FULL SCALE DEMONSTRATION AND ASSESSMENT OF ENZYMIC HYDROLYSIS PRE-TREATMENT FOR MESOPHILIC ANAEROBIC DIGESTION OF MUNICIPAL WASTEWATER TREATMENT SLUDGE

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ABSTRACT

A full-scale monitoring programme was undertaken to assess acidogenic pre-treatment as a bolt-on biological upgrade to mesophilic anaerobic digestion (MAD). The United Utilities Enhanced Enzymic Hydrolysis (EEH) MAD pre-treatment process was installed by Monsal Limited at the Blackburn (UK) wastewater treatment plant. This process combines mesophilic acid phase digestion with pasteurization at 55 ºC using low grade boiler heat derived from biogas production. The monitoring programme started in January 2006 and ended in June 2007. The monitoring data will be utilized in a comprehensive evaluation of this pre-treatment technology. The purpose of this paper is to show process performance data of scientific significance based on selected monitoring results that are being evaluated as a first step in the larger technical and economic assessment. Enhanced Enzymic Hydrolysis (EEH) achieved 6 log *E.coli* removal and elimination of *Salmonella*. The pre-treatment provided a consistent feed to MAD with the anticipated outcome of more stable methane production. The upgrade has enhanced VS destruction by around 10% with concomitant improvements of 24% in biogas production. The potential for VS destruction and gas production are currently limited by low influent TS levels (5 %DS) and the need for optimization of the MAD mixing regime. VFA production during EEH at Blackburn is limited by hydrolysis kinetics and by inhibition when VFA levels are in excess of 9 g VFA-COD/L. The final biosolids product was of consistent quality with metal levels well below the norms established by the EU and EPA. Further research is required to better characterize factors limiting the potential for VFA production during EH and to understand how the EH acidogenic environment contributes to pathogen elimination.

KEYWORDS

acidogenesis pre-treatment, biogas, enzymic hydrolysis, full-scale, pathogen removal, two-phase anaerobic digestion process, wastewater sludge management, upgrade, volatile fatty acids.

INTRODUCTION

This paper presents selected results from a full-scale monitoring program of a biological pre-treatment upgrade for mesophilic anaerobic digestion (MAD). The upgrade was carried out to achieve an overall improved process that could guarantee end-product quality for agricultural recycling. Agricultural recycling of biosolids has become regarded as the best practical environmental option in the UK. This perspective is also more widely advocated within Europe. The Sixth Community Environment Action Program includes the sustainable use of natural resources and management of wastes (Decision No 1600/2002/EC). Towards this objective, researchers, and owners and operators of municipal wastewater treatment works are encouraged to optimize aspects of the waste solids management, in particular:

1. The volatile solid reduction with concurrent benefits such as energy production (biogas), and
2. The production of safe, value added by-products for recycling, especially the recycling of nutrients and organic matter to agriculture.

Often existing infrastructure and investment in sludge management and disposal is already committed to MAD. In these cases, one route to augment biogas production and to improve digested biosolids quality while reducing quantity is with the use of a bolt-on pre-treatment technology prior to MAD. The choice of *which* pre-treatment technology for enhancing MAD is case specific and coloured by how the cost/benefit assessment of the capital investment with operations and management costs with energy and chemical inputs are weighted. Technology selection is also weighted by site specific needs, incentives, and stakeholders influenced by the available full-scale references, the local regional infrastructure and the established policies for sludge management at treatment facilities.

In the United Kingdom, the ban of sludge disposal to sea in 1998 forced re-evaluation of sludge with perspectives of both opportunities and concerns. Concerns about agricultural recycling of sludge came at the time of the BSE crisis fuelling a general atmosphere of public disquiet with respect to food safety. This concern led to the establishment of the *safe sludge matrix* (SSM, www.water.org.uk), a protocol agreed upon by the British Retail Consortium, the Water Industry, and the Department for the Environment, Food and Rural Affairs (DEFRA). The goal of the SSM was to set out clear guidelines for recycling to assure all stakeholders that the use of biosolids in agricultural was completely safe and fully sustainable. The SSM bans the agricultural use of untreated sludge and defines the quality requirement for conventionally treated and enhanced treated sludge. Conventionally treated sludge entails treatment that secures at least 99% elimination of pathogens. Enhanced treated sludge will be free from *Salmonella* and will have been treated so as to reach at least 6 log reduction in pathogens.

Although the prime driver in the UK for MAD upgrade has been the SSM, more recent escalating energy prices and growing interest in complimentary energy sources have also stimulated the trends and developments focused on augmenting the performance of sludge digestion revolving around minimizing the amount of wastewater sludge produced (Wei *et al.*, 2003) and reducing volumes of sludge for assimilation (Odegaard, 2004). There exist a number of strategies that could be coupled to MAD (Kelly, 2006; Mata-Alvarez *et al.*, 2000).

Sludge pre-treatment processes for enhancing MAD treatment performance must act to solubilize suspended sludge organic matter and achieve some level of hydrolysis of the more complex organic compounds. Thermal hydrolysis (Li and Noike, 1992), ultrasound (Tiehm *et al.*, 2001), ball milling (Baier and Schmidheiny, 1997), thickening-centrifugation cell lysis (Dohanyos *et al.*, 1997), ozonation (Yasui *et al.*, 2005), chemical (Ardic and Taner, 2005) and pressure (Dereix *et al.*, 2006) pre-treatments are some of the non-biological strategies that have been evaluated at different scales with respect to MAD enhancement. The principles of sludge conditioning methodologies have also been considered in combinations, such as chemical and ultrasound (Chiu *et al.*, 1997). The biological approach to enhance MAD is acidogenic pre-treatment (Demirel and Yenigun, 2002). Acid phase digestion as a pre-treatment to MAD represents a multistage anaerobic digestion system whereby processes of hydrolysis and volatile acid fermentation within the sludge are encouraged to proceed to as far as possible prior to the conventional MAD unit process (EPA, 2006). Acidogenic pre-treatment was a solution from its onset to problems of efficiency, stability and control encountered with MAD treatment (Liu and Ghosh, 1997; Ghosh *et al.*, 1995). While different physical, chemical and biological pre-treatment strategies are researched (Kelly, 2006), a number of developments have become commercially available (sonix™, MicroSludge®, Cambi THP, BIOTHELYS®, Bug Buster RnD®, Enzymic Hydrolysis; see for example 11th European Biosolids and Biowastes Conference Proceedings, 13-15th November 2006, Wakefield, UK). The present investigation concerns the full-scale monitoring of the biological approach to MAD pre-treatment that is based on the principles of Enzymic Hydrolysis (Mayhew *et al.*, 2002).

