentrations are also shown for comparison.

Table 5 summarises titration curve inflections, assigned equilibria and calculated concentrations for the other field samples analysed. This method offers a number of possibilities for the description of chemical components and equilibria in a test solution. In a single experimental procedure, all the major acid-base equilibria could be identified quantitatively. This would indicate many chemical conditions necessary for optimised struvite precipitation from the test water and provide direction for modelling and defining this situation (optimal struvite precipitation).

In many of the successive approximations to the derivative of a titration curve, a type of 'noise' (erratic, unstable point-to-point values) can be noted in certain pH ranges. The principal cause of this effect is erratic data in one of the titration replicates, or a poor point-to-point resolution in the titration data (relatively large gap between pH data points).

In some cases, this lack of resolution precludes the use of identified pH inflections for further calculations.
Table 4. Inflection pH, assigned equilibria and calculated component concentrations for the PES (0.01M) acid-base titration profiles and derivatives (see Appendix).

<table>
<thead>
<tr>
<th>Inflection pH</th>
<th>Appropriate equilibrium (selected from critical compilations [20-23])</th>
<th>$A_T$ (lower)</th>
<th>$A_T$ (upper)</th>
<th>Overall $T$ (ppm)</th>
<th>Measured conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4$</td>
<td>4.02</td>
<td>4.08</td>
<td>4.05</td>
<td>125.6</td>
</tr>
<tr>
<td>6.5</td>
<td>$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$</td>
<td>1.33</td>
<td>1.23</td>
<td>1.28</td>
<td>15.4</td>
</tr>
<tr>
<td>7.8</td>
<td>$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$</td>
<td>5.71</td>
<td>4.06</td>
<td>4.88</td>
<td>151.3</td>
</tr>
</tbody>
</table>

* $A_T$ = estimated total concentration of listed species (e.g. phosphates, carbonates, etc.)
1 Calculated as shown in paper for points below inflection, (e.g. $A = H_xCO_3^{y-}$ for pH 4.6 inflection above)
2 as for 1 for points above inflection

Table 5. Major inflection points identified and quantified from the titration data of this paper.

<table>
<thead>
<tr>
<th>Inflection pH</th>
<th>Predicted $A_T$ (mg L⁻¹)</th>
<th>Measured $A_T$ (mg L⁻¹)</th>
<th>Inflection pH</th>
<th>Predicted $A_T$ (mg L⁻¹)</th>
<th>Measured $A_T$ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PES (0.01M TITRANTS)</strong></td>
<td></td>
<td></td>
<td><strong>AES-2 (0.1M TITRANTS)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>125.6</td>
<td>46.3 PO₄-P</td>
<td>4.5</td>
<td>112.2</td>
<td>16.5 PO₄-P</td>
</tr>
<tr>
<td>6.5</td>
<td>15.4</td>
<td>81.6 CO₃-C</td>
<td>11.0</td>
<td>140.4</td>
<td>40.2 CO₃-C</td>
</tr>
<tr>
<td>7.8</td>
<td>151.3</td>
<td>46.3 PO₄-P</td>
<td>11.5</td>
<td>1159.4</td>
<td>128.3 PO₄-P</td>
</tr>
<tr>
<td><strong>PES (0.1M TITRANTS)</strong></td>
<td></td>
<td></td>
<td><strong>ADSSA (0.1M TITRANTS)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>107.6</td>
<td>46.3 PO₄-P</td>
<td>4.0</td>
<td>184.4</td>
<td>128.3 PO₄-P</td>
</tr>
<tr>
<td>6.4</td>
<td>172.8</td>
<td>81.6 CO₃-C</td>
<td>6.4</td>
<td>580.8</td>
<td>302.4 CO₃-C</td>
</tr>
<tr>
<td>8.1</td>
<td>254.2</td>
<td>46.3 PO₄-P</td>
<td>8.0</td>
<td>399.9</td>
<td>128.3 PO₄-P</td>
</tr>
<tr>
<td>11.3</td>
<td>230.4</td>
<td>81.6 CO₃-C</td>
<td>10.0</td>
<td>1115.8</td>
<td>460 NH₃-N</td>
</tr>
<tr>
<td><strong>AES-1 (0.01M TITRANTS)</strong></td>
<td></td>
<td></td>
<td><strong>ADSSB (0.1M TITRANTS)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>47.4</td>
<td>17.9 PO₄-P</td>
<td>4.1</td>
<td>155.3</td>
<td>29.9 PO₄-P</td>
</tr>
<tr>
<td>6.4</td>
<td>89.2</td>
<td>44.2 CO₃-C</td>
<td>6.5</td>
<td>831.6</td>
<td>390.2 CO₃-C</td>
</tr>
<tr>
<td>7.8</td>
<td>86.2</td>
<td>17.9 PO₄-P</td>
<td>8.0</td>
<td>846.3</td>
<td>29.9 PO₄-P</td>
</tr>
<tr>
<td><strong>AES-1 (0.1M TITRANTS)</strong></td>
<td></td>
<td></td>
<td><strong>AES-2 (0.01M TITRANTS)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>43.7</td>
<td>17.9 PO₄-P</td>
<td>9.8</td>
<td>1400.0</td>
<td>517.0 NH₃-N</td>
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<tr>
<td>9.3</td>
<td>104.0</td>
<td>52.0 NH₃-N</td>
<td>11.3</td>
<td>1884.8</td>
<td>29.9 PO₄-P</td>
</tr>
<tr>
<td>11.0</td>
<td>148.8</td>
<td>44.2 CO₃-C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AES-2 (0.01M TITRANTS)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>57.7</td>
<td>16.5 PO₄-P</td>
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<td></td>
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</tr>
<tr>
<td>6.5</td>
<td>83.3</td>
<td>40.2 CO₃-C</td>
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<td></td>
</tr>
<tr>
<td>8.3</td>
<td>86.8</td>
<td>16.5 PO₄-P</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is clear that only the most prominent acid-base equilibria are detected in this data. The minor acid-base equilibria (VFA’s, metal hydrolysis) are not significant enough to be isolated, due to such factors as masking by more prominent equilibria and in the case of metal hydroxide complexation, inappropriate pH range (these reactions for Ca and Mg have pK values near or above 12, [20-23]). Consequently, metal concentrations (most particularly Ca and Mg) can not be identified or derived from the data. This is unfortunate, since these quantities are of some importance in estimating struvite precipitation from a wastewater sample.

