Aim and Scope

The objective of the *Journal of Residuals Science & Technology* is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal and are also welcome.

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EDITORIAL

Selected Papers Presented During ECSM'08—European Conference on Sludge Management, Liège, September 1–2, 2008

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THESE last years, the management of residual sludge has become a key issue. According to stringent environmental regulations, the production of sludge from wastewater treatment plants has been continuously increasing worldwide for several years. The treatment of each so-called Equivalent Inhabitant leads to an annual production of about 20 kg of sludge, expressed on a dry basis. Taking into account the remaining water at the outlet of mechanical dewatering processes, the total mass is roughly 4 to 5 times higher.

Considering the recent ban on dumping non ultimate wastes, energy valorization and landspreading remain the two major issues for sewage sludge disposal. Besides research for new or improved valorization ways, some effort remains to be done to improve mechanical dewatering and drying processes.

This special issue of the Journal of Residuals Science and Technology gathers some of the papers presented during the first European Conference on Sludge Management (ECSM'08). This conference was organized at the University of Liège on September 1–2, 2008. About 150 delegates coming from 30 countries participated to this event. The 'hot' character of sludge management has been confirmed by the large participation of industrials, who were more than 60. The program of the conference was very dense, with 37 oral and 21 poster presentations, respectively. Most of them dealt with dewatering, drying, and thermal valorisation.

Taking into account the success of this event, the second ECSM conference will take place in September 2010 in Budapest, Hungary.

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Effect of CaO and Dolomite Additive on the Thermal Decomposition of Sewage Sludge in an Inert Atmosphere

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ABSTRACT: The synchronised and calibrated measurement system consisting of thermobalance coupled with mass spectrometer was used in the study of sewage sludge pyrolysis. A sample of dried and sieved sewage sludge had been mixed with mineral additives (calcium oxide or dolomite) in different proportions and then heated up to 1000°C with constant heating rate in the atmosphere of argon. The aim of this work was to compare the thermal decomposition of sewage sludge with and without addition of catalyst and to qualitatively describe phenomena occurred. Adding of CaO or dolomite to the sludge sample we achieved: decrease of residual mass and tars production, an increase of CO and H_2 amount.

INTRODUCTION

THE pyrolysis and gasification of sewage sludge are currently being investigated as an alternative to the problem of sewage sludge disposal. These two processes present certain advantages over the most widely used combustion or co-combustion technologies. The flue gas volume decreases significantly when changing from combustion to gasification [1] and the product of gasification, synthesis gas, is a useful raw material for chemical industries apart from being used as potential fuel.

Pyrolysis is the process of thermal decomposition of organic substances in an inert (oxygen free) atmosphere, at temperatures below 800°C. During the pyrolysis sewage sludge undergoes a sequence of physical and chemical steps, starting with the drying with maximum rate at about 120°C. Above this temperature a series of chemical and thermal reaction occurs. The major products that are formed after thermal degradation of the sludge in an inert atmosphere are the following:

- non-condensable gas (at normal conditions) containing mainly carbon monoxide, carbon dioxide, hydrogen, methane and several other hydrocarbons in smaller concentrations,
- tar and/or oil (liquid fraction),
- char, which is mainly carbon with small amounts of inert materials.

In gasification process the primary pyrolysis products, condensable and non-condensable vapours and mainly char undergo secondary reactions with a gasification reagent forming additional amounts of synthesis gas. In fact, pyrolysis and gasification are two separate or partly overlapping stages (depending on the gasifying agent used) because the conversion of char occurs at higher temperatures when most of thermal decomposition processes are finished.

Process of coal pyrolysis has been well known and utilized for many years, but pyrolysis and gasification of sewage sludge are still under development. One of the most important technical problem concerning these processes is tar formation. Tars are defined as all organic contaminants with a molecular weight larger than benzene. Tars are condensing on cooler parts of equipment causing its blocking and clogging. One of the method for decrease of tars production in pyrolysis of coal is an addition of catalysts [2]. Addition of some active bed materials has been also proven to be effective in the case of thermal decomposition of biomass [3]. By mixing of coal or biomass with catalyst we can achieve a decrease of tar production and simultaneously an increase of the amount of produced gas, what leads to increasing of process efficiency. Moreover, the activation energy of chemical reactions proceed in this process decreases.

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Limestone was one of the first additives used in the gasifier to improve the process, whereas dolomite is now one of the most popular and mostly studied in-bed additive [4,5]. Calcium, in the form of oxide or hydroxide, is often applied in the final stage of sewage sludge processing for hygienisation. The factors which influence the biocidality of a liming process are a high alkaline reaction and an increased temperature caused by the exothermal reaction of calcium oxide hydration [6]. Liming of sludge also enables stabilization and enhances dehydration [7]. The addition of calcined dolomite to biomass gasification reactor improves the quality of the product gas as well as reduces significantly the amount of tars [8,9]. CaO and dolomite catalysts are reported to be very effective not only for tar reduction, but also for decreasing the amount of HCl when gasifying a feedstock with a high content in chlorine [10].

Because in-bed addition of catalyst seems to be of potential importance for the thermochemical processing of sewage sludge more research is required for better understanding the fundamentals of the process and developing an efficient technologies. The aim of this work is to compare pyrolysis process of sewage sludge with and without addition of catalyst (CaO and dolomite) and to qualitatively describe phenomena occurring in this process.

EXPERIMENTAL

The Mettler-Toledo TGA/SDTA851 LF (temperature range 20 ÷ 1100°C, sample mass up to 5000 mg) thermobalance was coupled with Balzers ThermoStar Mass Spectrometer QMS 200 using a special TG-MS conversion kit. TG-MS system was successfully used in other similar investigations [11,12]. The gas supplying system consisting of three calibrated mass flow meters (Brooks model 4850S) was set to control the feed gas flow rate and gas composition.

The TG provides extensive information on the thermal decomposition of a solid substrate and the mass spectrometry analysis was used to monitor gas emissions. Both analytical methods result in a more complete picture of the ongoing reactions during the process—TG and DTG profiles, as well as the evolution of main gaseous product emissions.

In order to use the results obtained from TG-MS system for quantitative analysis of reaction products the MS profiles recorded as relative intensity must be converted into composition of evolved gases. Calibration methods of TG-MS system was described in details in another work [13].

In our study a sample of digested sewage sludge from municipal wastewater treatment plant in Lodz, Poland, (GOS) was used after drying (to about 97% dry mass). The sample was grinded and sieved (fraction ($< 40\ \mu m$) to achieve better homogeneity, then mixed in different proportions with calcium oxide or dolomite (the same particle size as for the sludge) and heated with a constant heating rate in thermobalance to the temperature 1000°C. The list of experiments performed is presented in Table 1.

In two experiments (KAN and KAW) samples of digested sewage sludge from Kalisz (Poland) wastewater treatment plant were studied—one of them (KAW) after stabilization by addition of lime in the form of suspension (about 30% of dry basis of sewage sludge) for hygienisation.

In Table 2 initial elemental composition of sewage sludge samples used in this work are compared.

Table 1. List of Experiments.