United Utilities PLC (Warrington, UK) together with Monsal Limited (Mansfield, UK) have established, at full-scale on a number of UK sites, a biological pre-treatment strategy based on plug flow hydrolytic acidogenic pre-fermentation. Plug flow designs for acidogenic pre-fermentation have been presented in the research literature from the perspective of volatile fatty acid production or benefits in the overall anaerobic digestion process (Bolzonella *et al.*, 2005; Liu and Ghosh, 1997; Sans *et al.*, 1995; Sans *et al.*, 1994). New focus is being directed towards specific benefits of pre-fermentation with respect to pathogen fate and removal (Salsali *et al.*, 2006).

In its initial inception the Enzymic Hydrolysis (EH) process was designed with six equal volume well-mixed tanks in series for mesophilic pre-fermentation (Figure 1). The system is designed with external heat exchange for the feed and draft tube type gas recirculation for mixing and sludge transfer between vessels. Sludge transfers of nominally 1/8 tank volume are made in semi-continuous batches that are sequenced in order to minimize short-circuiting. Vessel contents are mixed at least once between respective batch transfers. Transfers are made from both the upper and lower volume fractions of the cylindrical vessels due to potential for sludge stratification.

In order to achieve the SSM enhanced treatment standards, the EH process design was modified to include pasteurization at 55 ºC with a guaranteed minimum 5 hour batch hold (Figure 1). The Enhanced Enzymic Hydrolysis (EEH) process starts with EH mesophilic pre-fermentation in plug flow from tanks 1 to 3. A second external heat exchange loop after tank 3 brings the sludge contents of tank 4 up to 55 ºC. Tank 4 serves as a well-mixed staging reactor that delivers nominal 5/8 volume batches of heated sludge to tanks 5 or 6. Tanks 5 and 6 operate as parallel sequencing batch reactors. Thus, EEH combines pre-fermentation at 42 ºC with pasteurization at 55 ºC using only low grade heat from either a boiler or Combined Heat and Power system (CHP).

The EEH-MAD plant upgrade at the Blackburn Wastewater Treatment Plant (WWTP) was commissioned in January 2006. Blackburn (Lancashire, UK) is a major sludge handling centre for the Northern region. Every year the centre processes up to 13,500 tonnes sludge (tDS) by

MAD for 0.5M people from the Blackburn and South Lancashire area and safely recycles it to agriculture as fertiliser and soil conditioner. The Safe Sludge Matrix necessitated more stringent control of sludge pathogens. As most of the accessible land bank within 25 miles of the Blackburn works is grassland, the highest standard of treatment was called for. The upgrade became a technology demonstration project supported by the European Commission LIFE Programme. This EU-LIFE project (LIFE05 ENV/UK/00124) has entailed an extensive monitoring program of the full-scale facility and a technical assessment from an independent project partner. Monitoring commenced in February 2006 and was just completed in June 2007. From the recently completed dataset the detailed independent technical and economic assessment of the EEH process is underway. The objective of this paper is to provide insight of the EEH-MAD treatment process based on selected monitoring results that are being derived as a first step in the technical assessment.

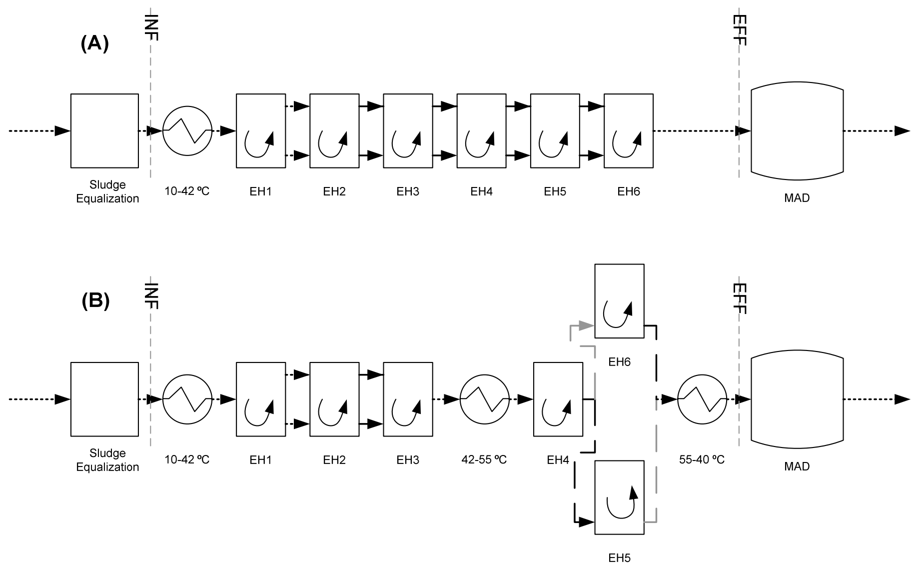

Figure 1 – Schematic diagrams for the United Utilities Enzymic Hydrolysis MAD pre-treatment process showing standard *EH-mode* (A) and enhanced *EEH-mode* (B) configurations and temperatures. Tank labels and locations for influent (INF) and pre-treatment effluent (EFF) are with reference the monitoring results presented below.

