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# Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion

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**Abstract**

In order to face excess waste activated sludge management problems, sludge anaerobic digestion with thermal pre-treatment is of great interest. If most of works agree on the optimal treatment temperature (160–180 °C), results of thermal pre-treatments in terms of biogas production are very dispersed. With the aim of analysing the impact of sludge samples, thermal pre-treatments were carried on five different waste activated sludge samples.

For temperatures lower than 200 °C, COD solubilisation was found to increase linearly with treatment temperature and all the different sludge samples behaved in the same way. For temperatures lower than 150 °C, carbohydrates solubilisation was more important than proteins solubilisation. Analyses of sludge apparent viscosity, settleabilty and dewaterability (CST) of pre-treated sludge pointed out a threshold temperature of 150 °C. Thermal treatments up to 190 °C allowed the biogas production to increase during batch anaerobic digestion of sludge. Biogas volume enhancement was linked to sludge COD solubilisation and to untreated sludge initial biodegradability; the lower the initial biodegradability, the higher is the impact of thermal treatment.



*Keywords:* Methanisation; Biogas; Viscosity; Filterability; Settleability; Proteins; Carbohydrates; Lipids

## 1. Introduction

Sludge represents the major solid waste from biological wastewater treatment processes. In response to the strengthening of the European legislation regarding the Urban Wastewater Treatments Directive (91/271/EEC), sludge production is increasing whereas disposal routes are more reduced. It is thus essential to develop processes to reduce sludge quantity. One of the most interesting processes is anaerobic digestion or methanisation. It leads to sludge stabilisation by converting a part of its organic matter into biogas which is valuable as a renewable energy source. The rate-limiting step of this biological process is organic matter hydrolysis. Methanisation process can thus be improved by a thermal pre-treatment in order to lyse sludge cells [1]. Moreover, thermal pre-treatments imply sludge sanitation and energy costs can be covered by biogas production [2]. Therefore, some industrial plants such as Cambi process [2] and *Bio*THELYS® [3] are commercialised and combination of thermal pre-treatments and anaerobic digestion is widely investigated in literature. Thermal treatments were first applied to sludge to improve their dewaterability [4]. Sludge dewaterability was reported to be improved after a treatment at a temperature higher than 150 °C [5] or higher than 180 °C [6]. But a large part of works deals with the effect of sludge thermal treatments on biogas production enhancement during anaerobic digestion. Table 1 presents some examples of such studies. At laboratory scale, anaerobic digestion is carried out either in batch reactors or in CSTR. It was operated in a fixed bed reactor in one industrial reference [16]. Most of the studies reported an optimal temperature in the range from 160 to 180 °C and treatment times from 30 to 60 min. However, treatment time is often shown to have little effect in this temperature range [4] and Dohanyos et al. [14] proposed a very fast thermal treatment, lasting only 60 s. On the other hand, thermal treatments at moderate temperature (70 °C) lasted several days [11]. If we consider their impact on biogas production, thermal treatments can be classified into two groups: treatments at temperatures of 70 °C or 121 °C which led to a 20–30% biogas production increase and treatments at 160–180 °C which led to a 40–100% biogas production increase. The 160–180 °C pre-treatments are thus most

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**Nomenclature**

| | |
|---|---|
| Bo | untreated sludge biodegradability (%) |
| BSA | bovine serum albumin (–) |
| COD | chemical oxygen demand (g $O_2$/l) |
| CODp | COD in particles (g $O_2$/l) |
| CODs | soluble COD (g $O_2$/l) |
| CST | capillary suction time (s) |
| CSTR | continuous stirred tank reactor (–) |
| Gluc | glucose (–) |
| HRT | hydraulic retention time (d) |
| $N\text{-}NH_4^+$ | ammonium nitrogen (g N/l) |
| $S_{COD}$ | COD solubilisation (–) |
| SVI | sludge volume index (ml/g) |
| TS | total solids (g/l) |
| TSS | total suspended solids (g/l) |
| VFA | volatile fatty acids (g/l) |
| VS | volatile or organic solids (g/l) |
| VSS | volatile or organic suspended solids (g/l) |
| WAS | waste activated sludge (–) |

*Greek letters*

| | |
|---|---|
| $\theta$ | temperature of treatment (°C) |
| $\mu_{ap}$ | apparent viscosity (Pa s) |

efficient to enhance sludge anaerobic digestion but they lead to very dispersed results in terms of increase in biogas production (from 40 to 100%). Such a wide range of results was obtained with different anaerobic digestion process conditions (batch processes of 7 to 24 days, CSTR with hydraulic retention time of 5 to 25 days). Moreover, we may wonder what is the impact of the sludge samples on the increase of biogas production due to thermal treatment. Or is it interesting to treat all types of waste activated sludge?

The objective of this study was to investigate the impact of thermal pre-treatment on five different sludge samples. In the first part, sludge solubilisation was analysed in terms of COD, total and volatile solids, proteins, carbohydrates and lipids solubilisation. The impact of thermal treatments on sludge viscosity, settleability and dewaterability (CST) was investigated in a second part. Finally, batch anaerobic biodegradation of pre-treated and untreated sludge was measured.

## 2. Experimental

### 2.1. Waste activated sludge samples characteristics

The experiments were carried out using five different WAS samples. Samples were collected from various plants located in the South of France. Table 2 presents sludge samples main characteristics. Samples used could be ranged according to two parameters: the process from which they originated and their organic content.

### 2.2. Thermal treatment conditions

The reactor used for thermal treatment was a Zipperclave (Autoclave France) controlled in temperature via a regulation using a proportional integral derivative (PID). Sample volume was around 0.7 l. Temperature of treatment varied from 90 to 210 °C according to the sludge samples. The rise in temperature lasted from 25 to 60 min, depending on the desired temperature. Once temperature was reached, treatments lasted 30 min.

In table or figure presentations, untreated sludge was arbitrarily associated to 20 °C temperature.

### 2.3. Samples analyses

#### 2.3.1. Sludge composition

In order to determine sludge composition, several measurements were made on samples according to Standard methods [19]. First, soluble and particulate fractions were obtained after centrifugation (Beckman J2 MC – 25,000 rpm, 15 min, 5 °C).