Table 5 shows moderate agreement between measured component concentrations and those calculated using the method of this discussion (cf. Appendix). Overall, the measured and calculated carbonate concentrations are in greatest agreement. This is a result of two factors. Firstly, the reactions of CO₃-C (H₂CO₃, HCO₃⁻ and CO₃²⁻) with H⁺ or OH⁻ are the most significant in the field solutions. They are the most clearly detected inflections in all titration curves. Secondly, the measured and calculated carbonate concentrations are both derived from the titration data, albeit through different calculations.

Samples in which the NH₃/NH₄⁺ equilibrium was clearly identified showed reasonable agreement between calculated and measured concentrations of NH₃-N (within a factor of 2). The agreement between measured and calculated concentrations of ortho-phosphate are somewhat variable. In some cases there is a variation of up to 3 orders of magnitude between the known PO₄-P concentration and those calculated for one or more of the orthophosphate H⁺ addition reactions.
The general lack of agreement between measured and calculated concentrations can be ascribed to a variety of factors. The masking effect of superimposed equilibria (two or more equilibria whose equivalence points are close together in pH) is certainly a major influence in the identification of pH inflections and quantifying component concentrations. In these field samples, there is at least some lack of distinction between the $\text{HPO}_4^{2-}$ - $\text{H}_2\text{PO}_4$ and $\text{CO}_3^{2-}$ - $\text{HCO}_3^{-}$ equilibria, whose log K values lie quite closely together (approximately 6-7.2 and 6.8-8.0 respectively, [20-23]). As a result of this ambiguity, both basic assumptions of the method are contravened and the calculation invalidated, or diminished in significance.

An important factor in the processing of titration data at higher pH (above 10) is the effect of precipitation. As mentioned previously, precipitation means that solution mass balance for a particular chemical component is not necessarily maintained. This would mean that the second basic assumption of the method is not satisfied and again that calculations would be of less significance.

The best use of the approaches presented here would be achieved by the combined use of chemical speciation modelling with the chemical and titrimetric data. In this case, deficiencies in component identification or titration profiles could be reasonably deduced by interpretation of the modelled speciation.

CONCLUSIONS

In terms of application of struvite chemistry in this paper, one major point is that the pH titration indicates that the amount of alkaline materials added to achieve optimum pH for struvite precipitation varies considerably from wastewater to wastewater, and hence the importance of its determination. Having done so the reduction of acidity can be done chemically or biologically, and the latter may be a more cost-effective way.

Optimised recovery of N and P by struvite precipitation for particular waste solutions is obtained by sufficient chemical and acid-base titration profile data. Interpretation of this data allows the determination of the extent of counter reactions and the best way to move solution chemical conditions to a favourable area for struvite or apatite precipitation.

The adjunct use of chemical speciation modelling would considerably bolster this approach and elucidate optimal precipitation conditions.