MATERIALS AND METHODS

Plant Operations and Process Description

The EH-MAD plant was operated in standard (EH) mode (Figure 1A) from January 15th to February 16th, 2006, and in enhanced (EEH) mode (Figure 1B) from March 6th 2006 onwards. The Blackburn WWTP (maximum 236 MLD) serves 328,000 PE with both domestic and industrial flows from the Blackburn area and accounts for about 5,000 tDS/yr. The onsite yearly sludge production is augmented in excess of 100 percent with tankered sludge imports from the region. The combined sludge is anticipated to be a 50:50 primary and secondary blend. Sludge produced onsite is thickened by gravity belt thickeners (GBT) up to approximately 7 % DS. Off-site sludge is delivered at 4 % DS, typically, and cannot be further processed by onsite GBT because of capacity constraints. The two sludge streams are combined in a 2000 m^3 holding-equalization tank (Figure 1) which feeds the EEH-MAD digestion process. It is important to note that due to the capacity for sludge storage onsite and the potential variability in the imported sludge, the age of the sludge entering the digestion process is anticipated to vary significantly from 2 to 5 days.

At Blackburn, the six EH tanks are identical cylindrical vessels with 256 m^3 working liquid volume (7.4 m surface level) plus additional headspace for foam control. The pasteurised sludge is cooled and distributed to four parallel MAD digesters with an estimated 2200 m^3 working volume each. EH feed and pre-treatment effluent flow rate is effectively continuous and can range from 100 to 740 m^3/day. At 740 m^3/day the hydraulic retention time (HRT) is 2.1 days which in EEH-mode means a batch holding time at 55 ºC of 5 hours in tanks EH5 and EH6 (Figure 1).

The monitoring program has focused on characterizing the performance of the EEH plant as a unit process and understanding the influence of the process in combination with MAD. Routine samples were taken across the sludge digestion process and assessed by standardized methods. The final biosolids product was evaluated quantitatively and qualitatively for its suitability as a recovered value added by-product.

Monitoring Program

From January 15th, 2006 to June 15th, 2007, grab samples were routinely acquired from respective monitoring points for the EH plant (INF, EH1 to EH6, and EFF, Figure 1) and the four MAD digesters. Sub-samples from the larger bucketed grab sample volumes were conveyed and analysed for pH, alkalinity, ammonia, TCOD, SCOD, DS, VS, TVFA, VFA composition, *E. coli*, and *Salmonella*. Reactor headspace gas-bag grab samples were obtained for gas quality analyses (methane, carbon dioxide, and oxygen by GC/TCD, and hydrogen sulphide using Draeger tubes). Sludge volumetric throughput and gas production rates were logged. The final digested pressed sludge cake product was assessed (pH, DS, VS, *E. coli*, Ar, Cd, Cr, Cu, F, Hg, Mo, N, Ni, P, Pb, S, Se, Zn). United Utilities further undertook to characterise the sludge composition (Carbohydrate, Protein, Fat) as an important point of reference for the acidogenic fermentation performance at Blackburn with respect to other EH facilities. The routine grab sampling and analyses were performed by personnel at the United Utilities Lingley Mere Laboratories, using established sampling and preservation protocols and accredited methods: solids by standard methods; metals by acid digestion and ICP; COD, TVFA and ammonia with Hach-Lange cuvette test kits; *E. coli* with either the membrane filter method (conventionally treated samples) or the Most Probable Number Method (enhanced treated samples); *Samonella* by MPN and PAB. Note that not all parameters and monitoring locations were assessed on each given sampling day.

The weekly routine of sampling and monitoring by United Utilities provided for the assessment of longer term trends in the process performance. At the same time, it was of interest to obtain a characteristic impression of the process on a given day. Therefore, over the periods July 12-13, 2006 and June 11-13, 2007, grab sample rounds from locations across the plant were undertaken with direct onsite sludge analyses by AnoxKaldnes. These *snapshots* of the plant performance were obtained over periods when the volumetric loading to the plant was relatively constant.

Sludge grab samples of approximately 5 litres were drawn from the available access points for raw sludge INF, EH reactors 1 to 6, and the MAD digesters (Figure 1). For each grab sample the ports were flushed through with nominally 10 litres of sludge. The sludge flush volume was discarded. A sampling round was made by taking grab samples in as quick a succession as possible starting from the raw feed and ending at the digesters. Aliquots from a well mixed grab sample were either pre-filtered or centrifuged and then filtered by gravity through Munktell, MGC 150 mm filters. Approximately 25 mL of filtrate were obtained from each respective grab sample. Three such sampling rounds were made over 48 hours on each of the two field trips.

Total and filtrate samples were analyzed directly for pH, alkalinity, COD, TVFA, TN, NH_4-N, TP, PO_4-P, TOC, and TIC, using HACH-Lange cuvette test kits (LCK 362, 014, 914, 114, 365, 338, 303, 350, 381), a Hach-Lange LT200 incubation block and a Lasa50 spectrophotometer. Requisite sample dilutions were made with a stock supply of deionised water from which blank control samples were also prepared. pH was measured (WTW pH/Oxi 340i) with reference to pH 4 and 7 standard buffers (Reagecon). Duplicate samples for GC-FID analysis of VFA compositions were prepared from the filtrate. Aliquots of 1350 µL filtrated were preserved with 150 µL concentrated phosphoric acid (Merck 85% ortho-phosphoric acid) in standard 2 mL GC-vials with Teflon lined screw cap. GC analysis was performed within 1 week. Volatile fatty acids (acetic, propionic, butyric and valeric acids) were analyzed with a Varian 3400 gas chromatograph equipped with a Chromosorb 101 (80/100 mesh) column (Length: 2.5 m, diameter: 2.3 mm) and a flame ionization detector (FID). Nitrogen gas saturated with formic acid was the carrier gas (30 mL/min). The temperature of the injector and detector were 240°C and 250°C, respectively. The column temperature was 170°C for the initial 2 min and was then increased with 10°C/min to 250°C and retained at 250°C for 3 min. Sample VFA concentrations were evaluated with respect to the response factors for individual peaks from a standard VFA mixture and were corrected for dilution with phosphoric acid.

