INFLUENCE OF PH ON THE HYDROLYTIC AND ACIDOGENIC PHASES DURING ANAEROBIC DIGESTION OF WASTE ACTIVATED SOLIDS IN A BATCH SYSTEM

B. M McDonald, D. J Gapes, J. P Strong

ABSTRACT

Fermentations of complex waste streams are sensitive to multiple environmental conditions, with pH being one key parameter. A laboratory-scale study was performed to describe the impact of pH on acidogenic fermentation of municipal wastewater treatment biosolids produced from a New Zealand nutrient removal plant. Duplicate batch fermentations were conducted, at two pH levels- pH 6 and 8. The effects of pH on hydrolysis and volatile fatty acid formation and purity were examined across a 15 day time series. It was expected that the pH 8 reactors would show a greater level of hydrolysis, but results indicated that volatile suspended solids destruction was greater at lower pH. Further, acidogenic formation of VFA was greater at low pH, also not an expected result. At pH6, methanogenic fermentation was suspected (but not confirmed) to impact on VFA productivity after 9 days fermentation, a phenomenon not observed at pH8.

Under more alkaline conditions, the kinetics of reaction did appear slower, with indications that the full extent of fermentation had not been reached by the end of the 15 day study. Acclimation of the microbiological community to the increased pH conditions may thus have been a significant factor in the hydrolysis/acidogenic efficacy of the system.

Certainly the results confirm that operational pH does have a significant impact on the acidogenic fermentation of biosolids, even across a moderately narrow span of pH, providing considerable potential for manipulation of product formation from these complex organic solids.

KEYWORDS

Methanogenesis, Acidogenesis, Acetogenesis, Waste activated sludge

1   INTRODUCTION

Anaerobic Digestion (AD) technology is utilised to target the production of biogas- a mixture of methane, carbon dioxide, and hydrogen (Poggi-Varaldo et al). There are four major steps to AD, these being hydrolysis, acidogenesis, acetogenesis and methanogenesis (Miyamoto, 1997).

In hydrolysis, polymeric material (e.g. protein, carbohydrate, fats) is broken down to smaller fragments. Subsequently, this material is transformed into small chain volatile fatty acid (VFA) such as acetic propionic and butyric acids). Interestingly, these two steps have direct relevance in the following areas outside methanogenic fermentation:

- in pre-fermentation within biological nutrient removal at municipal wastewater treatment plants
- in dark fermentation for bio-hydrogen production.

A number of factors impact on the performance of hydrolysis/acidogenesis. The effect of system pH on these initial steps can be profound and complex. Hydrolysis of primary solids from a wastewater treatment plant has

been shown to increase when working above the neutral pH range, with total VFA also increasing with pH (Wu et al. 2009). Alkaline fermentation up to pH 11 has been utilised to produce elevated levels of short chain fatty acids, again from primary sludge (Wu et al. 2010). Following glucose fermentation over pH range of 4.5-8, acetic acid yields were demonstrated to increase substantially with higher pH (Horiuchi et al. 2002; Temudo et al. 2007). This is consistent with work on food waste fermentation (Lim et al. 2008).

Thus, it would appear that increasing pH provides opportunity for increased hydrolysis and VFA production. However, fermentations remain difficult to predict, due to the complexity of the substrates and the strong potential for inhibition and thermodynamic control by fermentation products (Rodriguez et al. 2006).

Methanogenic fermentation appears to have optima between 6.5-7.2 (Appels et al. 2008). For fermentative control of methanogenic activity, operating far from this pH range in the hydrolysis/acidogenesis stage may have a substantial economic impact (pH/alkalinity adjustment costs). Thus, we have an interest in studying pH effects on acidogenic fermentation, but remaining within one pH unit of methanogenic optima.

In this work, we investigated the impact of pH on the fermentation of biosolids (primary/secondary blend) from a New Zealand municipal wastewater treatment plant. The focus of this work is to describe the hydrolysis and acid forming steps for this biosolid, to test the hypothesis that higher pH would provide a greater hydrolysis and VFA productivity, even for the small pH range of 2 units spanning neutrality (pH7).

2   MATERIALS AND METHODS

2.1   ANAEROBIC BATCH FERMENT

A blend of municipal waste activated sludge and primary sludge (here referred to as biosolids) was sourced from a local domestic wastewater treatment plant, which utilised a full biological nutrient removal process, with no AD processes for sludge reduction. This biosolid material was fermented under acidogenic conditions for 15 days in 6 L ferments. An AD inoculum was sourced from Tauranga District Council waste water treatment facility where a anaerobic digester is operated at pH 6.