COD measurement can permit to achieve pollution concentration, expressed in oxygen ($O_2$) consumed to oxidise matter. A known amount of oxidant is added to samples and, after reaction, the excess oxidant is analysed. By this difference in

Table 1
Literature review on impacts of thermal pre-treatments on waste activated sludge mesophilic anaerobic digestion

| Reference | Thermal treatment | Anaerobic digestion | Results |
|---|---|---|---|
| Haug et al. [7] | 175 °C, 30 min | CSTR, HRT = 15 d | Increase of $CH_4$ production from 115 to 186 ml/g $COD_{in}$ (+62%) |
| Stuckley and McCarty [8] | 175 °C, 60 min | Batch, 25 d | Increase of convertibility of COD to $CH_4$ from 48 to 68% (+42%) |
| Li and Noike [1] | 175 °C, 60 min | CSTR HRT = 5 d | Increase of gas production from 108 to 216 ml/g $COD_{in}$ (+100%) |
| Tanaka et al. [9] | 180 °C, 60 min | Batch, 8 d | Increase of methane production (+90%) |
| Fjordside [10] | 160 °C | CSTR, 15 d | Increase of biogas production (+60%) |
| Gavala et al. [11] | 70 °C, 7 d | Batch | Increase of $CH_4$ production from 8.30 to 10.45 mmol/g $VS_{in}$ (+26%) |
| Barjenbruch and Kopplow [12] | 121 °C, 60 min | CSTR, 20 d | Increase of biogas production from 350 to 420 ml/g $VSS_{in}$ (+20%) |
| Kim et al. [13] | 121 °C, 30 min | Batch, 7 d | Increase of biogas production from 3657 to 4843 l/m$^3$ $WAS_{in}$ (+32%) |
| Dohanyos et al. [14] | 170 °C, 60 s | Batch, 20 d Thermophilic | Increase of biogas production (+49%) |
| Valo et al. [15] | 170 °C, 60 min | Batch, 24 d | Increase of biogas production (+45%) |
| Valo et al. [15] | 170 °C, 60 min | CSTR, 20 d | Increase of $CH_4$ production from 88 to 142 ml/g $COD_{in}$ (+61%) |
| Graja et al. [16] | 175 °C, 40 min | Fixed film reactor, HRT = 2.9 d | 65% reduction of TSS |
| Bougrier et al. [17] | 170 °C, 30 min | Batch, 24 d | Increase of $CH_4$ production from 221 to 333 ml/g $COD_{in}$ (+76%) |
| Bougrier et al. [18] | 170 °C, 30 min | CSTR, 20 d | Increase of $CH_4$ production from 145 to 256 ml/g $VS_{in}$ (+51%) |

Table 2
Untreated WAS samples characteristics

| Sludge samples | A | B | C | D | E |
|---|---|---|---|---|---|
| Size of the plant (PE) | 500,000 | 90,000 | 10,000 | 33,000 | 60,000 |
| Process | High load | High load | Medium load | Medium load | Extended aeration |
| Wastewater | Urban and industrial | Urban and industrial | Urban | Urban | Urban and industrial |
| TS concentration (g/l) | 33.7 ± 0.2 | 15.3 ± 0.2 | 17.1 ± 0.2 | 15.0 ± 0.1 | 14.8 ± 0.2 |
| VS content (%TS) | 81 ± 2 | 76 ± 2 | 70 ± 2 | 82 ± 1 | 76 ± 2 |
| TSS content (%TS) | 93 ± 1 | 93 ± 2 | 80 ± 1 | 97 ± 1 | 95 ± 2 |
| Total COD (g/l) | 35.1 ± 0.1 | 14 ± 1 | 17.4 ± 0.5 | 10.5 ± 0.7 | 11.4 ± 0.4 |
| Soluble COD (g/l) | 1.52 ± 0.04 | 1.3 ± 0.2 | 0.47 ± 0.02 | 0.04 ± 0.01 | 0.04 ± 0.01 |
| Total proteins (g eqBSA/l) | 12.2 ± 0.3 | nd | nd | 4.3 ± 0.2 | 5.1 ± 0.4 |
| Soluble proteins [g eqBSA/l] | 0.31 ± 0.03 | nd | nd | 0.30 ± 0.05 | 0.20 ± 0.03 |
| Total carbohydrates (g eqGluc/l) | 2.66 ± 0.07 | nd | nd | 1.34 ± 0.02 | 1.45 ± 0.05 |
| Soluble carbohydrates (g eqGluc/l) | 0.13 ± 0.01 | nd | nd | 0.020 ± 0.001 | 0.02 ± 0.01 |
| Total lipids (g/l) | 1.5 ± 0.3 | nd | nd | nd | nd |
| VFA (g/l) | 0.23 ± 0.01 | nd | nd | 0.065 ± 0.001 | 0.016 ± 0.001 |

TS: total solids; VS: volatile solids (or organic solids); TSS: total suspended solids (solids concentration in the particular fraction of sludge); nd: not determinated.

the oxidant concentration, it is possible to calculate the oxygen quantity necessary to degrade pollution, that is to say the COD concentration. COD was measured on the total sludge and on the supernatant. For this paper, COD measured on supernatant will be called "soluble COD" (CODs) and the difference between total COD and soluble COD will be called "particulate COD" (CODp). The error due to this measure was around 10%.

Measures of total and organic solids (TS and VS) were realised on sludge and on solids of centrifugation (Total and Volatile Suspended Solids: TSS and VSS). Samples were heated at 105 °C for 24 h; water was evaporated. That led to total matter concentration. Then, samples were heated at 550 °C for 2 h. That led to mineral matter concentration. Organic matter concentration was then deduced. Solids concentration of the supernatant, that is to say the soluble phase, was deduced from the difference between total solids and suspended solids concentrations. All these concentrations led to the composition in the different parts of the sludge. The error due to this measure was around 3–5%.

Measures of ammonium nitrogen (N-$NH_4^+$) was realised in the soluble fraction by colorimetric dosage [19]. The error due to this measure was around 10%.

In order to better know solids and soluble fractions, proteins, carbohydrates and lipids concentrations were measured.

Protein concentration was determined on total sludge and on supernatant using the Lowry method [20]. The technique quantified the peptidic bounds. After reactions with salts and Folin reagent, absorbance of samples was determined at 750 nm, using a spectrophotometer (DV-640, Beckman). By using different known solutions of bovine serum albumin (BSA), a calibration curve was obtained and protein concentrations were determined in BSA equivalent gram per litre. The error due to this measure was around 15%.