Sample Designation	m_{sludge}	$m_{additive}$	Gas/Flow Rate	Heating Rate
	Mg		cm^3/min	°C/min
GOS/CaO_50	37.5	37.5	Ar / 50	20
GOSCaO_25	56.2	18.8	Ar / 50	20
GOS/CaO_10	67.5	7.5	Ar / 50	20
GOS/dol_25	56.2	18.8	Ar / 50	20
GOS	75	–	Ar / 50	20
GOS_CO2	75	–	Ar:CO_2 = 1:1 / 100	20
CaO	–	75	Ar / 50	20
CaO_CO2	–	75	Ar:CO_2 = 1:1 / 100	20
dol	–	75	Ar / 50	20
KAN	–	75	Ar / 50	20
KAW	–	75	Ar / 50	20

Table 2. Elemental Analysis of the Raw Sewage Sludge Samples

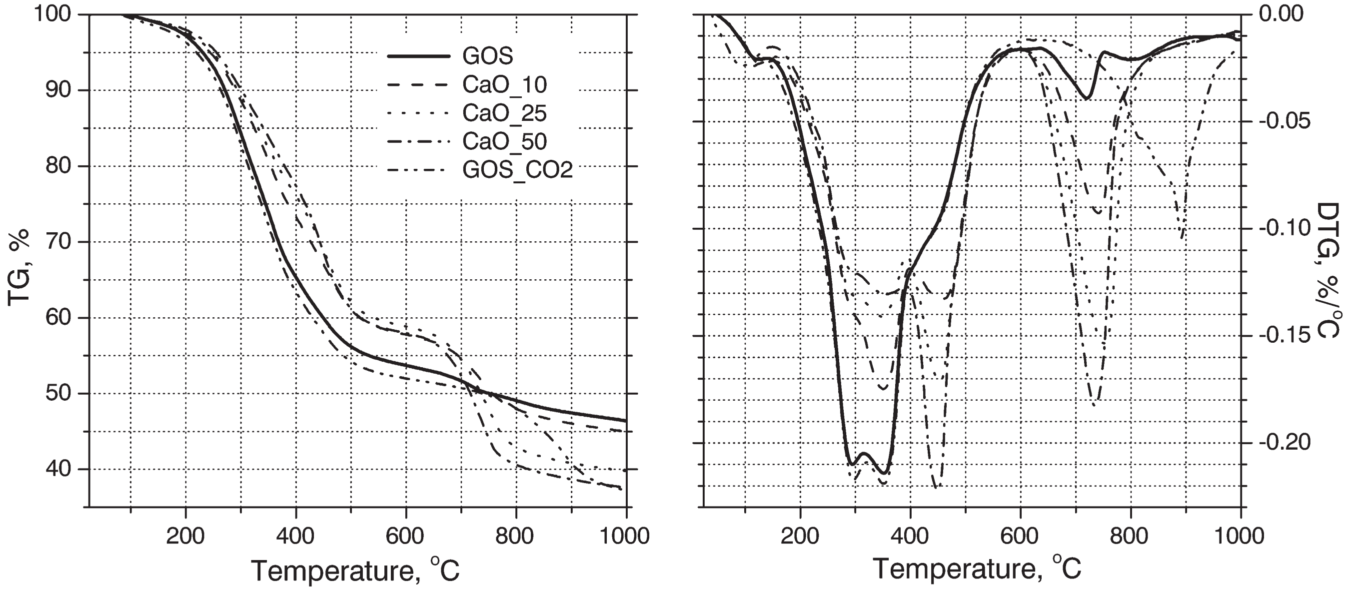
	C	H	O	N	S	Ash	H/C	O/C
Sample	**% of raw sample mass**						**mole**	
GOS	26.0	3.5	23.9	2.8	1.1	42.7	0.81	0.69
KAN	32.6	5.0	24.6	3.7	2.1	32.0	0.92	0.57
KAW	24.7	3.7	25.9	2.7	0.7	42.3	0.89	0.79

RESULTS AND DISCUSSION

CaO Addition

In Figure 1 the TG and DTG profiles for thermal treatment of sewage sludge containing various amounts of CaO are shown. For samples containing no CaO the data are presented as they were measured directly by thermobalance (experiment GOS and GOS_CO2). In other cases numerical values presented in the figure were obtained by subtracting the initial mass of CaO added from current mass of sample measured. The result of the subtraction represents the mass of sludge in the case when calcium is in the form of CaO only. It will be shown later that CaO can react with some pyrolysis products (H_2O, CO_2), and therefore, TG profiles for samples with calcium oxide show the current mass of sludge plus mass of pyrolysis product reacted with CaO. This is why the TG curves for these samples lie above the curves recorded for samples without any addition.

As can be seen from Figure 1(a), the smallest mass loss (53.6%) was observed for pyrolysis process of sewage sludge sample without any addition of CaO. A solid residue after pyrolysis is composed of inert ash and pyrolysis char, which undergoes gasification process in gaseous atmosphere of CO_2 (experiment GOS_CO2). Total mass loss after the gasification was 62.8% and it means that yield of char formed at the conditions applied was about 9.2% of the initial sample mass. When increasing amount of CaO added to sewage sludge an increase in mass loss is observed comparing to the pyrolysis experiment of sewage sludge without CaO. When using the mixture of CaO and sewage sludge in 1:1 mass ratio entire carbon from the sample is converted into gas and liquid fractions. Total mass loss of 62.4% measured in this experiment (CaO_50) was almost the same as for sewage sludge gasification in CO_2 atmosphere. It is worth to notice that the char gasification reaction in the atmosphere of CO_2 occurs above 750°C, whereas the process of char conversion in the sample containing CaO begins at much lower tempera-



(a) (b)