The pH was maintained at pH values of 6 and 8 - either side of the optimal methanogenesis region (pH 6.5 to 7.2). The chosen pHs were maintained through automated addition of 1N H_2SO_4 or 2N NaOH as required. The volume of the acid or base solution used was measured daily. Four reactors were operated under anaerobic conditions and controlled in duplicate to 2 pH set points, pH6 and pH8

The consistency of the biosolids was 3 % VSS, and the consistency of the anaerobic sludge inoculum was 1.0 % VSS. Samples were removed from the batch reactors at time 0 and after 3, 6, 9, 12 and 15 days for analysis.

Unless otherwise described, the results of the duplicate reactors are presented as an average of the two, for each pH level.

2.2   ANALYSIS

Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS):

100 ml was filtered and processed according to APHA Standard Methods *2540B (APHA, 1998).*

Volatile Fatty Acids

Volatile fatty acid concentrations were determined by an in-house method involving pH correction, with formic acid, followed by capillary gas chromatography with flame ionisation detection (GC-FID). The column used was a 30m Supelco 23327 column (0.5 μM ID) ramped from 40ºC to 180ºC. Butan-1-ol solution as internal standard, and turbid samples were pre-filtered through a PTFE syringe filter (0.45μm). The method was also used to determine low MW alcohol concentrations (i.e. MeOH and EtOH).

Total and Dissolved Organic Carbon (TOC & DOC)

Total organic carbon was calculated from the DOC plus VSS carbon assuming 0.53gC/gVSS from LECO C&N analyser

DOC Samples were filtered through 0.45 μm cellulose acetate syringe filters (Dismic – 25cs). 5 ml of the filtered sample was added to 45 ml of distilled water in a 50 ml falcon tube. This was immediately frozen until analysis

in a batch using the TOC machine (Elementar High TOC II analyser with autoinjector and magnetic stirrer bar). A calibration curve was constructed using standards for 0, 50, 100, 250, 500 mg/l. A 50 mg/l standard was placed after the middle and the final sample for quality control.

Total and Soluble Chemical Oxygen Demand (CODtot & CODsol)

1.5 ml GFC filtered supernatant was stored for CODsol analyses and 1.5 ml of the whole sample was stored for CODtot analyses. Whole samples were homogenised prior to analysis using standard an in house method based on APHA_AWWA_WPCF "standard methods" Section 5220D (19th ed. 1995) and on ASTM Standard Test Method D 1252-88 9Method B).

3   RESULTS AND DISCUSSION

3.1   HYDROLYSIS

3.1.1   SOLIDS DESTRUCTION

Figure 1 shows that VSS destruction in the pH6 reactors was greater than that in the pH8 reactors. The performance of the duplicate reactors followed each other closely, and VSS destruction peaked at day 9 at 50% – 58% where after VSS stabilised until the end of ferment at day 15. The pH8 reactors showed similar VSS destruction in the first three days with the performance of the two duplicate pH 8 reactors again following each other closely. After a period of slower VSS destruction from day 3 to day 9, the rate of destruction increased until the end of ferment at day 15, by which time this had reached 41% - 46%.

VSS destruction in the pH 6 reactors was more rapid than at pH 8. This indicated that the acclimation period to the more acidic conditions was more rapid than to those at slightly more basic conditions. After 9 days the bacterial communities in the pH 8 reactors started further solids degradation, indicative of some form of acclimation requirement. In the same period the majority of the destruction at pH 6 occurred. The overall rate that was achieved at pH 8 was slower than that achieved in the pH 6 reactors although pH8 reactors did show signs of converging performance at cessation of the trial.