As well as proteins, carbohydrate concentration was determined on total sludge and soluble fraction. The anthrone method [21] was used. It dosed carbohydrates concentration by quantifying the carbonyl functions (C=O). After reaction with anthrone and sulphuric acid, absorbance of samples was determined at 625 nm using a spectrophotometer (DV-640, Beckman). By using different known solutions of glucose (Gluc), a calibration curve was obtained and carbohydrate concentrations were determined in glucose equivalent gram per litre. The error due to this measure was around 10%.

Lipid concentration was determined using two techniques. First, fatty solids concentration was measured by extraction by hexane according to Bridoux et al. [22]. Samples were acidified in order to maintain fatty acids in the non-dissociated form. Hexane was added to samples which were agitated; fatty acids transferred from sludge to hexane fraction. Then the hexane phase was collected and evaporated (Rotavapor R, Büchi). By weighting the extracted compounds, and by knowing the initial volume of sludge, it was possible to determine fatty solids concentration. The error due to this measure was around 15%.

Beside, volatile fatty acids (VFA) concentrations were determined in the soluble fraction by gas chromatography (GC800, Fisons Instruments). The internal standard method allowed to measure total VFA concentration (acetic, propionic, butyric and *iso*-butyric, valeric and *iso*-valeric acids) in the range 0.25–1 g/l. The error due to this measure was around 3%.

### 2.3.2. Sludge physical properties

Viscosity measurements were carried out using a RT 10 Rotovisco (Haake Fisons) connected to a computer. The system was a coaxial cylinder system with a gap of 0.925 mm. Measures were realised by increasing the shear stress from 3 to 10 Pa and were duplicated.

Settleability was estimated using the sludge volume index (SVI). Sludge was diluted several times (twice, four times). One litre was introduced in test tubes. After 30 min, the settled volume was measured.

The filterability was measured using the capillary suction time (CST). The apparatus was a Triton type 319 Multi-CST (Triton Electronics Ltd.). The CST permits to estimate the sludge ability to dewater; water is absorbed by CST paper by capillary. The CST measure corresponds to the time needed for water to cross a fixed distance in the filter paper.

### 2.4. Batch anaerobic digestion

Batch anaerobic digestion tests were carried out to assess sludge biodegradability. For these experiments the inoculum was a sludge treating a mixture of wine effluents (80%) and sludge (20%). The inoculum was diluted to 4 g/l of volatile suspended solids (VSS – equivalent to organic suspended solids). For each pre-treatment, samples of treated or untreated sludge were added to 400 ml of inoculum. The pollution to degrade was equivalent to 0.5 g COD/g VSS of inoculum. Plasma bottles were agitated (200 rpm). Several control samples were realised: a blank (water), an ethanol sample (completely biodegradable compound) and an untreated sample (untreated WAS added). Produced biogas volume was measured by movement of liquid (water, pH = 2, NaCl 10%). Experiments lasted from 17 to 24 days according to sludge samples.

Enhancement of biodegradability was evaluated by comparison of biogas volumes produced by treated and untreated samples. Biogas ratio is biogas volume produced with treated sludge divided by biogas volume produced with untreated sludge. Moreover, the biodegradability percentage was estimated by comparing the biogas volume produced with sludge (treated or not) to the biogas volume produced with ethanol. For all substrates, volumes of biogas were reported to the COD introduced in the bottle (quantity of pollution to degrade).

### 2.5. Partial least square analyses

Partial least squares (PLS) regression technique is based in constructing PLS factors (also called principal components) by minimising the covariance between the dependent variables (Y block) and the explicative variables (X block). Then, the prediction of the Y block was calculated with a multivariable linear regression on X block through PLS1 models using the software R version R 1.2.2 for Windows and by using PLS functions developed by Durand [23]. The algorithm constructs orthogonal PLS factors in each block by minimising the covariance between the X and Y blocks. The first PLS factor contains the highest percentage of variance, and the following factors account for decreasing amounts of variance. The number of PLS factors (also called dimensions, dim) of the model was determined by minimising the mean squared prediction error (PRESS) through a cross-validation procedure.

## 3. Results and discussion

### 3.1. Effects of thermal treatments on sludge solubilisation

In this study, the term "solubilisation" was used in order to describe the transfer from the particular fraction to the supernatant of centrifugation. Solubilisation of COD, proteins and carbohydrates has been defined as the ratio of the soluble fraction minus the initial soluble fraction divided by the initial particulate fraction. For example, COD solubilisation was

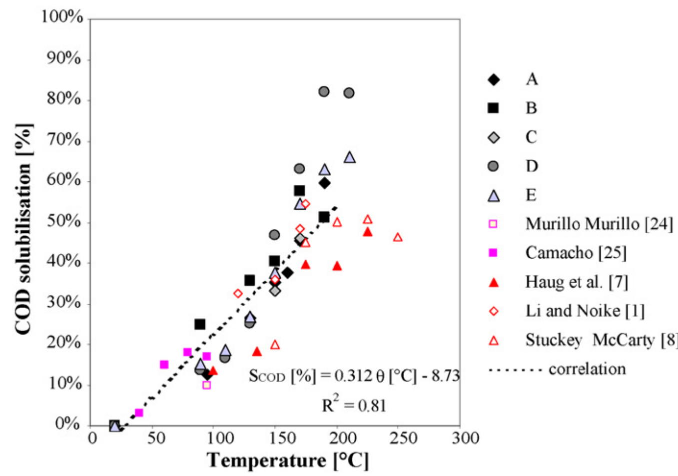


Fig. 1. Effect of thermal treatment on COD solubilisation for the various sludge samples and comparison with literature. The points at 20 °C correspond to untreated sludge.

expressed by:

$$S_{COD} = \frac{CODs - CODs_0}{COD_0 - CODs_0} = \frac{CODs - CODs_0}{CODp_0} \quad (1)$$

#### 3.1.1. COD solubilisation

Fig. 1 presents results obtained for COD solubilisation of the five sludge samples. All the points, obtained from this study or in the literature, seemed to be put in almost a line. But, for temperature higher than 200 °C, results seemed to be more dispersed.

Therefore, COD solubilisation was linked to temperature of pre-treatment whatever be the sludge samples characteristics.