RESULTS AND DISCUSSION

General Operating Conditions

The sludge feed at Blackburn was characterised by an estimated carbohydrate to protein to fat balance of 58:31:11 (±5) and a calorific value of 14 MJ/kgDS. The calorific value remained constant during EEH but decreased to approximately 11 MJ/kgDS after MAD. Over EEH and MAD, the organic makeup of the sludge in terms of carbohydrate, protein and fat remained constant within the measurement variability observed from 3 grab samples taken over one week during June 2006. This indication that rates for carbohydrate, protein and fat hydrolysis and acidification were similar is also inferred from the analysis of the VFA composition which was relatively stable whilst VFA levels increased across the EH plant (see Figure 6 below). Different substrates for acidogenesis contribute to different VFAs as products (Batstone *et al.*, 2002) and different rate constants have been observed for different organic substrates (Jeyaseelan, 1997). If acidogenesis proceeded at different rates or with different preferences with respect to the major organic fractions then trends in composition in a plug flow process would be anticipated. Hydrolysis of the suspended solids as a whole is rate limiting the VFA production rate.

Start-up and commissioning of the EH plant went smoothly. Since January 2006, apart from brief interruptions due to issues with faulty control valves, volumetric loadings from 200 m^3/d up to the maximum design level of 740 m^3/d were achieved without any difficulties. After a month running EH in standard mode (6 tanks in series at 42 ºC), the pre-treatment was switched over to enhanced mode. Unfortunately, operational experience downstream of the EH plant was problematic up until the last 4 months of the monitoring program. One digester was out of service for the first 4 months of 2006 due to a mixer problem. From mid April to December 2006 all digesters experienced intermittent mixing failures. During this period all 4 digesters were kept as best as possible in service but with only 50% mixing duty. This compromise influenced performance in VS destruction but allowed the digesters to achieve full throughput pending the arrival of new mixers which were ordered. Service and installation of the digester mixers were completed in the beginning of 2007 and the full EEH-MAD system was brought into a state of intended operation in February 2007. In order to exploit as much as possible the information embodied by the available monitoring data the most representative data segments were applied with respect to specific aspects of the process of interest. The dataset could be divided into three time periods referred to as A, B, and C as follows:

A. EH with problematic MAD performance: January 15, 2006 to February 16, 2006.
B. EEH with problematic MAD performance: March 6, 2006 to March 2, 2007.
C. EEH with stable MAD performance: March 15, 2007 to June 15, 2007.

The operating conditions depicting these three time periods are given in Table 1. The dataset was scrutinized for inadmissible values arising from entry errors or occasional experimental errors in sample processing and analyses. Whenever possible, such errors were corrected for but have otherwise been removed in the results being presented. Based on trends in either observed normal or lognormal distributions that tended to represent the measurement variability for the parameters at respective sampling locations, obvious outliers in the dataset were also removed. MAD performance data from the 4 digesters were averaged together.

In addition to the routine monitoring periods reported in Table 1, two *snapshots* (S1 and S2) in triplicate of the EEH process were taken within periods B and C with sampling over two days in July 2006 and June 2007. The operating conditions based on data from the week before and the week of S1 and S2 are given in Table 2.

In conjunction with the service to the MAD mixers at the end of period B, the GBTs were also refurbished. The overall process performance is known to improve with dried solids concentration and the target is 7 % DS. However, in spite of the improvement to thickening of sludge produced on site, the solids level was dominated by the low concentration of the imported sludge entering the equalization tank. By period C the gas production yield increased from levels of about 14.6 during A and B, reaching 16.7 m^3 biogas per m^3 solids treated (Table 1). Thus indications were that the overall process was coming into its own during period C as the MAD vessels came into service with improved mechanical performance and reliability. In spite of this period involving a number of shut down and start up organic loading rate disturbances to the individual digesters, the digesters were otherwise stable as suggested by the pH data over periods B and C (Figure 2). In general, MAD is sensitive to fluctuations in the quality of the influent organic matter and the process environmental conditions. If EEH serves to make the MAD influent organic content more uniform then EEH-MAD should be a more robust biological process in comparison to MAD alone.

Table 1 – Time periods and nominal operating conditions as delineated by EH or EEH modes and MAD operations.

Period	A 060115-060216	B 060306-070302	C 070315-070615
EH Plant Mode	EH	EEH	EEH
MAD Digesters in Service	3	1 to 4	4
MAD Service	Ok	Mixer Problems	Ok
Dry Solids (%)	4.7±0.8	4.8±0.7	4.9±0.6
Mean Feed Rate (m^3/d)	630	429	544
EH/EEH HRT (d)	2.4	3.6	2.8
MAD HRT (d)	10.2	13.5	16.8
Gas Production Rate (m^3/d)	9076	6365	9070

Table 2 – Time periods and nominal operating conditions as delineated by EH or EEH modes and MAD operations.

Period	S1 060703-060717	S2 070604-070618
EH Plant Mode	EEH	EEH
MAD Digesters in Service	2	4
MAD Service	Mixing Problems	Ok
Dry Solids (%)	4.7±0.4	4.7
Feed Rate (m^3/d)	389	477
EH/EEH HRT (d)	3.9	3.2
MAD HRT (d)	11.4	19

Hydrolytic and Acidogenic Activities

The pH levels across the EH plant were stable but increased slightly due to buffering capacity from alkalinity and ammonia release with respect to SCOD production (Figure 3 and Figure 4). Increase in buffering capacity compensated for tendencies for pH drop due to accumulation of VFAs during acidogenesis (Figure 5). The trends in VFA production were found to be most reliable with samples that were filtered and preserved directly after sampling. In addition, while the Hach-Lange (LCK 365) TVFA assay exhibited trends that were proportional to the GC/FID derived VFA data, it was observed that the LCK 365 assay was not accurate due to matrix interference.