***Figure 1.** Comparison of TG (a) and DTG (b) curves for sewage sludge with and without the addition of CaO.*

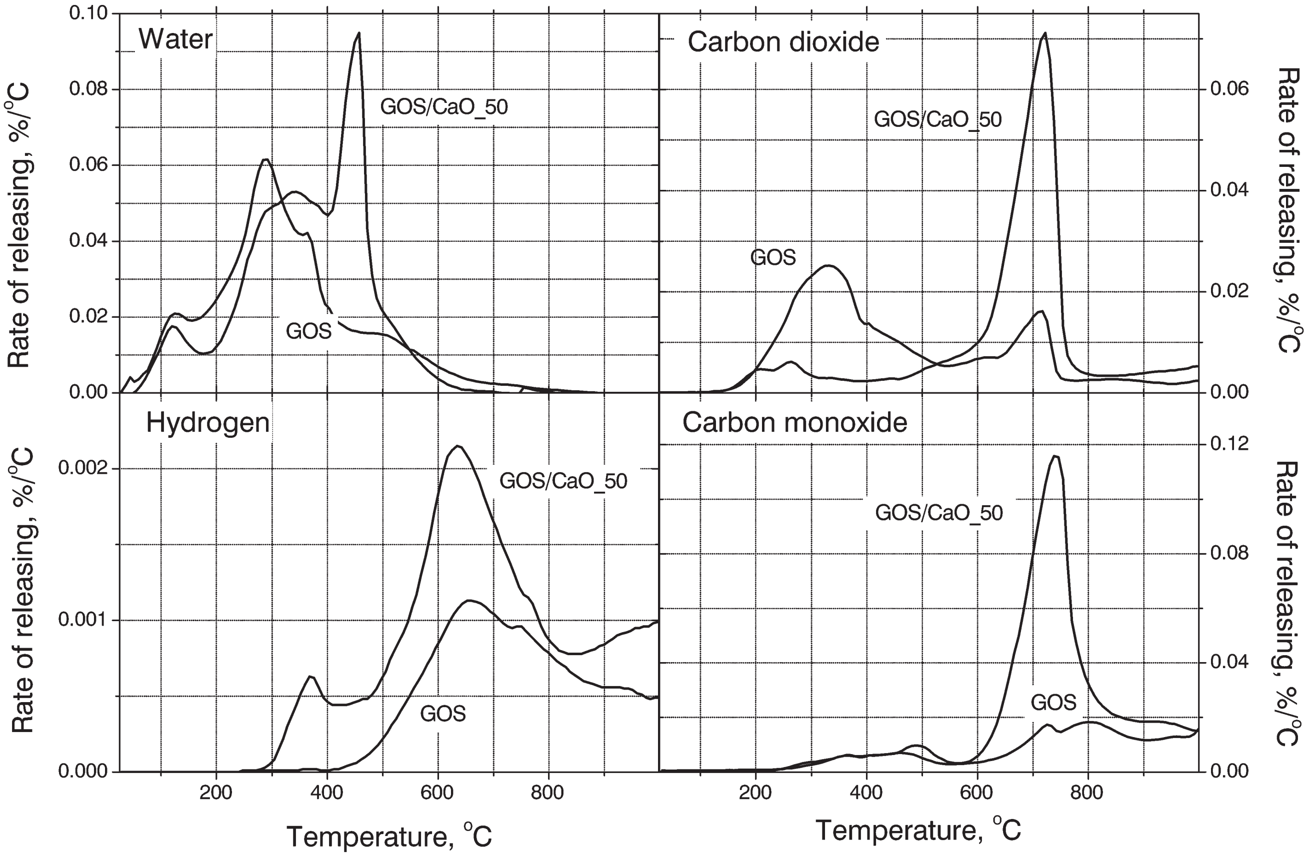


Figure 2. *Effect of CaO addition to sewage sludge sample on the formation rate of major gas products.*

tures. The highest DTG values for the peak representing gasification of char by CO_2 can be observed at 890°C [see Figure 1(b)] while for samples with CaO in an inert atmosphere the maximum of gasification rate shifts to 740°C.

Figure 1(b) reveals more details of the pyrolysis process of sewage sludge mixed with calcium oxide taking place in the main devolatilisation steps at temperatures between 150 and 500°C. Lower DTG values for the first double peak that can be observed for samples with CaO are a consequence of the above mentioned chemical reactions between primary pyrolysis products and calcium oxide. The third devolatilisation step represented by the partly overlapped peak with maximum at about 450°C becomes very intensive now and a maximum DTG value characterizing this peak increases with increasing amount of CaO in the sample.

In Figire 2 the evolution of main gaseous products emissions from samples GOS and GOS/CaO_50 obtained based on of profiles recorded by mass spectrometer are compared. In both experiments H_2O was observed to be given off within the temperature below 600°C. However, the profiles of water emission differ significantly in these experiments. Comparing to pyrolysis of sewage sludge (experiment GOS) less water was released from the sample containing CaO below 300°C and much more above this temperature. It is clear that the high sample mass loss in temperature range 400–500°C observed for sample CaO_50 is related to the faster water vapor emission. It is also interesting that total amount of water released from sample was bigger for sample CaO_50 (about 17% instead of 14% of the initial mass of sewage sludge in the case of sample GOS).

A similar situation occurred for carbon dioxide: a significant amount of CO_2 produced during pyrolysis at lower temperatures is used for the carbonisation of CaO (250–500°C), and then it is released at higher temperatures (600–800°C). Total amount of CO_2 released was 9% and 7% for samples GOS/CaO_50 and GOS, respectively. The addition of CaO caused also a significant increase in carbon monoxide formation. Total amount of CO in the gas phase changed from 7% to about 17% of the initial mass of sludge in the sample. The temperature range where CO was released covers with that recorded for CO_2. CO_2 released at these temperatures is responsible for the auto-gasification of pyrolysis char, resulting in a significant increase in the carbon monoxide production rate. In consequence, a further decrease in the mass of the sample was observed. Similar processes, but to a lesser extent, are observed for the samples without any addition of CaO. This phenomenon is due to the presence of CaO in every sewage sludge (typically from 3 to 15% of dry basis) [14].

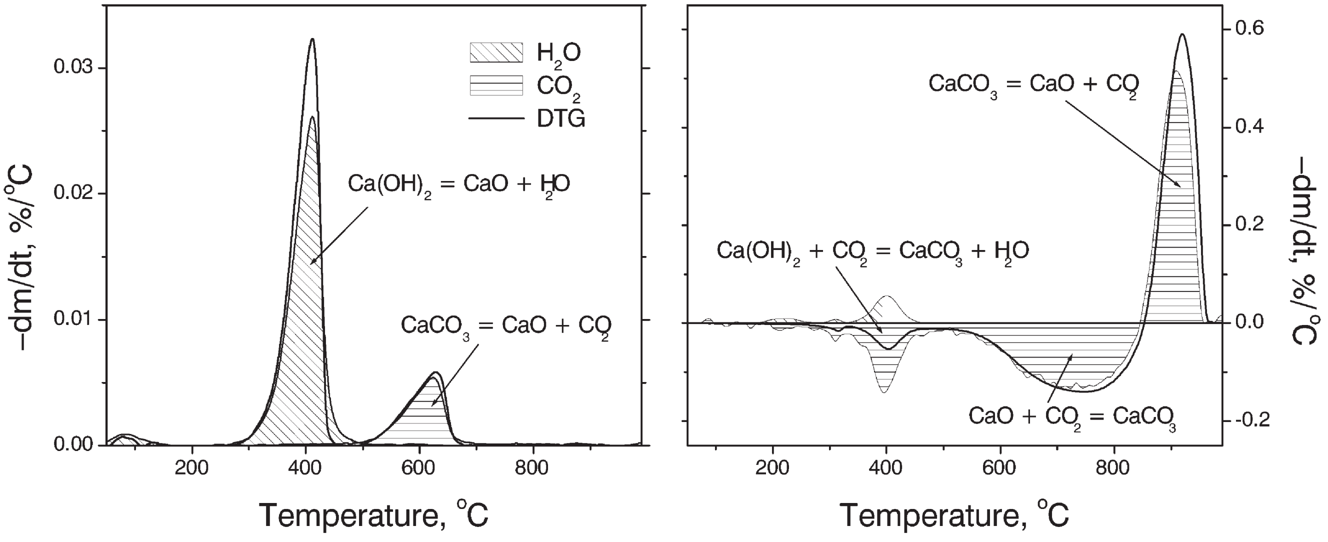
Elevated emission of H_2O, CO, CO_2 and H_2 from the samples with CaO addition should result in lower formation of tars. Based on mass spectrometer data it was estimated that amount of tars was reduced from about 23% of initial mass of sludge to 15.5% when CaO was added to sewage sludge in mass ratio of 1/1. We believe that apart from the aforementioned chemical reactions in which same primary pyrolysis product are involved, other unidentified processes of the type:

$$C_xH_yO_z + 2H_2O + CaO \rightarrow$$
$$CaCO_3 + 2H_2 + (CO, CH_4, C_mH_n, \text{tars})$$

catalysed by Ca and its compounds take place. As a result less tar and more gaseous product is produced instead.

To get better insight into processes occurring in the samples containing calcium oxide additional experiments were performed, in which pure CaO was heated in argon or carbon dioxide (experiments CaO and CaO_CO2). The results of these experiments are presented in Figure 3. Pure CaO heated in an inert atmosphere should not undergo any chemical reaction. However the sample of CaO was not calcinated just before experiment, so it could contain small amounts of hydroxide and calcium carbonate. As can be seen in Figure 3(a), water is released in temperatures between 300 and 500°C, whereas the second small peak appearing in temperature range of 500–700°C is related to carbon dioxide desorption. Total mass loss of the sample heated in Ar was 2.3%. Mass of the same sample of CaO heated in a reactive atmosphere of CO_2 was increasing up to 134.5% of its initial value at 850°C and then quickly dropped to the level of 97.7% of its initial value—the same as for sample heated in argon. CO_2 adsorption occurs in temperatures 600–800°C [see Figure 3(b)], although some CO_2 was also adsorbed at about 400°C. At this temperature adsorption was accompanied by dehydration process. When the test was carried out in atmosphere containing carbon dioxide the carbonation peak shifted to higher temperature comparing to the experiment performed in argon because of the equilibrium of this reversible reaction.