The levels of VSS destruction observed here are consistent with the expectation for anaerobic digestion provided in a comprehensive review by Appels (2008), who suggest 50-60% volatile solids destruction for a high rate anaerobic fermentation with retention time of 10-15 days.
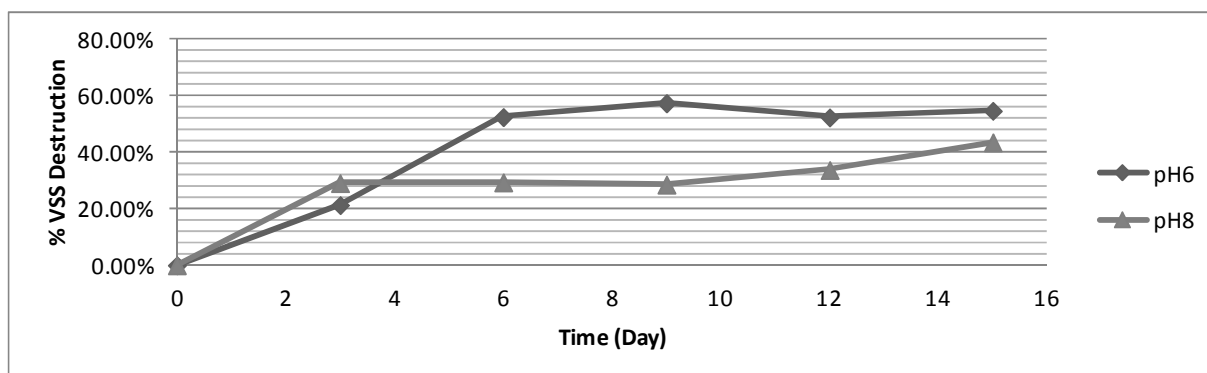

Figure 1: VSS Destruction for Batch Ferment

Figure 2 shows that there was a higher ratio of VSS:TSS for the pH 8 reactors than there was for the pH 6 reactors and reactors at both pH set points tended to decrease with time. This is consistent with the hydrolysing activity of the system, increasing the ash content of the residual biomass over the time-period of the fermentation.
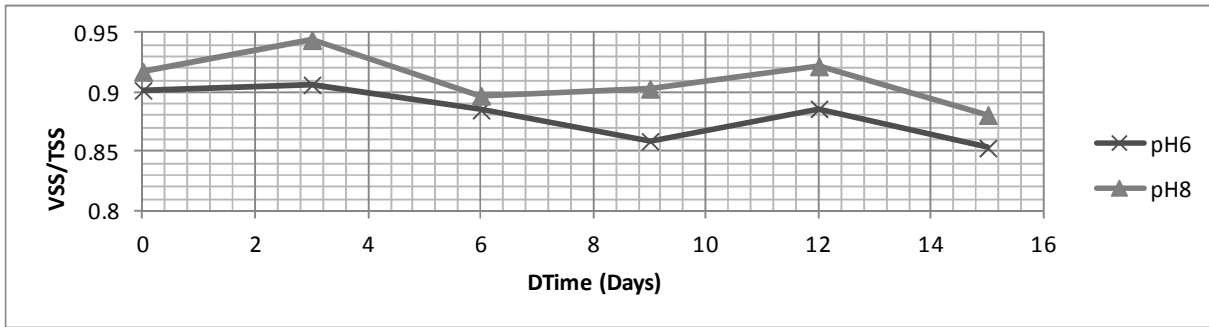
Figure 2: VSS to TSS Ratio for Batch Ferment.

3.1.2 ORGANIC CARBON AND CHEMICAL OXYGEN DEMAND

Figure 3 shows the development of soluble organic compounds within the fermentations. The pH 8 reactors initially showed a higher DOC than the pH6 reactors at 4680 mg/l of carbon on day 3, but thereafter decreased in DOC to 3220 mg/l followed by a modest but steady increase throughout the remainder of ferment time. The reactors at pH 6 showed a steady rise in DOC through to day 12, but by day 15 had decreased from 4650 to 3350 mg/l.

The soluble COD was remarkably consistent between the two pH conditions. The pH 6 ferment did show signs of depletion between days 10 and 15, consistent with observations from the DOC data
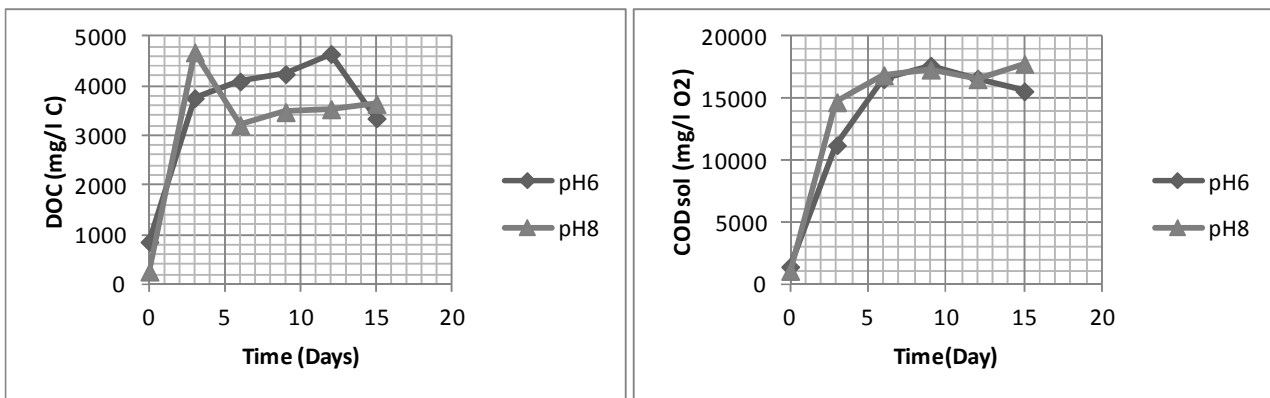