The EEH *snapshots* S1 and S2 (Table 2) provided for important perspective with respect to VFA production during pre-treatment. Feed sludge for S1 was deemed to be significantly *fresher* due to the relatively lower feed SCOD and TVFA levels (5.6 g/L SCOD and 4.7 g/L VFA-COD) when compared to S2 (9.1 g/L SCOD and 8.2 g/L VFA-COD). The progress of VFA production for S1 exhibited inhibition at about 9 g/L VFA-COD that was coincident with temperature increase to 55 ºC in tank 4. Thus S1-VFA data in isolation supported findings that a thermal shock to the acidogenic microbial community with EEH pasteurization can significantly impair potential in VFA production (Demirel and Yenigun, 2002). However, the results of S2 indicated that temperature shock was an inadequate explanation for the observed reduced yield in VFAs over 9 g/L VFA-COD. The optimum retention time in a thermophilic acidogenic reactor has been determined to be 3 to 3.5 days with net acidogenic growth rates of 0.25 d^{-1} (Puchajda and Oleszkiewicz, 2006). Therefore, VFA production activity should proceed in EEH given a sufficient fraction of temperature tolerant acidogenic activity present in the mesophilic biomass. NH_4-N can also be inhibitory to acidogenic activity but levels of the order 0.6 g NH_4-N/L are well below the observed threshold of 1.2 g NH_4-N/L (Yang *et al.*, 2004). Sulphur compounds (Lin and Hsiu, 1997) and metals (Yu and Fang, 2001) are known to inhibit acidogenic activity. However, it is most likely that the onset of inhibiting conditions for VFA production is due to inhibition from increase in the VFA levels in combination with pH (Babel *et al.*, 2004).

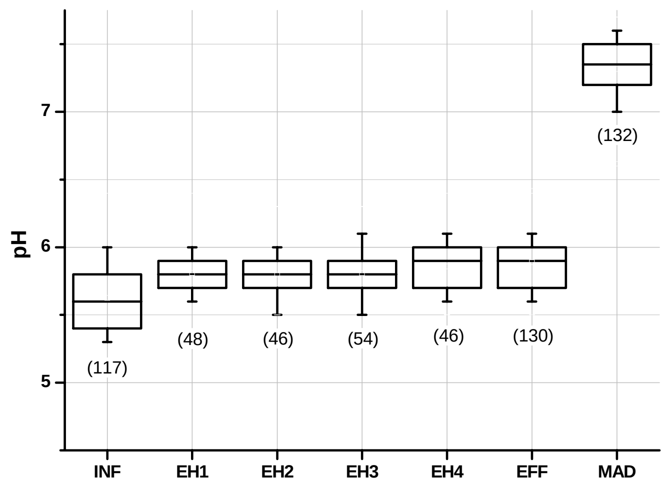

Figure 2 – Summary of pH levels with median (line), 25-75 percentile (box), 10-90 percentile (whiskers), and number of observations (in brackets) for periods B and C.

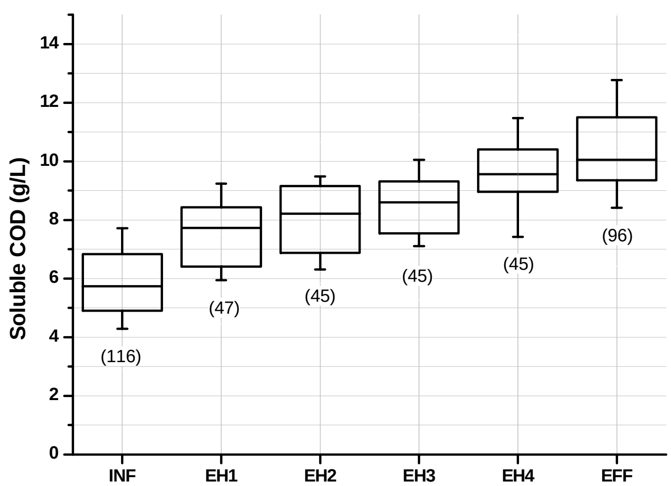

Figure 3 – SCOD production during EEH with median (line), 25-75 percentile (box), 10-90 percentile (whiskers), and number of observations (in brackets) for periods B and C.

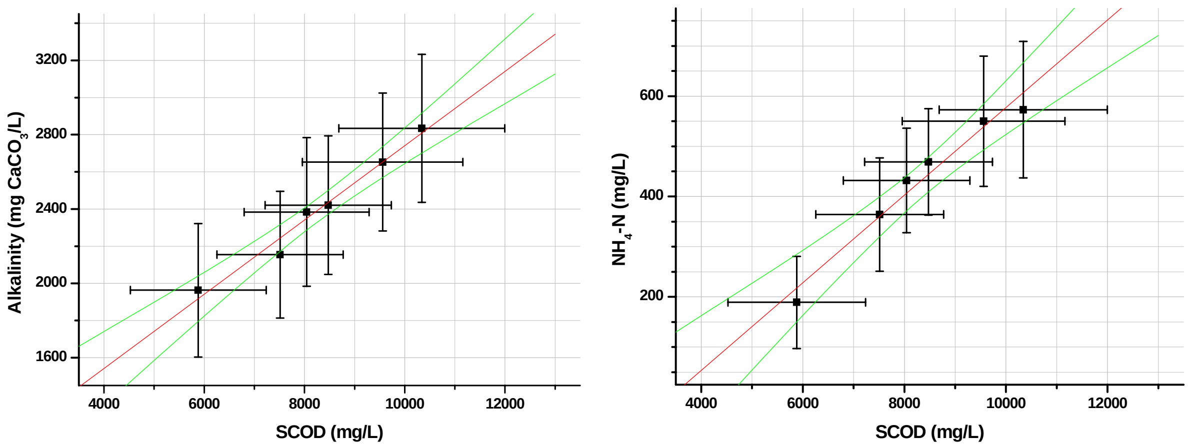

Figure 4 – Trends in alkalinity and ammonia release with increase in soluble organic matter as SCOD during EEH (Periods B and C). Averages are reported together with standard deviations.