In Figure 4 DTG profiles for pyrolysis of sewage sludge samples GOS, KAN and KAW are compared. Samples GOS and KAN do not contain any additives but their DTG profiles differ significantly due to different ash contents (see Table 2). The high temperature reaction steps in the case of sample KAN are slower probably because of lower content of CaO in the mineral fraction of the sludge. The DTG profile for sample KAW with lime are very similar to that observed for GOS sewage sludge mixed with CaO [compare Figure 1(a)].



(a) (b)

Figure 3. *DTG and gas emission profiles for heating of pure CaO in Ar (a) and CO_2 (b).*

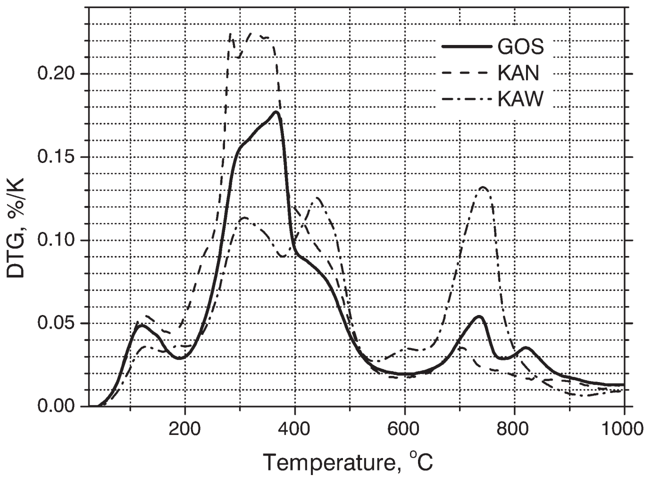


Figure 4. *DTG curves for pyrolysis of sewage sludges from Lodz (GOS) and Kalisz (KAN & KAW).*

Additive of Dolomite

In Figure 5(a) the TG curves for the pyrolysis process of the GOS sewage sludge sample and the sludge mixed with dolomite $CaMg(CO_3)_2$ in a mass ratio 1:3 are presented (experiments GOS and GOS/dol, respectively). Comparing these two profiles it must be taken into account, that the mass of sewage sludge in the sample GOS/dol is only 75% of the sample mass and total mass loss observed for this sample is caused partly by the thermal decomposition of sludge, and only partly by the decomposition of dolomite. We conclude this from Figure 5(b), where DTG and gas emission profiles for thermal decomposition of dolomite are shown (experiment depicted with dol). This mineral decomposes at temperatures above 600°C with the emission of CO_2. Total mass loss at a temperature range of 600–1000°C amounts to 45.4% of initial mass of dolomite. Assuming that the mass loss of dolomite in the mixture with sewage sludge was exactly the same as for pure mineral the mass loss of sewage sludge can be estimated. According to these calculations, this mass loss amounts to 55.8%, which is higher than for mass loss measured in the experiments GOS with no dolomite addition (53.6%). Initial part of TG curve for GOS/dol sample can be also recalculated in the same way and it is drawn in Figure 5(a). The line showing mass changes of sludge in the sample GOS/dol is slightly below the TG curve for GOS and this is due to higher moisture content in the sample GOS/dol (see water emission profile in Figure 6).

Mass spectrometry analysis was used to monitor main gas product emissions. Figure 6 shows the evolution of H_2, H_2O, CO and CO_2 emissions from GOS and GOS/dol samples. At temperatures below 600°C the main products were H_2O and CO_2 and, in smaller quantities of CO (some methane and other hydrocarbons were also detected but these are not discussed here). At higher temperatures mainly CO and CO_2 were evolved. During the pyrolysis of the sludge/dolomite mixture more CO_2 was formed due to the decomposition of dolomite. More CO was also characteristic for this case. Carbon monoxide appears in parallel with CO_2, being the result of char auto-gasification reaction. Conversion of pyrolysis char into gas explains higher yield of pyrolysis process when dolomite addition to sewage sludge is used.

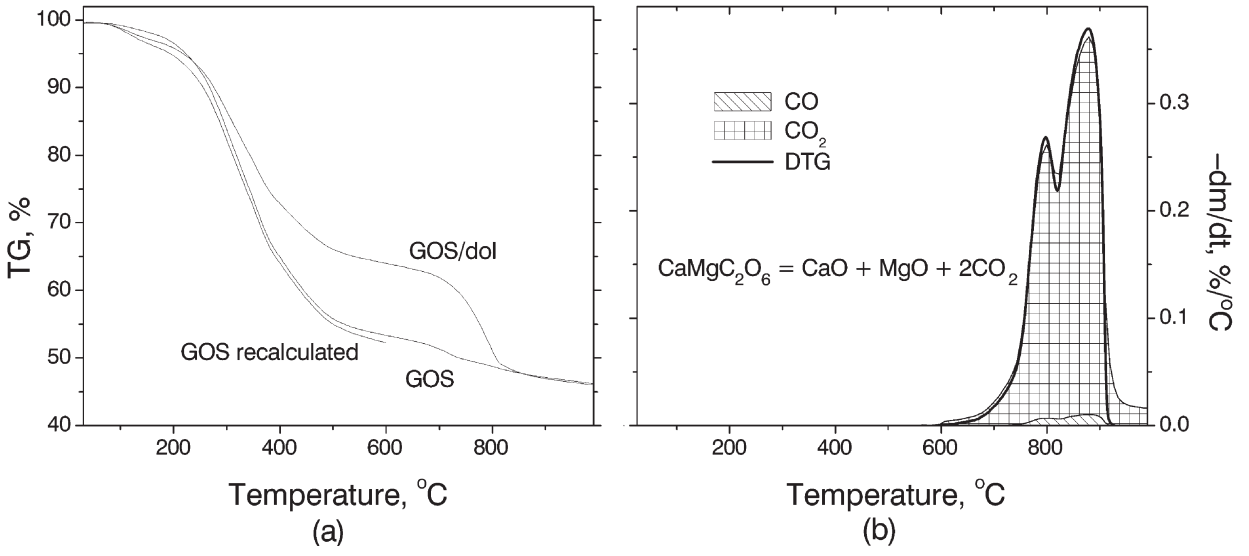


Figure 5. *TG curves recorded in experiments for GOS and GOS/dol_25 (a) and DTG and gas emission profiles for pure dolomite (b).*