Figure 3: DOC and soluble COD for Batch Ferment.

Figure 4 describes the total (unfiltered) carbon and COD levels over the time series of the experiment. The figure shows a gradual decline in TOC with pH 6 reactors having the largest reduction (around 30% loss, as opposed to 20% for pH 8 conditions). In contrast, no significant change in total COD could be described for either pH condition. Despite the slight difference between these two measures, the results indicate that little organic material was being lost as gaseous product, over the time course of the experiment, and that the organics associated with the solid fraction was being effectively converted into soluble components.
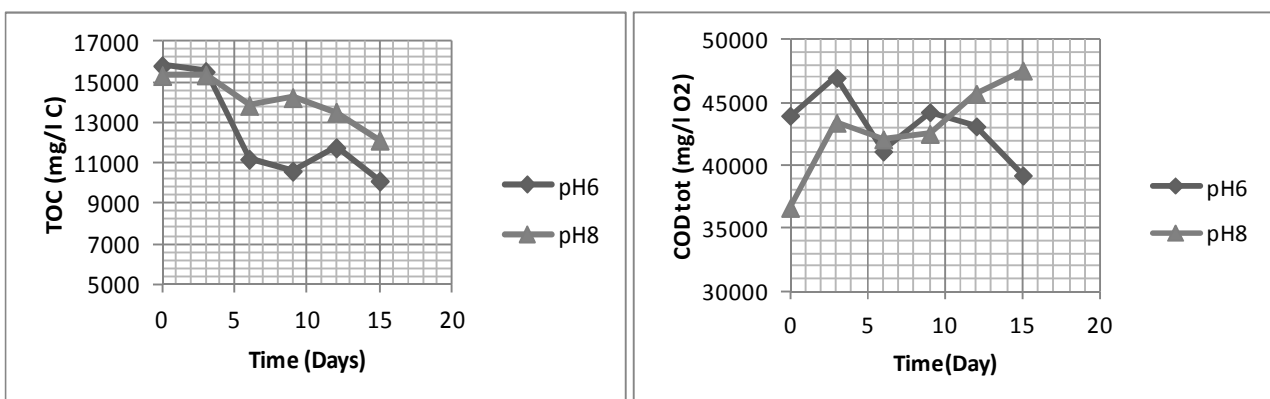
Figure 4: TOC and COD for batch ferment.

3.2   PRODUCT FORMATION

The formation of VFA product is described in Figure 5, for both duplicates of each pH level. Acetic acid and total VFA development **Error! Reference source not found.**reveals increasing concentrations for pH6, up to day 10. Beyond this, there is a significant decrease in concentration. A likely reason for this decrease is the onset of methanogenic activity (not measured).