#### 3.1.2. Solids solubilisation

At the same time, solids solubilisation was observed. Table 3 presents results obtained for the five sludge samples tested. For all sludge samples, TSS/TS ratio decreased with treatment temperature, as well as the ratio VSS/TSS. Therefore, solid concentration in particles decreased and particles became more mineral. For all sludge tested, the solubilisation level increased

Table 3
Solubilisation of solids due to thermal treatments

| Temperature (°C) | 20 | 95 | 110 | 130 | 150 | 170 | 190 | 210 |
|---|---|---|---|---|---|---|---|---|
| Sludge sample | | | | | | | | |
| TSS/TS (%) | | | | | | | | |
| A | 93 | 82 | | 74 | 64 | 57 | | |
| B | 93 | 77 | | 70 | 54 | 33 | 27 | |
| C | 80 | | | 64 | 49 | 29 | | |
| D | 97 | 84 | 79 | 72 | 63 | 59 | 46 | 45 |
| E | 95 | 83 | 87 | 77 | 68 | 58 | 45 | 47 |
| VSS/TSS (%) | | | | | | | | |
| A | 82 | 81 | | 79 | 74 | 72 | | |
| B | 79 | 76 | | 70 | 65 | 66 | 68 | |
| C | 82 | | | 77 | 79 | 64 | | |
| D | 83 | 80 | 82 | 78 | 74 | 71 | 65 | 61 |
| E | 78 | 71 | 73 | 72 | 68 | 66 | 68 | 56 |

20 °C data corresponds to untreated sludge.

regularly with the rise in temperature. A treatment of 170–190 °C led to a solubilisation level of almost 40–60% for sludge A, D and E and to a solubilisation level of 75–80% for sludge B and C. No global parameter seemed to explain this difference between sludge samples.

Due to thermal treatments, solids were solubilised, especially organic solids. Organic solids were very affected by treatment; for a temperature of treatment higher than 150 °C, organic solids solubilisation was more than 43% for all sludge samples tested. But, according to literature [26], it seemed that all organic compounds did not react in the same way. For instance, Barlindhaug and Odegaard [27] emitted the hypothesis that carbohydrates were more easily degraded than proteins, but that proteins were better solubilised. In order to better understand behaviour of each kind of compounds, carbohydrate, protein and lipid concentrations were determined in the sludge samples before and after thermal treatment.

### *3.1.3. Carbohydrates and proteins solubilisation*

Further to thermal treatment, proteins and carbohydrates were solubilised. Fig. 2 shows proteins concentration (curves in black) and carbohydrates concentration (curves in grey) in the whole sludge sample A and in the soluble fraction. Experiments have also been realised on two other sludge samples (D and E). Results were in agreement with conclusions exposed here.

Total proteins concentration seemed to increase. This could be explained by a better quantification of proteins after heating. However, as the error of measure was around 15%, the total proteins concentration could also be considered as constant and equal to almost 12.5 g eqSAB/l (sd: 1.2 g/l). Soluble proteins concentration increased strongly: from 0.31 g eqSAB/l (sd: 0.03 g/l) for untreated sludge to 5.9 g eqSAB/l (sd: 0.8 g/l) for sludge treated at 170 °C. On the contrary, total carbohydrates concentration seemed to decrease; whereas soluble carbohydrates concentration first increased strongly: from 0.13 g eqGluc/l (sd: 0.01 g/l) for untreated sludge to 1.04 g eqGluc/l (sd: 0.12 g/l) for sludge treated at 130 °C. Then the soluble carbohydrates concentration decreased in order to reach 0.78 g eqGluc/l (sd: 0.13 g/l) for sludge treated at 170 °C.

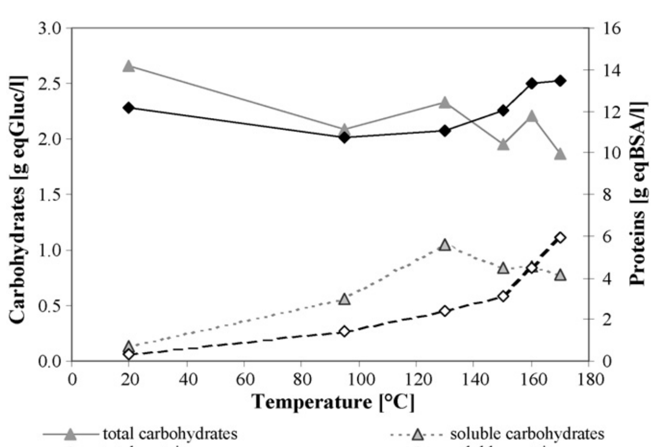


Fig. 2. Proteins and carbohydrates concentrations in the sludge sample A after thermal treatment. The points at 20 °C correspond to untreated sludge.

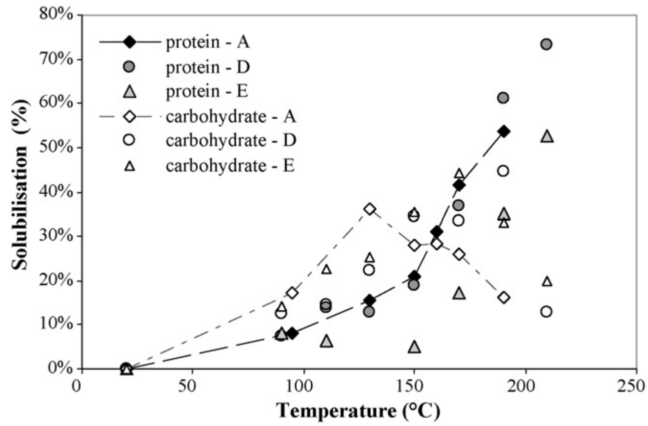


Fig. 3. Proteins and carbohydrates solubilisation for three sludge samples (A, D and C). The points at 20 °C correspond to untreated sludge.

This decrease in carbohydrates concentrations could be explained by the measurement method. Indeed, carbohydrates were measured by spectrophotometry by quantifying the carbonyl function (C=O). If carbohydrates had reacted with other carbohydrates ("burnt sugar" reactions) or with proteins (Maillard reactions), these carbonyl functions disappeared and compounds were not measured.

Nevertheless, it seemed that carbohydrates were in a first time more easily solubilised than proteins. Fig. 3 presents solubilisation rate calculated for proteins and carbohydrates for the three sludge samples tested. For all samples, solubilisation of carbohydrates was initially higher than proteins one. Then, for temperature higher than 130 °C or 170 °C (depending on samples), proteins solubilisation became higher.