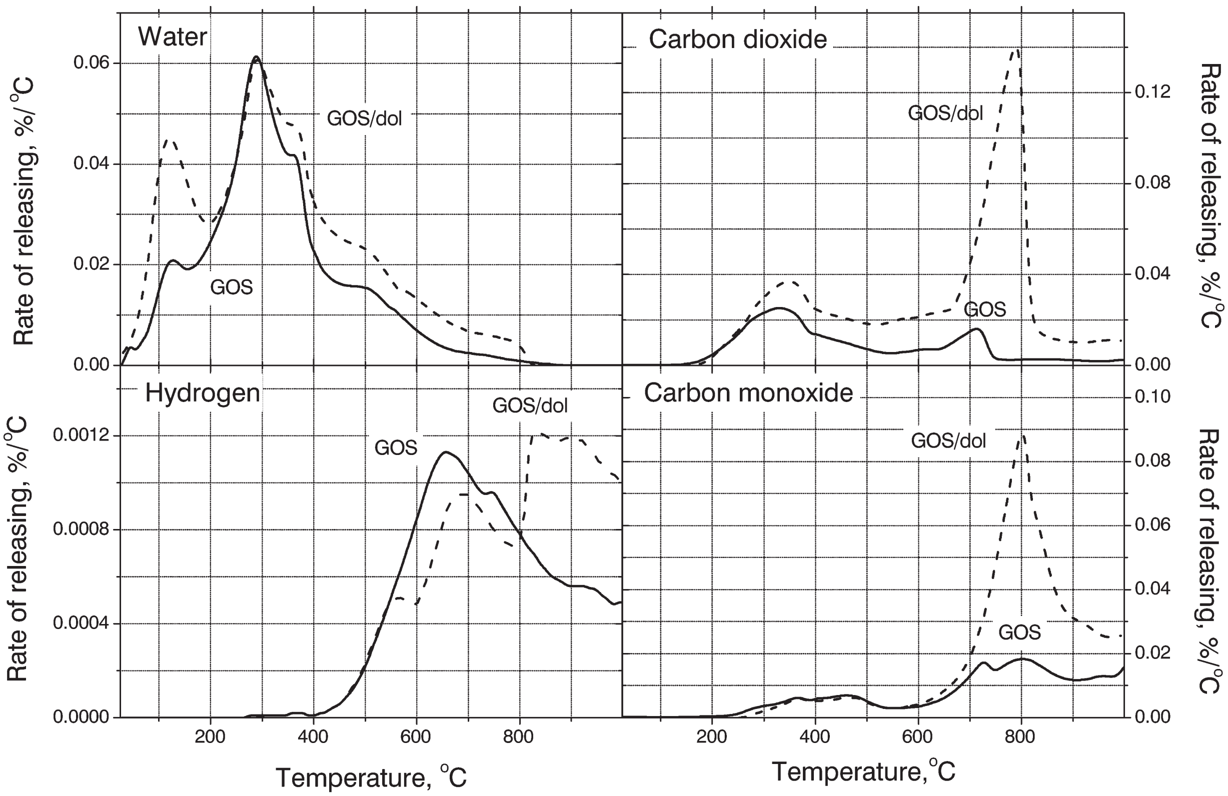


Figure 6. *Effect of dolomite addition to sewage sludge sample on the formation rate of major gas products.*

H_2 is formed in measurable quantities only above 400°C reaching a maximum at 600–650°C. In the case of the sludge/dolomite mixture the second peak also appears above 800°C. This peak is caused by release of H_2 from char, which undergoes the auto-gasification reaction. A total quantity of released H_2 from the sludge/dolomite mixture is about 15% higher than for sewage sludge without additives. It can be seen from Figure 5 that evolution curves for other compounds below 600°C are very similar, although slightly higher concentration of water and carbon dioxide were detected in the gas phase at the temperature range from 300 to 600°C. Because at this stage tars are formed, bigger amount of H_2O and CO_2 detected suggests lower quantity of tars. Taking into account the results obtained by using thermobalance and mass spectrometer we were able to estimate total amount of tars formed during pyrolysis. This estimation shows that dolomite reduced tar formation for about 2%.

CONCLUSIONS

In this paper we focused on the effect of CaO and dolomite addition on the process of sewage sludge pyrolysis. Relatively high amounts of additives were used in this study to make the observed effects more pronounced. It is obvious that such amounts of additives are not economically justified because of significantly high increase in solid residue remaining after the process.

Calcium oxide acts not only as a stabilizing agent for sewage sludge, but it is also a great catalyst in processes of pyrolysis and gasification of this waste. It was observed that increasing content of CaO in the sample we can achieve:

- Higher conversion of carbonaceous material into gas fuels.
- Increase of beneficial gaseous products such as CO and H_2.
- Decrease of unbeneficial liquid products (tars).

These results are possible as the effect of catalytic reactions (cracking, reforming), but also due to equilibrium chemical reactions between CaO and H_2O or CO_2, which are primary products of pyrolysis process.

Dolomite which is consider as a typical tar breaking catalyst in pyrolysis process appears to be less active than calcium oxide.

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Enhancement of Thermophilic Anaerobic Sludge Digestion by 70ºC Pre-Treatment: Energy Considerations

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ABSTRACT: The objective of this work was to investigate the effect of a low temperature pre-treatment (70°C) on the thermophilic anaerobic digestion of sewage sludge. Experimental results were used for the calculation of theoretical energy balances of full-scale digesters with and without pre-treatment step. The 70°C sludge pre-treatment increased sludge solubilization by 10 times and enhanced volatile fatty acids generation. Biogas production increased up to 30–40% and methane content in biogas from 64 to 68–70%. Theoretical calculations showed that additional surplus energy production would be expected by incorporating a 70°C pre-treatment step to a thermophilic reactor.

INTRODUCTION AND OBJECTIVES

THERMOPHILIC ANAEROBIC DIGESTION is more efficient than mesophilic anaerobic digestion in terms of biogas production, volatile solids removal and pathogens destruction [1]. Heat requirements in thermophilic sludge digestion are about twice those of mesophilic digestion, but they may be covered with a combined heat and power (CHP) unit fuelled with biogas, together with heat regeneration from the effluent sludge [2]. The conversion of full-scale two-stage digesters from mesophilic to thermophilic operation has shown that heat requirements are fully covered by increased biogas production; and that additionally surplus electric energy is yielded [3].

Since hydrolysis is the rate limiting step of sludge digestion, the process might be further accelerated by sludge pre-treatment through mechanical, thermal or chemical processes [4], being low temperature pre-treatments (< 100ºC) amongst the least energy consuming. Such pre-treatments have been pointed out as effective at increasing biogas production from sewage sludge [4–8]. In theory, extra energy requirements of a thermal pre-treatment step should be fully covered by the extra methane production [7,8].

The objective of this work was to assess the effect of a low temperature pre-treatment (70ºC) on the efficiency of thermophilic anaerobic digestion of sewage sludge in terms of net energy production. Firstly, the effect of sludge pre-treatment time (9–72 h) was evaluated by the increase in volatile dissolved solids (VDS), volatile fatty acids (VFA) and biogas production in thermophilic batch tests. Secondly, semi-continuous process performance was studied in a 5 L continuous stirred tank reactor (CSTR) working at 55ºC and 10 days solids retention time (SRT). Finally, the results were used for the calculation of theoretical energy balances (i.e. full-scale thermophilic digesters with and without pre-treatment step).

MATERIALS AND METHODS

Sewage Sludge

The mixture of thickened primary sludge (PS) and waste activated sludge (WAS) used for this work was obtained from a municipal wastewater treatment plant (WWTP) near Barcelona (Spain). In this WWTP, PS and WAS are thickened and mixed before undergoing

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mesophilic anaerobic digestion. The sampling point was located at the centrifuge pumping the sludge mixture to the digesters. Samples were collected weekly and stored at 4ºC until use.