REFERENCES

Mathematical Relationships used to Calculate the Primary Derivative and Successive Approximations to the Derivative of a Titration Curve

Consider the titration data set \((T_i, pHi)_i, i = 1, ..., n\) with increasing pH, where \(T_i\) represents the molar quantity of acid or base added per L of waste solution for a specific pH. \(pHi\) is the equilibrated pH value after addition of that quantity of acid or base. The following relationships apply,

**Arithmetic Means (AM),**

\[
\begin{align*}
\text{AM}_1 &= (T_1 + T_2)/2 \\
\text{AM}_2 &= \log_{10}(2) - \log_{10}(10^{-pH1} + 10^{-pH2}) \\
\end{align*}
\]

(for first 2 data points)

**Second Arithmetic Means (2AM),**

\[
\begin{align*}
\text{2AM}_1 &= (\text{AM}_1 + \text{AM}_2)/2 \\
\text{2AM}_2 &= \log_{10}(2) - \log_{10}(10^{-\text{2AM}_1} + 10^{-\text{2AM}_2}) \\
\end{align*}
\]

(for first 3 data points)

**Third Arithmetic Means (3AM),**

\[
\begin{align*}
\text{3AM}_1 &= (\text{2AM}_1 + \text{2AM}_2)/2 \\
\text{3AM}_2 &= \log_{10}(2) - \log_{10}(10^{-\text{3AM}_1} + 10^{-\text{3AM}_2}) \\
\end{align*}
\]

(for first 4 data points)

**Geometric Means (GM),**

\[
\begin{align*}
\text{GM}_1 &= (T_1 \cdot T_2)^{1/2} \\
\text{GM}_2 &= \log_{10}(10^{0.6931} + \log_{10}(10^{-pH1} + 10^{-pH2})) \\
\end{align*}
\]

(for first 2 data points)

The successive approximations to the arithmetic mean and the geometric mean can in turn be used to make approximations to the derivative of the titration data. These are defined as,

**Primary derivative (0D),**

\[
\begin{align*}
\text{0D} &= (pH2 - pH1)/(T2 - T1) \\
\end{align*}
\]

**First arithmetic approximation to the derivative (1DA),**

\[
\begin{align*}
\text{1DA} &= (\text{AM}_1 - \text{AM}_2)/(\text{AM}_2 - \text{AM}_1) \\
\end{align*}
\]

**Second arithmetic approximation to the derivative (2DA),**

\[
\begin{align*}
\text{2DA} &= (\text{2AM}_1 - \text{2AM}_2)/(\text{2AM}_2 - \text{2AM}_1) \\
\end{align*}
\]

**Third arithmetic approximation to the derivative (3DA),**

\[
\begin{align*}
\text{3DA} &= (\text{3AM}_1 - \text{3AM}_2)/(\text{3AM}_2 - \text{3AM}_1) \\
\end{align*}
\]

**First geometric approximation to the derivative (1DG),**

\[
\begin{align*}
\text{1DG} &= (\text{GM}_1 - \text{GM}_2)/(\text{GM}_2 - \text{GM}_1) \\
\end{align*}
\]

A Method to Estimate the Total Solution Concentration of a Component Identified as a Titration Curve Inflection

Basic assumptions of the method are -

- An inflection represents 1 dominant chemical equilibrium over the given sub-range of pH.
- The amount of H⁺ or OH⁻ added within a selected inflection and pH sub-range reacts directly in the conversion from the acid to base form or vice-versa.

With these assumptions, it is possible to use exact algebraic relationships to determine the concentration of a component, provided that (a) mass balance is preserved and (b) ion (charge) balance is preserved. In the solution systems studied in this experiment, these conditions are not totally satisfied since precipitation occurs in the solutions and the solutions are not completely chemically characterised. The following empirical calculation is therefore appropriate.

**General form of the calculation**

- Symbols: \(\Delta pHi = \) change in pH from inflection pH to upper/lower pH
- \(HA = \) proton associated form of ion A
- \(A = \) conjugate base form
- \(\chi = \) equimolar concentration of ion A = acid form HA (M units)
- \(\Delta T = \) moles acid/base added per litre of solution to reach upper/lower pH

**Figure 2 illustrates the conventions applied to an inflection point.**

![Figure 2. Naming conventions applied to an inflection point](image)

Using the Henderson-Hasselbalch equation [24,25],

\[
\begin{align*}
\text{pH} - pK &= -\log([HA]/[A]) \\
\end{align*}
\]

If it is assumed that the inflection pH selected (as above) represents pK for the equilibrium under analysis and pH is the lower or upper pH, xiv may be re-written as;

\[
\begin{align*}
\Delta pHi &= -\log([HA]/[A]) \\
\end{align*}
\]

the following re-arrangements and substitutions follow -

\[
\begin{align*}
\chi &= \{(10^{-\Delta pHi} + 1)\Delta T/(10^{-\Delta pHi} - 1)\} \\
\end{align*}
\]

hence the total concentration of species A, \(A_T\) is 2\(\chi\)

\[
\begin{align*}
A_T &= 2\chi = \{(2(10^{-\Delta pHi} + 1)\Delta T/(10^{-\Delta pHi} - 1)) \}
\end{align*}
\]

from this molar concentration, mg L⁻¹ (ppm) concentrations can be calculated for the particular species involved.