Thus, this could suggest a hypothesis on the location of these compounds. It seemed that carbohydrates were mainly located in the exopolymers of sludge structure whereas proteins were mainly located inside the cells. So, for "low" temperatures, only exopolymers were affected by thermal treatment: carbohydrates were solubilised and also few proteins. For higher temperatures, cell walls were lysed; proteins were no more protected and were strongly solubilised. At the same time, soluble carbohydrates reacted (with themselves or with soluble proteins) and formed organic compounds which were not quantified. We could suggest that these new compounds were like Amadori compounds or melanoidins and that they coloured the supernatant of sludge in brown.

At the same time, in order to know if proteins were degraded by heat, $N\text{-}NH_4^+$ measures were realised. $N\text{-}NH4^+$ concentration first increased with treatment temperature and then remained constant: from 0.35 g N/l (sd: 0.05 g/l) for untreated sludge to almost 0.7 g N/l (sd: 0.1 g/l) for temperatures higher than 90 °C. Therefore, it seemed that a small part of proteins were completely degraded. So, proteins were solubilised and only few degraded due to thermal treatment.

### *3.1.4. Lipids solubilisation*

Lipids concentration was determined by solvent extraction (hexane) for long chains fatty acids (what were called "lipids")

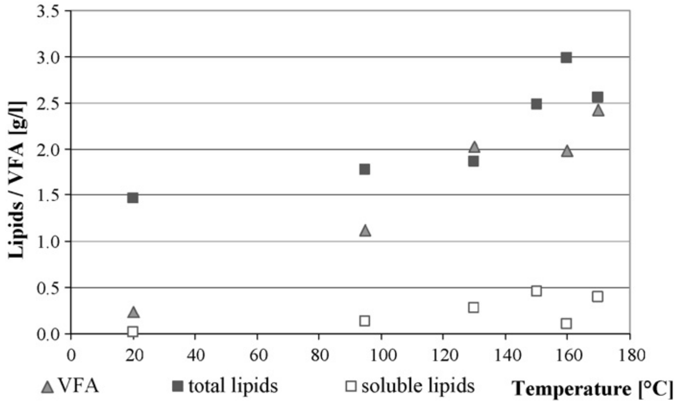


Fig. 4. Lipids and VFA concentrations in sample A after thermal treatment. The points at 20 °C correspond to untreated sludge.

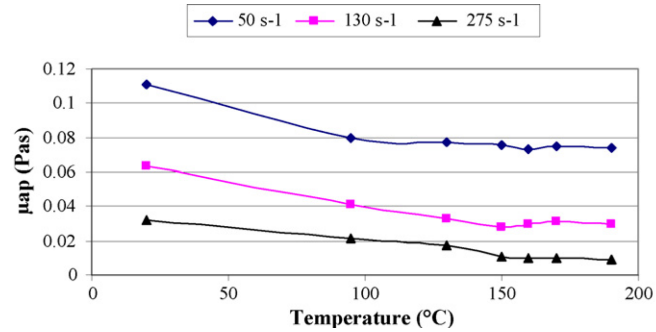


Fig. 5. Apparent viscosity of sludge sample A at different shear rate after thermal treatment. The points at 20 °C correspond to untreated sludge.

and volatile fatty acids concentration (VFA) was determined by gas chromatography. Fig. 4 shows lipid (total and soluble) and VFA concentrations in the sludge sample A. The total lipids concentration increased with thermal treatment. This increase could be due to a better extractability of lipids and a better affinity between hexane and heated lipids. Flocs were destructurated by thermal treatments. Then, the mixing between sludge and solvent was more efficient and the transfer of lipids towards the hexane phase was facilitated. Therefore, the total lipids concentration was better determined. At the same time, the soluble lipids concentration remained low: less than 0.5 g/l. That suggests that lipids, due to their high hydrophobicity, were not solubilised in the aqueous phase. Nevertheless, VFA concentration strongly increased with treatment: from 0.2 g/l for untreated sludge to almost 2.4 g/l for sludge treated at 170 °C. We may suppose that this increased was linked to lipids degradation [28]. Indeed, due to thermal treatment, long chains fatty acids may be reduced to form fatty acids of lower molecular weights, which themselves may be degraded in low chain fatty acids (i.e. VFA) and acetic acid. But, due to the difficulty in determining the total lipids concentration, it was impossible to determine a solubilisation rate of lipids. VFA production may also originate from proteins degradation.

### 3.2. Sludge physical properties

Thermal treatment led to modifications on sludge characteristics.

For instance, pH has also been measured during experiments with sludge from B and C (Table 4). For both sludge samples, pH values first increased (from 6.9 to 7.1 or 7.4 at 150 °C) and then decreased with temperature of treatment (to 6.4 or 7.1 at 170 °C). The pH increase could be due to proteins desorption or acidic compounds volatilisation [24]. And then, pH decreased could be linked to degradation of macromolecules into acidic compounds.

Table 4
pH variation for sludge samples B and C

| Temperature (°C) | 20 | 130 | 150 | 160 | 170 |
|---|---|---|---|---|---|
| Sample B | 6.9 | 7.15 | 7.4 | 7.8 | 7.1 |
| Sample C | 6.8 | 7.25 | 7.1 | / | 6.4 |

Thermal treatment had effects on sludge viscosity. Untreated sludge was pseudo-plastic fluid. Fig. 5 presents apparent viscosity of sludge sample A after thermal treatment, for different shear rates. Apparent viscosity of sludge decreased with treatment temperature. Moreover, for a temperature higher than 150 °C, apparent viscosity remained constant, for a given shear rate.

This comes along with modifications on sludge settleability. Indeed, sludge volume index decreased with the rise in temperature. For sludge A (Fig. 6), SVI was almost 140 ml/g for untreated sludge. It was equal to 47 ml/g for a temperature of 150 °C, then it seemed stabilised around 36 ml/g for higher temperatures. Thus, thermal treatment enhanced sludge settleability. This is due to modification in sludge structure. Neyens et al. [26] explained this by EPS solubilisation. EPS are hydrated compounds which can absorb huge quantity of water. Thanks to EPS solubilisation, a part of linked water is also released. Moreover, it seemed that 150 °C was a temperature threshold.