Low Temperature (70ºC) Pre-treatment

The low temperature pre-treatment was carried out at 70ºC in order to enhance thermal solubilization of particulate material, as well as enzymatic hydrolysis. Beakers containing 0.5 L of sludge were submersed in a thermostatic bath at 70ºC during 9, 24, 48 and 72 h. The beakers were covered with plastic film, to avoid water evaporation, and gently stirred (Heidolph RZR1) to ensure temperature homogeneity. Samples of raw and pre-treated sludge were analysed for total solids (TS), volatile solids (VS), total dissolved solids (TDS), VDS, VFA and pH. The effect of pre-treatment time was assessed by the increase in VDS and VFA. Sludge solubilization was evaluated by the increase in the ratio soluble to total volatile solids (VDS/VS).

Anaerobic Batch Tests

Biogas production was initially determined by means of thermophilic batch tests, using the device described in Ferrer *et al.* [9]. The inoculum was thermophilic digested sludge from a 5 L CSTR. The substrate was either pre-treated sludge (at 70ºC for 9, 24, 48 and 72 h) or raw sludge (control treatment). Each treatment was performed in triplicate. Each bottle-reactor (300 mL, SIGG®) was filled with 100 g of inoculum and 50 g of substrate (the blank treatment contained 150 g of inoculum only) and was subsequently purged with N_2 and sealed. The bottles were incubated at 55ºC and biogas production was followed by the pressure increase in the headspace by means of a SMC Pressure Switch manometer (1 bar), until biogas production ceased. Accumulated volumetric biogas production (mL) was calculated from the pressure increase in the headspace volume at 55 ºC and expressed under normal conditions (20ºC, 1 atm).

Lab-scale Thermophilic Anaerobic Digestion

The effect of 70ºC sludge pre-treatment on semi-continuous process performance was studied in a 5 L CSTR. The experimental set-up is described elsewhere [10]. Prior to the experiments with pre-treated sludge, the reactor was operated at 55ºC for one year, at decreasing SRT from 30 to 10 days. It was then maintained under steady-state conditions at 10 days SRT for 2 months (control treatment). The digester was subsequently fed with pre-treated sludge (at 70ºC, for 9, 24 and 48 h), with a total experimental duration of 6 months (approximately 2 months per pre-treatment). The daily flow rate was 500 mL of sludge, which was pre-treated following the protocol described above (Low temperature (70ºC) pre-treatment Section). The process was followed by on-line measurement of biogas production and by periodical analyses of influent and effluent sludge (TS, VS, VFA, pH and alkalinity) and biogas (% CH_4).

Analytical Methods

The solids content of sludge was determined according to Standard Methods [11]. TS and VS were determined directly from sludge samples, whereas TDS and VDS were determined from the supernatant of samples centrifuged at 7000 rpm. Supernatants underwent vacuum filtration through 1.2 μm nominal pore size glass fibber filters. pH, alkalinity and VFA (acetic, propionic, iso-butyric, n-butyric, iso-valeric and n-valeric acids) were also analysed from the filtrate supernatant. Samples for VFA analysis were further filtered through a 0.45 μm nylon syringe filter. VFA and biogas composition were determined by gas chromatography (Perkin-Elmer AutoSystem XL Gas Chromatograph).

Energy Balance

Theoretical energy balances were calculated by extrapolating experimental data to full-scale digesters.

Description of the System

The digesters were designed as cylindrical tanks with a width to eighth ratio 2:1 [12]. The sludge volume in the digesters (V) was supposed to be 80% of the total volume; leaving the remaining 20% for gas collection. It was assumed that digestion tanks were made of concrete, wall insulation reducing the heat transfer coefficient from 5 to 1 W m^{-2} $ºC^{-1}$ [12]. The pre-treatment step was conceptually defined as the first digester of a two-stage process, and not as a batch pretreatment followed by a single-stage digester.

Two alternatives were assessed in terms of energy recovery: a system with energy recovery from the biogas produced; and a system with energy recovery from the biogas produced and from the effluent sludge. In all cases it was assumed that biogas was fuelled to a CHP unit, generating electricity and heat. Output electricity would cover electricity requirements for sludge pumping and mixing, whereas output heat would be used to heat influent sludge by means of a sludge-to-water heat exchanger. In the system with heat recovery from the effluent sludge, influent sludge would also be heated by means of an additional heat exchanger; while cooling the digested sludge prior to dewatering [13].

Two environmental temperatures were considered, corresponding to warm seasons (20ºC) and cold seasons (0ºC) in a Mediterranean location like Barcelona Metropolitan Area. The minimum sludge temperature was assumed to be 10ºC when environmental temperature was 0ºC [2, 12].

Energy Requirements

Energy requirements of heated completely mixed anaerobic reactors may be divided into input electricity and input heat, calculated according to Equations (1) and (2). Input electricity for sludge pumping and for the stirring of the digester were estimated as 1.8×10^3 kJ m^{-3}_{sludge} and 3×10^2 kJ $m^{-3}_{reactor}$ d^{-1}, respectively [7].

Heat requirements were calculated using Equation (2) which includes the amount of heat needed to raise the influent sludge temperature from ambient to process temperature; and to compensate for heat losses through the walls of the digester [14]. Heat requirements to raise the influent sludge temperature can be calculated assuming that sludge specific density and specific heat are the same as those of water, thus 10^3 kg m^{-3} and 4.18 kJ kg^{-1} $ºC^{-1}$, respectively [12]. An efficiency of 85% for heat recovery from the effluent sludge was assumed [7]. Heat losses depend on the surface area of the reactor, the heat transfer coefficient and environmental conditions. For the purposes of this study, only the heat losses through the walls of the digester were calculated, since they account for the major energy loss of the system [12].

$$E(input,\ electricity) = Q\theta + V\omega \tag{1}$$

$$E(input,\ heat) = Q\rho\gamma(T_r - T_{sludge})(1 - \lambda) + kA(T_r - T_{env})86.4 \tag{2}$$

where:

$E(input,\ electricity)$ = total electricity requirement ($kJ\ d^{-1}$)
$E(input,\ heat)$ = total heat requirement ($kJ\ d^{-1}$)
Q = sludge daily flow rate ($m^3_{sludge}\ d^{-1}$)
V = volume of sludge in the reactor ($m^3_{reactor}$)
θ = electricity consumption for pumping ($kJ\ m^{-3}_{sludge}$)
ϖ = electricity consumption for stirring ($kJ\ m^{-3}_{reactor}\ d^{-1}$)
ρ = specific density of sludge ($kg\ m^{-3}_{sludge}$)
γ = specific heat of sludge ($kJ\ kg^{-1}\ ºC^{-1}$)
T_r = process temperature (ºC)
T_{sludge} = influent sludge temperature (ºC)
λ = heat recovered from effluent sludge (%)
T_{env} = environmental temperature (ºC)
k = heat transfer coefficient ($W\ m^{-2}\ ºC^{-1}$)
A = surface area of the reactor wall (m^2)
86.4 = conversion coefficient of W into $kJ\ d^{-1}$

Energy Output

Output electricity and heat were calculated according to Equations (3) and (4). It was assumed that the biogas was fuelled to a CHP unit, with conversion efficiencies of 35% and 55% for electricity and heat, respectively; energy loss accounting for the remaining 10 % [2]. The energy content of methane is 35,800 kJ m^{-3} [12].

$$E(output,\ electricity) = P_{CH_4} V\xi\eta \tag{3}$$

$$E(output,\ heat) = P_{CH_4} V\xi\psi \tag{4}$$

where:

$E(output,\ electricity)$ = the electricity produced ($kJ\ d^{-1}$)
$E(output)$ = the heat produced ($kJ\ d^{-1}$)
P_{CH4} = the methane production rate ($m^3_{CH4}\ m^{-3}_{reactor}\ d^{-1}$)
V = the volume of sludge in the reactor ($m^3_{reactor}$)
ξ = the lower heating value of methane ($kJ\ m^{-3}_{CH4}$)
η = the efficiency of CHP for electricity generation (%)
ψ = the efficiency of CHP for heat generation (%)

Calculation of the Energy Balances

In this work, the term energy balance is used to express the difference between the energy output and input of the process, which is calculated by Equations (5)–(7).

$$\Delta E(total) = E(output) - E(input,electricity) - E(input,heat) \tag{5}$$

$$\Delta E(electricity) = E(output,electricity) - E(input,electricity) \tag{6}$$

Table 1. Parameters used for the Calculation of Theoretical Energy Balances from Experimental Data in Table 3.