The pH8 fermentations produced generally lower VFA concentrations, but the time-course of production showed no significant decline with time, and indeed continued to trend upwards on cessation of the experiment at 15 days. Thus, product formation had not attained a maximum for this higher pH condition. This may assist in explaining the contrast between the results found in this work, and the body of literature which indicates elevated VFA productivity with increasing pH (e.g. Wu et al 2009, 2010). It may be that an inoculum effect was present at this elevated pH, whereby a longer acclimation time was required for the microorganisms to increase their activity and fermentation performance.
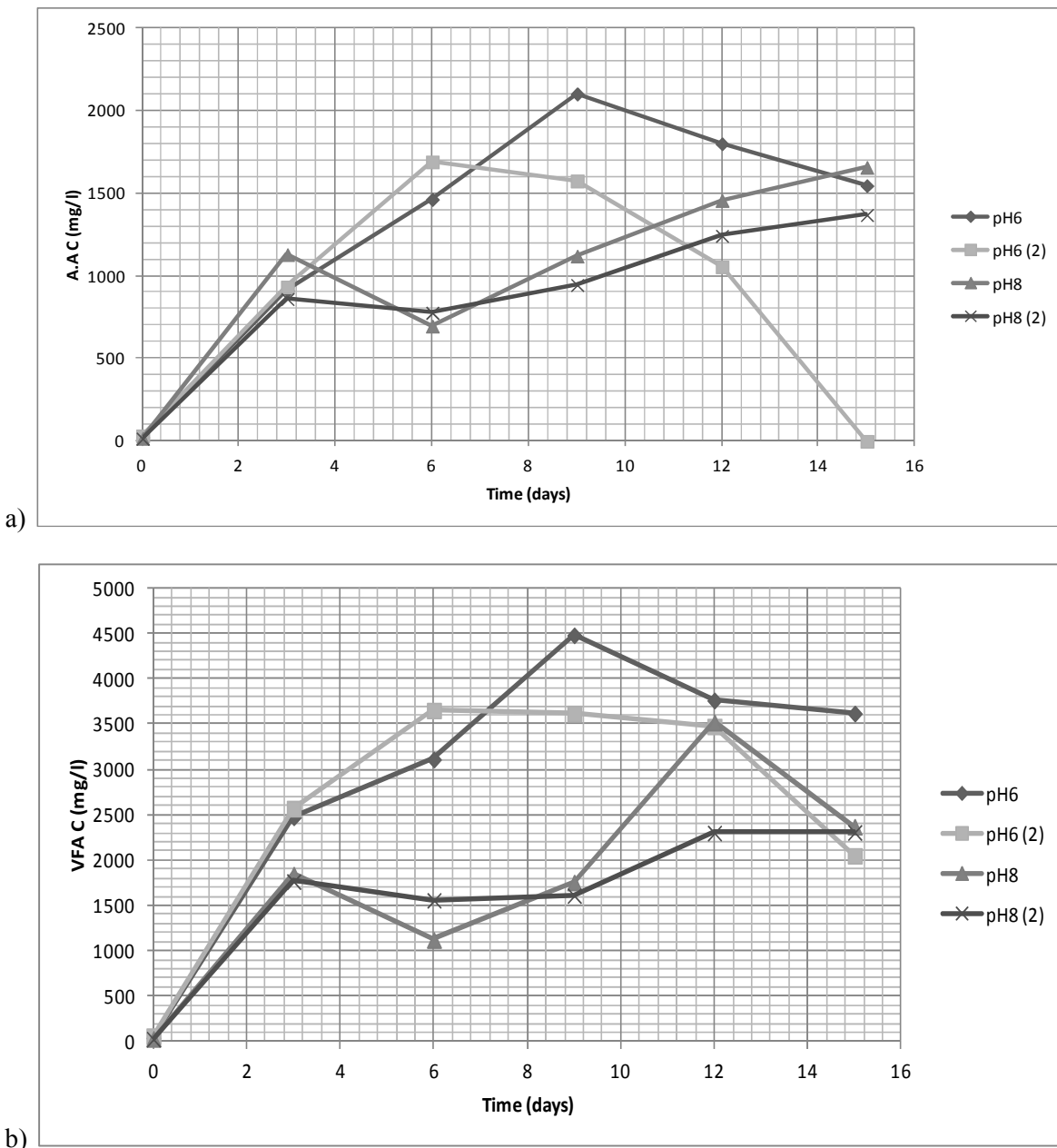

a)

b)

Figure 5: Product formation with time in fermentation a) acetic acid; b) total VFA. Both presented as carbon content of component of interest (mg/l)

The VFA production as a fraction of the total dissolved organic carbon is expressed in Figure 6. The figure reveals a low amount (less than 20%) of non-VFA carbon for the pH6 reactors for both days 6 and 15. This

contrasts to the results for the pH8 reactions, where up to 50% of the soluble carbon was unaccounted for in the fermentation. Interestingly, this fraction was reducing with fermentation time.