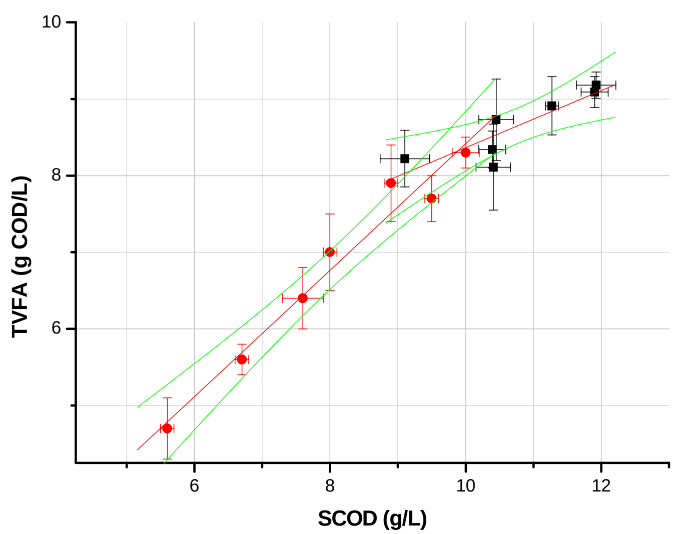

Figure 5 – Trends in TVFA (as COD) production with increase insoluble organic matter (SCOD) during EEH (S1 (●) and S2 (■), Table 2) . Average values are reported with standard deviations (3 replicates). TVFA-COD is estimated from the measured concentration of the speciated VFAs (HAc, HPr, HBu, HVa) determined by GC/FID (Figure 6).

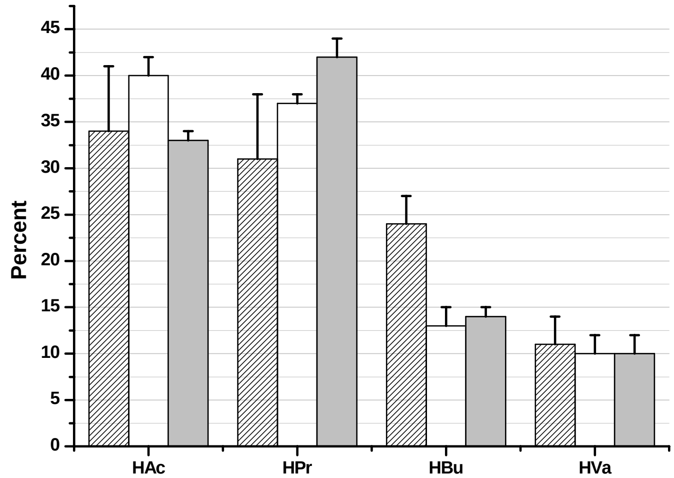

Figure 6 – Average VFA compositions from EH1 to EH6 for period A (Left), S1 (Middle) and S2 (Right).

Volatile Solids Destruction

Care must be taken in inferring changes to specific solid fractions from aggregate measurement methods in anaerobic digestion processes. Total solids (TS) estimates are biased by interferences due to losses of volatile organic components (such as VFAs and methane) and inorganic components (such as ammonium carbonate and hydrogen sulfide) (Switzenbaum *et al.*, 2003; Beall *et al.*, 1998). The volatile solids fraction of TS may in turn be biased by the interferences to TS and the loss of moisture from hydroscopic compounds in the dried sludge matrix. Chemical oxygen demand is biased by the presence of hydrogen sulphide. Inferences of trends for the sludge matrix are therefore best supported by cross confirmation through different strategies of measurement of, for example, the organic fraction of the sludge matrix.

Assessment of the volatile solids destruction through the EEH-MAD process was considered from mass balance considerations based on the estimated fate of volatile solids through the process (Figure 7). Based on the average trend in VS, the EEH-MAD process at Blackburn exhibited a 50% destruction of volatile solids. These data also suggested an average 16% VS removal across the EEH plant. However, the observed VS loss during EEH can not be simply interpreted as organic matter destruction. Measurements of total COD during the same period indicated insignificant changes across EEH and a 53 percent loss in TCOD for the EEH-MAD process (Figure 7). Similarly, measurements of TOC across the plant (S2) indicated no significant change in organic carbon across the EEH plant and a 55% reduction in the solids organic carbon content after MAD. TOC measurement of the sludge solids through the process is likely to give the most accurate indication of the EEH-MAD performance. The average gas composition during period C was 66±1 % methane and 33±1 % carbon dioxide.

In a recent internal audit of sludge digestion performance undertaken by United Utilities (Barber, 2007) with treatment dominated by conventional MAD (16 to 22 d HRT, 4.6 % DS, OLR 1.9 kgVS/m^3/d), the average VS reduction from 24 sites run by United Utilities and based on mass balance was 46±4%. In the audit, the historical data for Blackburn (one of the 24 sites) suggested an average of about 41% VS removal. With this audit as the historical reference before the pre-treatment upgrade, period C monitoring provides for strong indication of an average increase in the order of 10% VS destruction which corresponds to a 24% enhancement in biogas production for the EEH-MAD upgrade at Blackburn. The impact of the upgrade could be expected to increase with higher proportions of primary solids in the sludge.

Proper mixing is one of the most important considerations in achieving optimum process anaerobic digestion performance (Metcalf & Eddy Inc., 2003). Although the digester mixers were replaced, the mixing system was not upgraded and therefore the MAD operation was not considered as optimum. Digester mixing optimisation is being planned by United Utilities. More effective mixing is expected to further improve VS destruction and gas production at Blackburn.