Beside, filterability of sludge was evaluated by CST (Fig. 7). It varied with temperature of treatment. First, CST values increased: for instance, for sample A, it increased from 1300 s to 2030 s for a temperature of 130 °C. Then for temperature higher than 150 °C, CST strongly decreased and reached very low values: 31 s for a temperature of treatment of 190 °C for sample A and 13 s for samples D and E. Thus, for temperatures lower than 130 °C, filterability of sludge was deteriorated. This could be linked to sludge solubilisation and the amount of small particles. Nevertheless, this hypothesis has not been verified.

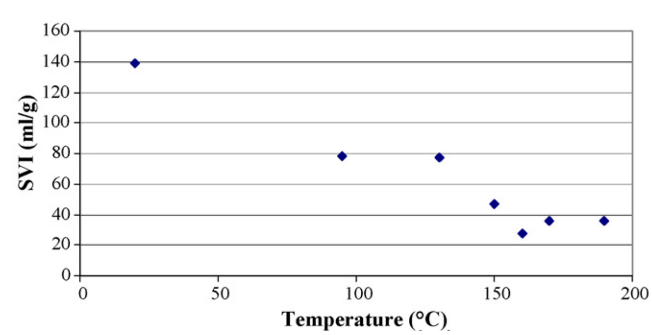


Fig. 6. Sludge volume index of sludge sample A after thermal treatment. The point at 20 °C corresponds to untreated sludge.

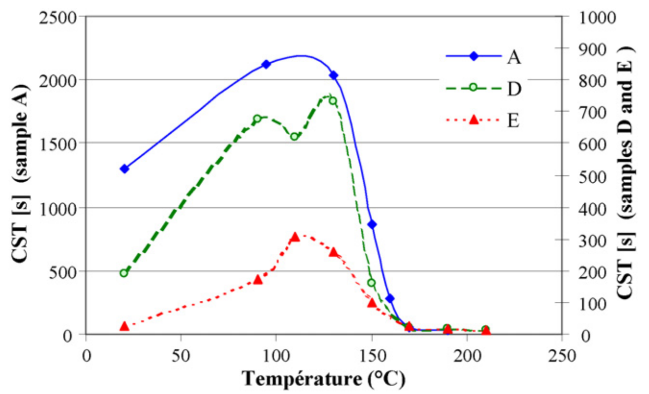


Fig. 7. CST Measurement for sludge samples A, D and E after thermal treatment. The points at 20 °C correspond to untreated sludge samples.

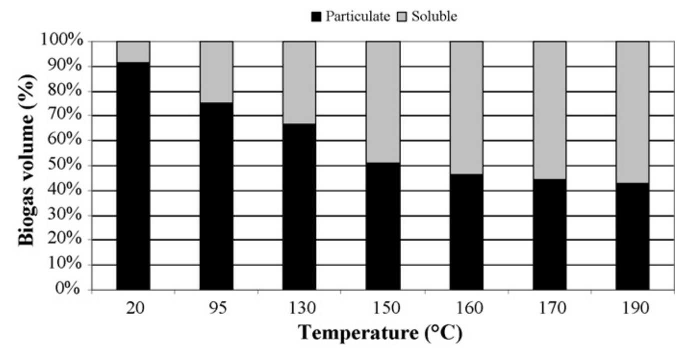


Fig. 9. Biogas production from sludge particulate and soluble fractions, sludge sample A.

On the contrary, for temperatures higher than 150 °C, filterability was improved. This could be explained by the modification of sludge structure and the released of linked water [26]. The observed threshold temperature of 150 °C is in agreement with the one reported by Fisher and Swanwick [5].

*3.2.1. Batch anaerobic digestion*

For all sludge samples, all pre-treatments from 90 °C to 210 °C led to higher sludge biodegradabilities than the untreated sludge ones, as shown in Fig. 8. Sludge biodegradability increased with pre-treatment temperature for temperatures up to 190 °C and it slightly decreased after a pre-treatment of 210 °C.

This decrease in sludge biodegradability has already been observed for temperatures higher than 175 °C which enhanced sludge solubilisation but not biogas production [8,29]. This was explained by the formation of inhibitory or toxic compounds. Moreover, Pinnekamp [30] observed a sharp decrease of biogas production and ascribed it to the products of Maillard reactions. Indeed, reaction of carbohydrates with amino acids forms melanoidins which are difficult or impossible to degrade.

Biogas composition was not measured in this study. However, another work [31] carried out with semi-continuous anaerobic reactors fed with untreated or treated WAS samples showed that thermal pre-treatment (at 135 °C or 190 °C) had no significant effect on biogas composition. Indeed, methane content was 73 ± 3% for the reactor fed with untreated WAS, 74 ± 3% and 73 ± 4% for reactors fed with sludge samples treated at 135 °C and 190 °C, respectively.

Some batch anaerobic digestion tests were carried out in order to evaluate biogas volumes produced by the soluble and particulate fractions of sludge samples. Three test bottles were realised for each sample; a given volume of total sludge was introduced in the first one. The same volume of the sample was centrifuged. Sludge particulate fraction was introduced in the second bottle and the soluble fraction was introduced in the last one. The sum of biogas volumes produced by the particular soluble fractions was equal to the biogas volume produced by the total sludge, the error being less than 10%. Fig. 9 shows the repartition of biogas volume between soluble and particular fractions. For untreated sludge, biogas was produced at 91% from particulate matter, whereas for sludge sample treated at 190 °C, only 43% of biogas came from particulate fraction. Thus biogas volume produced from the sludge soluble fraction increased with temperature pre-treatment but this increase was more important for temperatures higher than 130 °C.

The biogas volume produced by each fraction is plotted versus the amount of introduced COD in Fig. 10 that shows that biogas volume was proportional to the amount of introduced COD, except for the last point for soluble fraction. This point

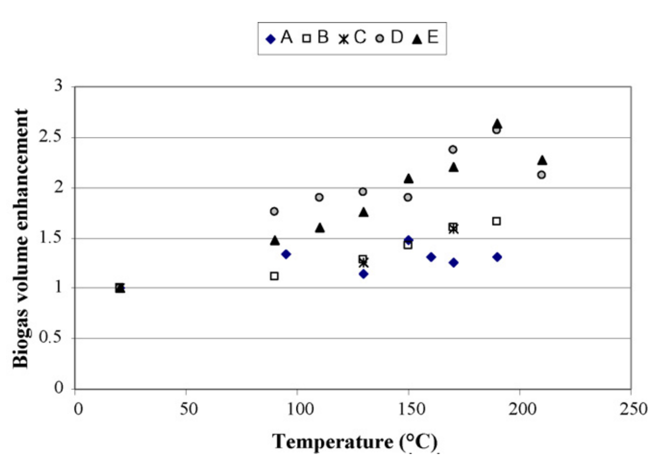


Fig. 8. Biodegradability enhancement (at 17 to 24 days of batch experiments) of pre-treated sludge. Sludge samples A, B, C, D and E.