Parameter	Value	Source
Pre-treatment temperature + process temperature (°C)	70 + 55	This work (Table 3)
Pre-treatment SRT (h) + process SRT (d)	9, 24, 48 + 10	This work (Table 3)
Sludge daily flow rate (m^3_{sludge} d^{-1})	100	Defined for calculation
Environmental temperature, cold season / warm season (°C)	0 / 20	Defined for calculation
Heat transfer coefficient, insulated / non-insulated (W (m^2 °C)$^{-1}$)	1 / 5	[12]
Energy consumption for pumping (kJ m^{-3})	1.8×10^3	[7]
Energy consumption rate for stirring (kJ·m^{-3}·d^{-1})	3×10^2	[7]
Specific density of sludge (kg m^{-3})	10^3	[12]
Specific heat of sludge (kJ (kg °C)$^{-1}$)	4.18	[12]
Lower heating value of methane (kJ m^{-3})	35,800	[12]
Efficiency of the CHP unit for electricity generation (%)	35	[2]
Efficiency of the CHP unit for heat generation (%)	55	[2]
Efficiency of heat recovery from effluent sludge (%)	85	[7]

$$\Delta E(heat) = E(ioutput,heat) - E(input,heat) \tag{7}$$

Parameters and input data used for the calculation of energy balances are summarised in Table 1.

RESULTS AND DISCUSSION

Low Temperature (70ºC) Pre-treatment

The expected effect after thermal pre-treatment of sludge was an increase in soluble materials (i.e. VDS). The disruption of the complex activated sludge floc structure may release biopolymers such as proteins or sugars from the floc into the soluble phase [15]; while the disruption of microbial cells from WAS should lead to their solubilization into carbohydrates, proteins, lipids and VFA [16]. As shown in Table 2, the concentration of VDS increased from around 1.5 g VDS L^{-1} in the raw sludge to 11.9–13.8 g VDS L^{-1} after 9, 24 and 48 h thermal pre-treatment, resulting in an increase in VDS/VS ratio from 0.05 to 0.44–0.48. In this way, the proportion of soluble to total organic matter increased by almost 10 times, from 5% to 50%. The VFA content increased from about 0 to nearly 5 g L^{-1} after 72 h pre-treatment.

Comparing the evolution of VDS and VFA, there is a sharp increase in VDS, followed by a progressive generation of VFA after 24 h. Sludge solubilization after 70ºC pre-treatment seems to occur rapidly, reaching a maximum VDS within 9–24 h. While some studies suggest even shorter periods (30–60 min) for WAS solubilization at 60–80ºC [16,17], longer pre-treatments at 70ºC may favour the activity of thermophilic or hyperthermophilic bacteria, promoting enzymatic hydrolysis and resulting in a predigestion step [6,7].

Table 2. Composition of the Raw Sludge (0 h) and Sludge Pre-treated at 70ºC (9, 12, 48 and 72 h).

	Pre-treatment Time (h)				
Parameter	0	9	24	48	72
TS (g L^{-1})	38.97	38.58	38.70	36.61	32.34
VS (g L^{-1})	28.87	28.12	28.78	26.20	22.74
VS/TS	0.74	0.73	0.74	0.72	0.70
TDS (g L^{-1})	2.54	13.97	15.72	13.91	9.32
VDS (g L^{-1})	1.51	12.49	13.79	11.91	8.11
VDS/TDS	0.59	0.89	0.88	0.86	0.87
VDS/VS	0.05	0.44	0.48	0.45	0.36
Total VFA (g L^{-1})	0.11	0.32	0.62	2.86	4.86
Acetate (g L^{-1})	0.06	0.25	0.44	1.25	1.89
Propionate (g L^{-1})	0.05	0.07	0.15	0.63	0.94
iso-Butyrate (g L^{-1})	0.00	0.00	0.00	0.17	0.41
n-Butyrate (g L^{-1})	0.00	0.00	0.00	0.29	0.73
iso-Valerate (g L^{-1})	0.00	0.00	0.00	0.52	0.89
n-Valerate (g L^{-1})	0.00	0.00	0.00	0.00	0.00

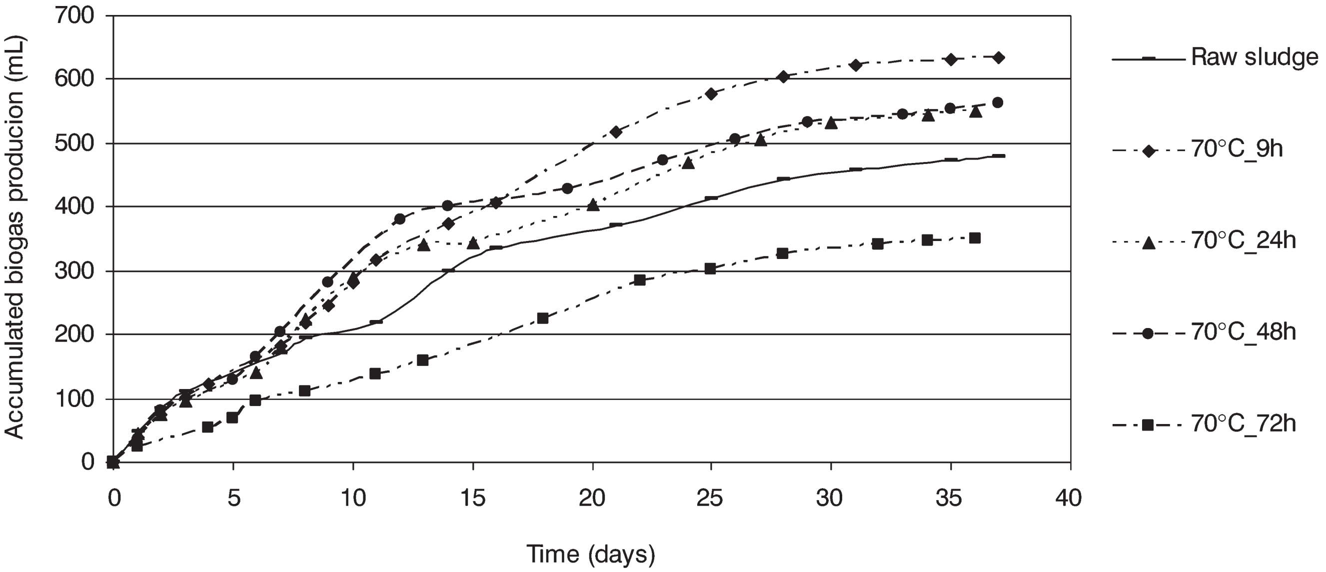

***Figure 1.** Biogas production in thermophilic anaerobic biodegradability tests with raw and 70°C pre-treated sludge (9, 24, 48 and 72 h).*

Anaerobic Batch Tests

Figure 1 shows the evolution of accumulated biogas production during thermophilic batch tests. Initial biogas production rate up to day 7 was similar in all cases, except for the 72 h pre-treated sludge. However, at day 10 (i.e. SRT of the CSTR) accumulated production was nearly 300 mL for 9, 24 and 48 h pre-treated samples, almost 50% higher than for the control treatment (200 mL) while it was considerably lower for the 72 h pre-treated. The lowest biogas production obtained with the 72 h pre-treatment could be attributed to a certain biodegradation of organic compounds during the pre-treatment step, which is in accordance with lower VS and VDS concentrations in the sludge (Table 2).