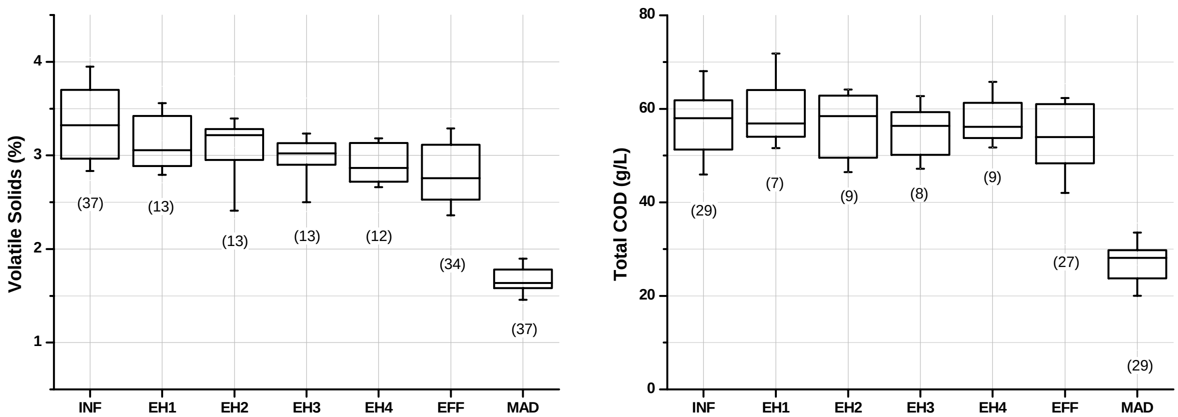

Figure 7 – Trends in VS (left) and TCOD (right) reduction during EEH-MAD with median (line), 25-75 percentile (box), 10-90 percentile (whiskers), and number of observations (in brackets) for period C.

Pathogen Fate and Removal

E. coli and *Salmonella* removal during mesophilic pre-treatment followed first order removal kinetics. The EH-mode of pre-treatment consistently removed *E. coli* by 3 log and *Salmonella* by 1 log (Figure 8). Median pathogen levels after mesophilic pre-treatment were not significantly influenced by MAD. For enhanced pre-treatment, the observed median *E. coli* removal was 6 log and *Salmonella* were eliminated. The temperature increase obviously has a marked impact on the kinetics of pathogen removal. At the same time, VFAs, ammonia, and carbonate that are generated during EH are known to contribute to removal or inhibition of pathogenic organisms (Theron and Lues, 2007; Salsali *et al.*, 2006; Shin *et al.*, 2006; Park and Diez-Gonzalez, 2003). The importance of these other factors in EH pre-treatment could help towards further establishing the minimum operational requirements for achieving enhanced treatment standards reliably.

At the influent *E. coli* levels of 3×10^6, a 6 log removal meant that the *E. coli* numbers reached levels that became problematic for reliable quantification. In addition, due to the background environment, additional care and precautions in sampling were necessary to avoid false positive readings due to contamination. The probability plot of the *E. coli* data for pre-treatment feed fit well to a lognormal distribution. The MAD effluent *E. coli* numbers could also be considered to be represented by a lognormal distribution if observations below detection were ranked but not included in the probability plot. If enhanced treatment is to ensure pathogen reduction to levels that might be commensurate to food industry standards, strategies and statistical approaches for the product assurance might well be drawn from the food sciences (Montville and Schaffner, 2004).

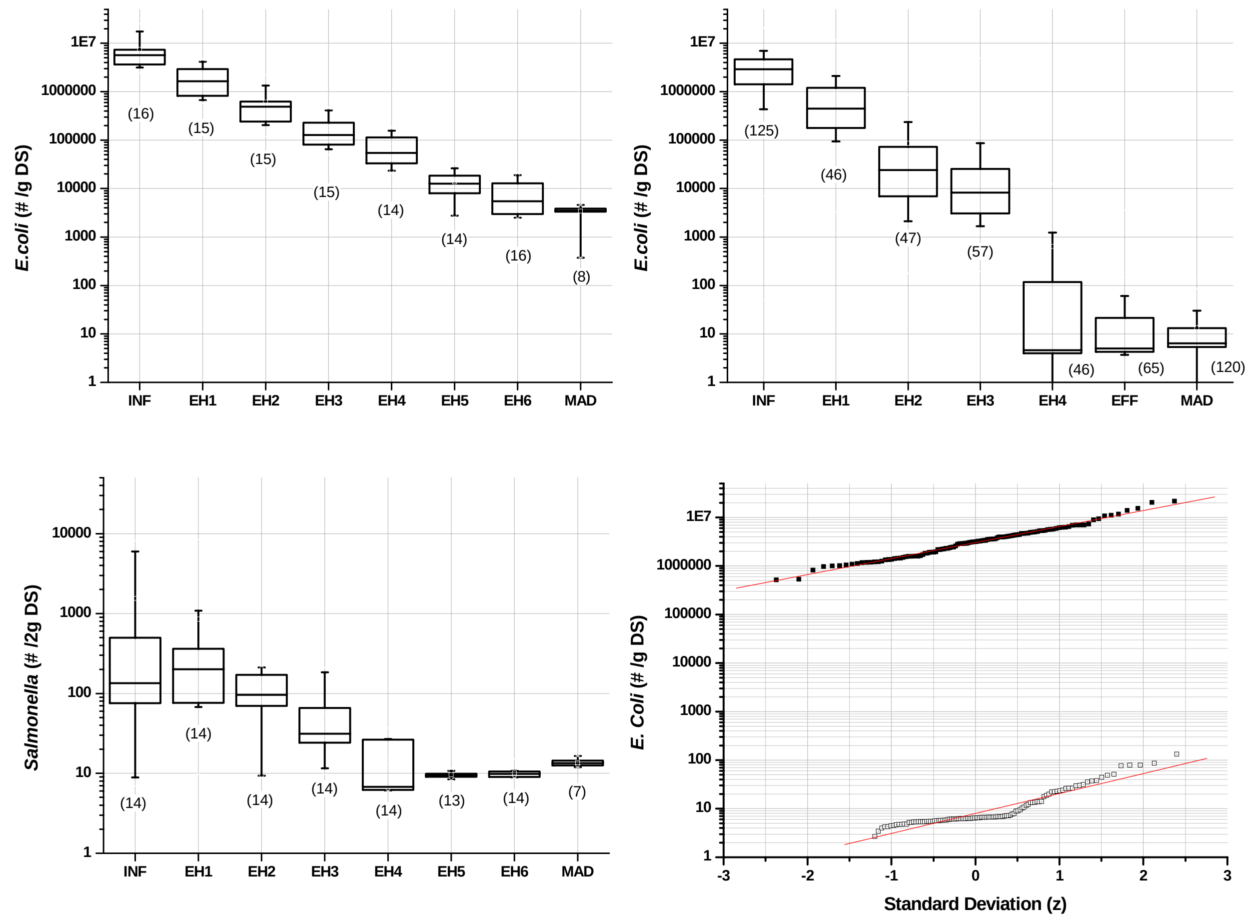

Figure 8 – Summary of pathogen fate during EH/EEH-MAD pretreatment. Top Left: *E. coli* reduction during EH-MAD (Period A). Top Right: *E. coli* reduction during EEH-MAD (Periods B and C). Bottom Left: *Salmonella* reduction during EH-MAD (Period A). Bottom Right: Probability plot showing feed (upper) and MAD effluent (lower) *E. coli* observations (Periods B and C). Box plots show median (line), 25-75 percentile (box), 10-90 percentile (whiskers), and number of observations (in brackets).