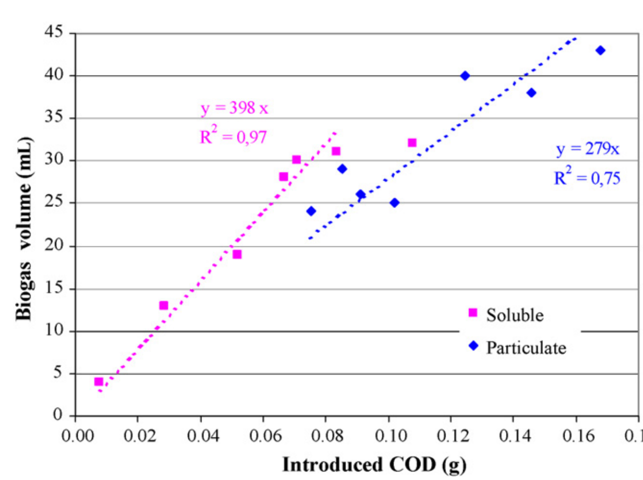


Fig. 10. Relationship between produced biogas volume and the amount of introduced COD for particulate and soluble fractions, sludge sample A.

corresponded to 190 °C treatment and showed the presence of non biodegradable compounds in the soluble phase (notably, products of Maillard reactions). Thus, for temperatures lower than 170 °C, 1 g of COD introduced in the test bottle led to the production of 398 ml of biogas. The conversion was lower for the particulate fraction as 1 g of COD led to the production of 279 ml of biogas. This shows that organic matter present in the soluble fraction was more biodegradable than particulate matter. It has also to be noticed that data corresponding to untreated sludge (lowest amount of soluble COD and highest amount of particulate COD) could be represented by the same lines as the data for pre-treated samples at temperatures lower than 170 °C. This means that biodegradability matter present in both fractions was not significantly changed by thermal treatments (at temperatures lower than 170 °C). The increase in biogas production was due to the transfer of organic matter from the particulate fraction to the soluble fraction.

Fig. 8 gathers experimental biogas volume enhancements obtained for the five studied sludge samples. We tried to analyse the impact of the sludge sample on the biogas volume enhancement. In a first time, a PLS analysis was carried out to see the correlation between different measured explicative variables. Three sludge samples were taken into account (samples A, C and D for which all the measures were available) and temperature, COD solubilisation, TS solubilisation, VS solubilisation, proteins solubilisation, carbohydrates solubilisation and untreated sludge biodegradability (Bo) were considered. As expected, all these parameters, except untreated sludge biodegradability were correlated. Thus, COD solubilisation was kept as an overall parameter to represent organic matter solubilisation. In a second time, a PLS regression was carried out considering the five sludge samples. The Y block was constituted of biogas volume enhancements (27 points). The X block was constituted of sludge initial biodegradability (Bo) and COD solubilisation ($S_{COD}$). The result was a dimension 2 model with an average prediction error of 25%.

$$\text{Biogas volume enhancement} = 2.156 + 1.155\, S_{COD} - 2.348\, \text{Bo} \quad (2)$$

The results of this model are plotted in Fig. 11, which shows the good agreement between experiment and calculated data. Thus, for temperatures lower or equal to 170 °C, the impact of thermal treatments on batch anaerobic biogas production can be simply represented by considering sludge COD solubilisation and untreated sludge initial biodegradability. The higher the COD solubilisation, the higher is the biogas production. Besides, the impact of pre-treatment was more important when it was applied to sludge samples with a low initial biodegradability. However, untreated sludge biodegradability did not seem to be linked to the sludge samples compositions. Indeed, sludge samples A and D had the same organic solids concentration (81–82% of TS) and their initial biodegradabilities were 53% and 33%, respectively. In the same way, sludge samples B and E had an organic solids concentration of 76% and initial biodegradabilities of 48% and 29%, respectively. If wastewater treatment plants processes are considered, sludge from both high load processes (A and B) had a high initial biodegradability and sludge from extended aeration (E) process had a poor initial biodegradability (29%). On the other hand, sludge samples from medium load processes had either a high (C) or a low (D) initial biodegradability.

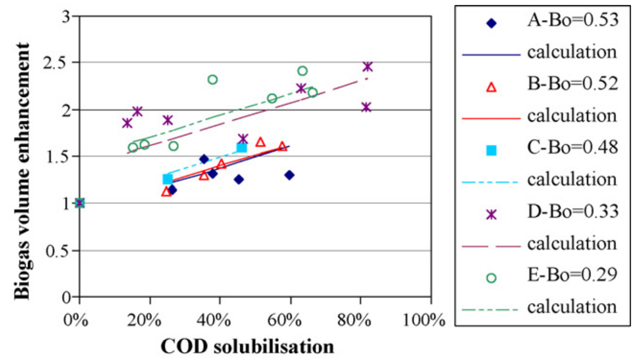


Fig. 11. Biodegradability enhancement (at 17 to 24 days of batch experiments) versus COD solubilisation and untreated sludge biodegaradability (Bo). Sludge samples A, B, C, D and E.

## 4. Conclusion

Thermal treatments are efficient to solubilise sludge. For temperatures lower than 200 °C, COD solubilisation was found to increase linearly with treatment temperature and all the different sludge samples behaved in the same way. For temperatures above 200 °C, solubilisation results seemed to be more dispersed. For temperatures lower than 150 °C, carbohydrates solubilisation was more important than proteins solubilisation as carbohydrates are located in exopolymers whereas proteins are mainly inside the cells. Moreover, carbohydrates concentration decreased at high temperature as they reacted with other carbohydrates or solubilised proteins.

Analyses of physical characteristic of sludge pointed out a threshold temperature of 150 °C. Indeed, sludge dewaterability was improved above this temperature but deteriorated for lower temperatures. Moreover, sludge apparent viscosity and sludge volume indexes were reduced first with temperature and then remained almost constant for temperatures higher than 150 °C.