Acetic acid fractions decreased with time in the pH6 fermentations, but increased to up to 42% of the total DOC at day 15 of the pH8 fermentation. The decrease in the former may be put down to the initiation of methanogenesis (see above), whilst the increasing dominance of acetic in the pH8 reactors is consistent with literature observations (e.g. Wu et al 2009, 2010).
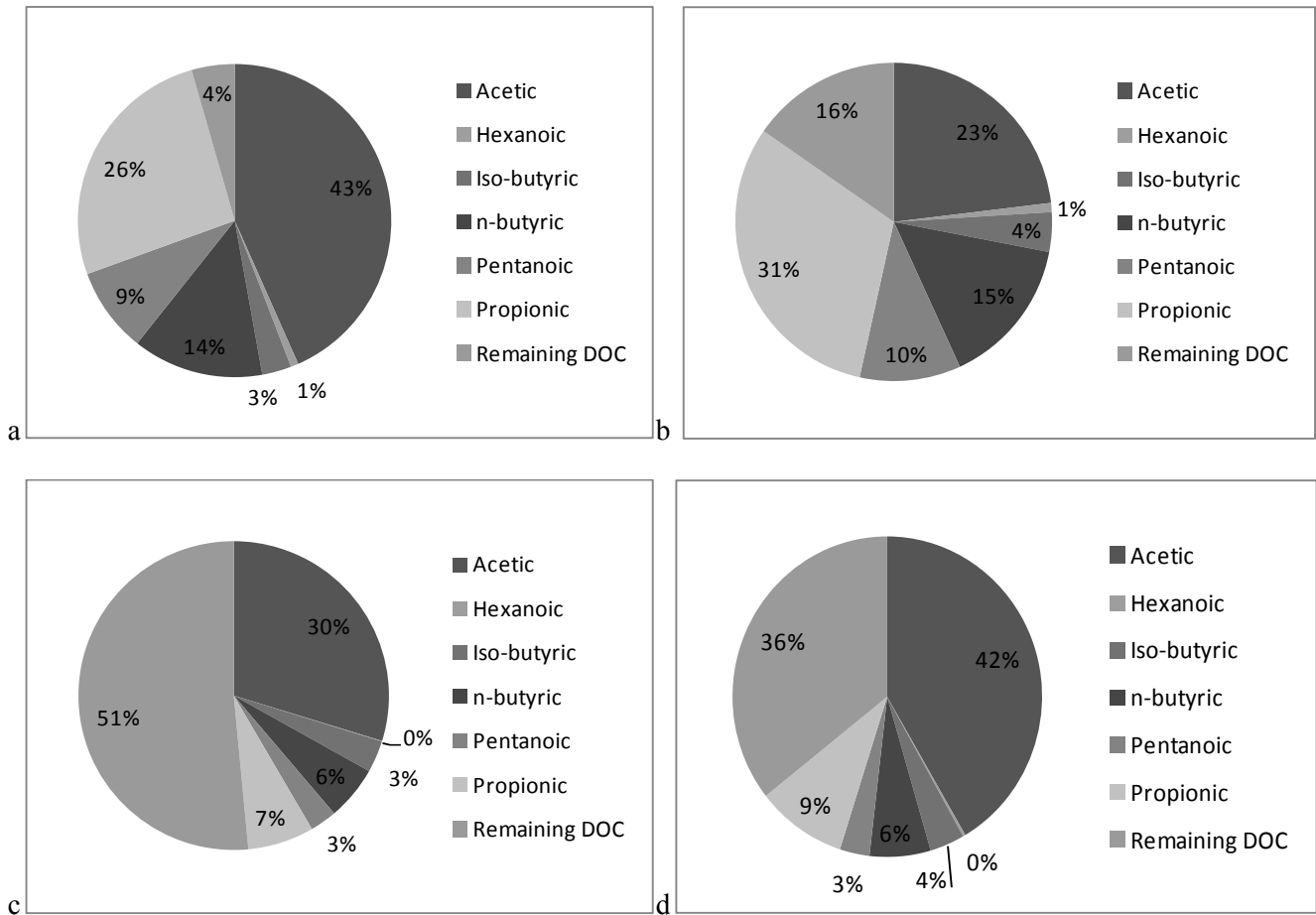
Figure 6: Product formation (as percentage of dissolved organic carbon) for a) pH 6 Day 9; b) pH 6 Day 15; c) pH 8 day 9; d) pH 8 day 15

4   CONCLUSIONS

This study has demonstrated the effect of pH on the acidogenic fermentation of municipal wastewater biosolids. The work did not strongly support the hypothesis of a positive impact of increasing hydrolysis extent or VFA product formation on increasing pH from 6 to 8. Under batch fermentations there was greater hydrolysis occurring in the pH6 reactor, and a higher and more sustained level of dissolved organic carbon. At pH6, methanogenic fermentation was suspected (but not confirmed) to impact on VFA productivity after 9 days fermentation, a phenomenon not observed at pH8.

Under pH8 conditions, the kinetics of reaction did appear slower, with indications that the full extent of fermentation had not been reached by the end of the 15 day study. Acclimation of the microbiological community to the increased pH conditions may thus have been a significant factor in the hydrolysis/acidogenic efficacy of the system.

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