Final Product Quality

From routine monthly press cake samples, the quality of the sludge press cake has been consistent over the monitoring period from A to C. Attributes of the cake are given in Table 3 and the average metal content is reported in Table 4. With respect to HACCP, *Salmonella* was consistently not detectable. *E. coli* levels in the cake followed a lognormal distribution with an average count of 367 #/g DS (Figure 9).

To date the treated cake has been used as a seedbed fertiliser for maize and cereal crops. The sludge cake has proven to be of low odour and has provided the opportunity for surface spreading on grassland, even in close proximity to residential areas. The added level of VS destruction as a result of pre-treatment must influence the final product stability by reducing risks for production of malodours.

Table 3 – Sludge Cake Properties (Periods A, B, and C). Mean, median and the standard deviation (σ) are reported along with the number of observations (n).

		g/ 100 mL		g/Kg		
	pH	**TS**	**VS**	**N**	**P**	**S**
Mean	7.8	24	13	39	25	9
Median	7.8	24	13	39	25	9
σ	0.1	3	2	6	4	2
n	2	24	24	24	24	3

Table 4 – Sludge Cake Metal Content (Periods A, B, and C). Mean, median, and standard deviations are given for the available number of measurements (n) with all concentrations expressed as mg/Kg. The European Council Directive 86/278/EEC Sewage Sludge Metal Level Standards (EU) and US Environmental Protection Agency (EPA) heavy metal limits in biosolids for agricultural use are also included for reference.

	As	**Cd**	**Cr**	**Cu**	**F**	**Pb**	**Hg**	**Mo**	**Ni**	**Se**	**Zn**
Mean	6.7	1.7	73	296	108	164	1.0	9.3	36.8	2.2	769
Median	6.8	1.5	73	292	111	170	1.0	9.3	36.3	2.2	770
σ	0.3	0.4	12	53	6.7	24	0.3	1.1	5.9	0.1	86
n	3	24	24	24	3	24	24	24	24	3	24
EU	-	20	1000	1000	-	750	16	-	300	-	2500
EPA	75	85	-	4300	-	840	57	75	420	100	7500

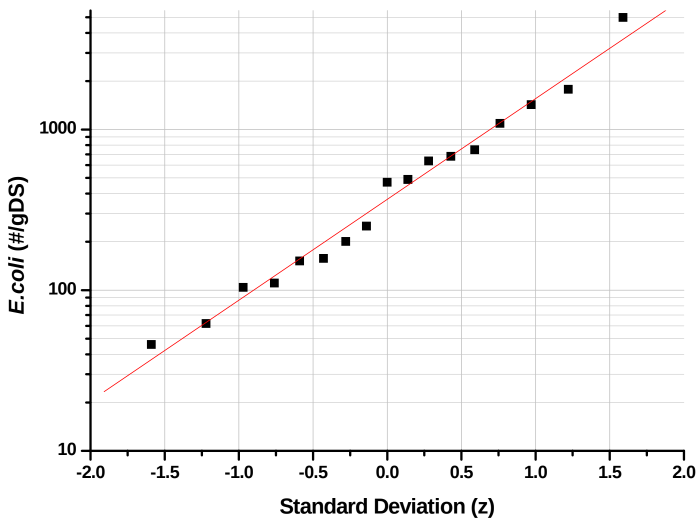

Figure 9 – Results of HACCP biosolids analysis. Probability plot for final press cake *E. coli* levels (Periods A, B, C).

CONCLUSIONS

Enhanced Enzymic Hydrolysis (EEH) pre-treatment upgrade to mesophilic anaerobic digestion at the Blackburn WWTP achieves 6 log *E.coli* removal and elimination of *Salmonella*. The pre-treatment acts to provide a consistent feed to MAD with the anticipated outcome of more stable methane production. The upgrade has enhanced VS destruction by around 10% with concomitant improvements of 24% in biogas production. The potential for VS destruction and gas production are currently limited by low influent TS levels (5 %DS) and the need for optimization of the MAD mixing regime. VFA production during EEH at Blackburn is limited by hydrolysis kinetics and by inhibition when VFA levels are in excess of 9 g VFA-COD/L. The final biosolids product was of consistent quality with metal levels well-below the norms established by the EU and EPA. Further research is required to better characterize factors limiting the potential for VFA production during EH and to understand how the EH acidogenic environment contributes to pathogen elimination.

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NONMENCLATURE

COD	Chemical Oxygen Demand	INF	EHH Feed
DS	Dry Solids	MAD	Mesophilic Anaerobic Digestion
EFF	EHH Pre-treatment Effluent	SCOD	Soluble COD
EH	Enzymic Hydrolysis	tDS	tonnes Dry Solids (metric)
EEH	Enhanced Enzymic Hydrolysis	VFA	Volatile Fatty Acids
EHi	Enzymic Hydrolysis Tank "i"	TN	Total Nitrogen
HACCP	Hazardous Analysis Critical Control Points	TIC	Total Inorganic Carbon
		TOC	Total Organic Carbon
HAc	Acetic Acid	TP	Total Phosphorus
HBu	Butyric Acid	TS	Total Solids
HPr	Propionic Acid	TSS	Total Suspended Solids
HVa	Valeric Acid	TCOD	Total COD
HRT	Hydraulic Retention Time	TVFA	Total VFA

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