Thermal treatments up to 190 °C allowed the biogas production to increase during batch anaerobic digestion of sludge. Biogas volume enhancement was linked to sludge COD solubilisation and to untreated sludge initial biodegradability, the lower the initial biodegradability, the higher is the impact of thermal treatment.

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## References

[1] Y.Y. Li, T. Noike, Upgrading of anaerobic digestion of waste activated sludge by thermal pretreatment, Water Sci. Technol. 26 (1992) 857–866.
[2] U. Kepp, I. Machenbach, N. Weisz, O.E. Solheim, Enhanced stabilization of sewage sludge through thermo hydrolysis – three years of experience with full scale plant, Water Sci. Technol. 42 (9) (2000) 89–96.

[3] J. Chauzy, D. Cretenot, L. Patria, P. Fernandez, P. Sauvegrain, J.P. Levasseur, Bio Thelys: a new sludge reduction process. Biosolids 2003, wastewater sludge as a resource, Trondheim, 23–25 June 2003, pp. 473–479.

[4] E. Neyens, J. Baeyens, A review of thermal sludge pre-treatment processes to improve dewaterability, J. Hazard. Mater. 98 (1–3) (2003) 51–67.

[5] R.A. Fisher, S.J. Swanwick, High temperature treatment of sewage sludge, Water Pollut. Control 71 (3) (1971) 255–370.

[6] N.J. Anderson, D.R. Dixon, P.J. Harbour, P.J. Scales, Complete characterisation of thermally treated sludges, Water Sci. Technol. 46 (10) (2002) 51–54.

[7] R.T. Haug, D.C. Stuckey, J.M. Gossett, P.L. Mac Carty, Effect of thermal pretreatment on digestibility and dewaterability of organic sludges, J. Water Pollut. Control Fed. (1978) 73–85.

[8] D.C. Stuckey, P.L. Mc Carty, Thermochemical pretreatment of nitrogenous materials to increase methane yield, Biotechnol. Bioeng. Symp. 8 (1978) 219–233.

[9] S. Tanaka, T. Kobayashi, K.I. Kamiyama, L.N. Bildan, Effects of thermochemical pretreatment on the anaerobic digestion of waste activated sludge, Water Sci. Technol. 35 (8) (1997) 209–215.

[10] C. Fjordside, An operating tale from Naeested Sewage Treatment plant, Municipal Wastewater Treatment Nordic Conference, Copenhagen, 17–19 January 2001.

[11] H.N. Gavala, U. Yenal, I.V. Skiadas, P. Westermann, B.K. Ahring, Mesophilic, thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature, Water Res. 37 (2003) 4561–4572.

[12] M. Barjenbruch, O. Kopplow, Enzymatic, mechanical and thermal pretreatment of surplus sludge, Adv. Environ. Res. 7 (3) (2003) 715–720.

[13] J. Kim, C. Park, T.H. Kim, M. Lee, S. Kim, S.W. Kim, J. Lee, Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, J. Biosci. Bioeng. 95 (3) (2003) 271–275.

[14] M. Dohanyos, J. Zabranska, J. Kutil, P. Jenicek, Improvement of anaerobic digestion of sludge, Water Sci. Technol. 49 (10) (2004) 89–96.

[15] A. Valo, H. Carrère, J.P. Delgenès, Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion, J. Chem. Technol. Biotechnol. 79 (2004) (2004) 1197–1203.

[16] S. Graja, J. Chauzy, P. Fernandes, L. Patria, D. Cretenot, Reduction of sludge production from WWTP using thermal pretreatment and enhanced anaerobic methanisation, Water Sci. Technol. 52 (1–2) (2005) 267–273.

[17] C. Bougrier, C. Albasi, J.P. Delgenès, H. Carrère, Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability, Chem. Eng. Proc. 45 (8) (2006) 711–718.

[18] C. Bougrier, J.P. Delgenès, H. Carrère, Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogaz yield, Process Saf. Environ. Protect. 84 (B4) (2006) 280–284.

[19] American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard methods for the examination of water and wastewater, in: L.S. Clesceri, A.E. Greenberg, R.R. Trussel (Eds.) 18th ed., APHA, 1992.

[20] O.H. Lowry, N.J. Rosebrough, A.L. Fau, R.J. Randall, Protein measurement with the Folin reagent, J. Biol. Chem. 193 (1951) 265–275.

[21] R. Dreywood, Qualitative test for carbohydrate material, Ind. Eng. Chem. Res. 18 (1946) 199.

[22] G. Bridoux, P. Dhulster, J. Manem, Greases analysis in waste water treatement plant, Techniques-Sciences-Méthodes 5 (mai 1994) (1994) 257–262 (in French).

[23] J.F. Durand, Partial least-squares regression: from linearity to nonlinear additive spline modeling Web site: http://jf-durand-pls.com/.

[24] M. Murillo Murillo, Characterisation of the effect of a hydrogen peroxide treatment of a sludge. Application to the reduction of sludge production, Ph.D. thesis, INSA Toulouse, 2004 (in French).

[25] P. Camacho, Study of sludge reduction processes by combibingchemical or physical treatments and biological treatments, Ph.D. thesis, INSA Toulouse, 2001 (in French), cited by Murillo-Murillio [24].

[26] E. Neyens, J. Baeyens, R. Dewill, B. De Heyder, Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, J. Hazard. Mater. 106B (2004) 83–92.

[27] J. Barlindhaug, H. Odegaard, Thermal hydrolysis for the production of carbon source for denitrification, Water Sci. Technol. 34 (1–2) (1996) 371–378.

[28] A. Shanableh, S. Jomaa, Production and transformation of volatile fatty acids from sludge subjected to hydrothermal treatment, Water Sci. Technol. 44 (10) (2001) 129–135.

[29] R.T. Haug, T.J. Le Brun, D. Tortorici, Thermal pretreatment of sludges: a field demonstration, J. Water Pollut. Control Fed. 55 (1) (1983) 23–34.

[30] J. Pinnekamp, Effect of thermal pretreatment of sewage sludge on anaerobic digestion, Water Sci. Technol. 21 (1989) 97–108.

[31] C. Bougrier, J.P. Delgenès, H. Carrère, Impact of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge, Biochem. Eng. J. 34 (2007) 20–27.