Performance of Thermophilic Anaerobic Digestion at 10 days SRT

The results with pre-treated sludge (Table 3) clearly show that the process was more efficient in terms of biogas production and yield in all cases, with increases in the range of 30–40%, following the tendency observed in the batch tests. Lower increase with the 24 h pre-treatment (10%) may be attributed to lower VS content in the influent sludge obtained from the WWTP during this period. It is observed that, in spite of the variability of solids concentration in the influent sludge, solids concentration in the effluent is fairly similar for all treatments. Apparently, the higher the VS fed, the higher the VS removed, and the higher the biogas production. According to this, increasing the solids concentration in the influent sludge up to of 55 g TS L^{-1} and 30 g VS L^{-1}, allows to increase biogas production (i.e. energy production) maintaining the quality of the effluent. Biogas yield was also enhanced in all cases, being some 30% higher with pre-treated sludge (0.28–0.30 L gVS_{fed}^{-1}) than with raw sludge (0.22 L gVS_{fed}^{-1}). The same pattern described for biogas production applies to methane production. Moreover, methane content in biogas was also always higher after sludge pre-treatment, around 69% vs. 64% with raw sludge.

According to the results, it seems that 70ºC sludge pre-treatment has similar effects in subsequent thermophilic digestion regardless of pre-treatment time. If no additional benefits are obtained, the shorter the pre-treatment time, the lower the costs related to energy consumption and reactor volume. Therefore, 9 h pre-treatment should be enough to enhance thermophilic digestion of sludge at 10 days SRT. Two-stage systems coupling a hyperthermophilic digester (68–70ºC, 2–3 days SRT) and a thermophilic digester (55ºC, 12–13 days SRT) have also been found to be more efficient than single-stage thermophilic digesters (55ºC, 15 days SRT) [6,7]. In such studies, positive effects of low temperature pre-treatments are attributed to accelerated hydrolysis-acidogenesis promoted by the activity of thermophilic bacteria, resulting in the so-called predigestion step. Our study shows that 70ºC pre-treatment time as well as the overall SRT of thermophilic anaerobic digestion can be further reduced, maintaining the efficiency in terms of biogas and methane production.

Energy Considerations

Figure 2 shows the electricity, heat and total energy balances of the single-stage (10 days SRT) and two-stage system; composed of a first 70ºC step (9, 24 or 48 h SRT) and a second 55ºC step (10 days SRT). Graph (a) corresponds to the system with energy recovery from the biogas and graph (b) to energy recovery from the biogas and from the effluent sludge. Within each graph, the balances for environmental temperatures of 20 and 0ºC, for digesters with and without wall insulation, are shown.

According to theoretical calculations, sludge digestion always results in surplus electricity generation. Output electricity obtained by cogeneration with biogas is much higher than electricity consumption for sludge pumping and mixing; thus electricity balances are always positive. The results are better for the 9 and 48 h pre-treatments, which is in accordance with higher biogas and methane production (Table 3). Contrary to electricity balances, heat balances are much affected by environmental temperature and tank insulation. All heat balances and overall energy balances are negative when only energy from biogas is recovered [Figure 2(a)]. The results are worse for the two-stage system, as a result of extra heat requirements for the 70ºC pre-treatment step.

Nevertheless, when energy recovery from the effluent sludge is also accounted for [Figure 2(b)], all balances become positive; except for the non-insulated reactor at 0ºC, which has a negative heat balance but positive overall balance, due to surplus electricity generation. At 20ºC without digester insulation, energy production is almost half of that with insulated digesters, making evident the necessity of digester insulation. Provided that digesters are insulated, environmental temperature (0–20ºC) has little effect on net energy production. By heat regeneration from the effluent, input heat is reduced, hence net energy production results from the stabilisation of sludge in such system. Therefore, successful thermophilic sludge digestion requires energy recovery from the effluent, as suggested by other authors [2,13].

In such a case, the two-stage system would result in higher energy production (Figure 2), which is in accordance with higher methane production rates (Table 3). If we compare the results of mesophilic and thermophilic two-stage systems (data not shown), the highest net energy production (almost double) is obtained with the results of the present work, which corre-

Table 3. Performance of Anaerobic Digestion (55ºC, 10 days SRT) with Raw and 70ºC Pre-treated Sludge.

70°C Treatment Time (h)	**0**	**9**	**24**	**48**
Influent Composition				
TS (g·L^{-1})	38.53 ± 6.26	55.47 ± 11.75	38.33 ± 9.90	54.43 ± 4.43
VS (g·L^{-1})	30.08 ± 2.89	30.45 ± 3.59	26.59 ± 6.63	27.88 ± 2.12
pH	6.92 ± 0.18	6.67 ± 0.46	7.28 ± 0.29	7.15 ± 0.18
Effluent Composition				
TS (g·L^{-1})	31.17 ± 4.93	34.87 ± 5.92	33.95 ± 5.43	36.88 ± 5.64
VS (g·L^{-1})	19.93 ± 1.88	18.95 ± 2.29	19.64 ± 3.52	18.56 ± 1.69
Total VFA (g·L^{-1})	2.40 ± 0.42	1.27 ± 0.38	2.07 ± 0.45	1.42 ± 0.34
Acetate (g·L^{-1})	0.32 ± 0.13	0.15 ± 0.10	0.67 ± 0.23	0.40 ± 0.29
Propionate (g·L^{-1})	1.14 ± 0.12	0.88 ± 0.09	1.11 ± 0.17	0.86 ± 0.10
iso-Butyrate (g·L^{-1})	0.30 ± 0.13	0.05 ± 0.08	0.09 ± 0.04	0.07 ± 0.04
n-Butyrate (g·L^{-1})	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00
iso-Valerate (g·L^{-1})	0.53 ± 0.09	0.18 ± 0.13	0.19 ± 0.14	0.11 ± 0.02
n-Valerate (g·L^{-1})	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
pH	8.22 ± 0.10	8.27 ± 0.10	8.32 ± 0.13	8.25 ± 0.12
Removal Efficiency				
TS removal (%)	26.89 ± 6.07	31.16 ± 15.44	28.35 ± 15.38	30.66 ± 8.70
VS removal (%)	33.23 ± 5.49	36.55 ± 5.72	24.64 ± 9.09	32.61 ± 4.27
Biogas Characteristics				
Biogas production (L·LR^{-1}·day^{-1})	0.63 ± 0.06	0.87 ± 0.17	0.69 ± 0.18	0.81 ± 0.15
Biogas yield (L·gVS$_{fed}^{-1}$)	0.22 ± 0.04	0.30 ± 0.04	0.28 ± 0.05	0.29 ± 0.05
Biogas yield (L·gVSr$_{emoved}^{-1}$)	0.61 ± 0.16	0.82 ± 0.17	0.81 ± 0.13	0.94 ± 0.14
Methane content (%)	63.73 ± 3.52	69.77 ± 3.36	68.73 ± 5.48	67.84 ± 5.13

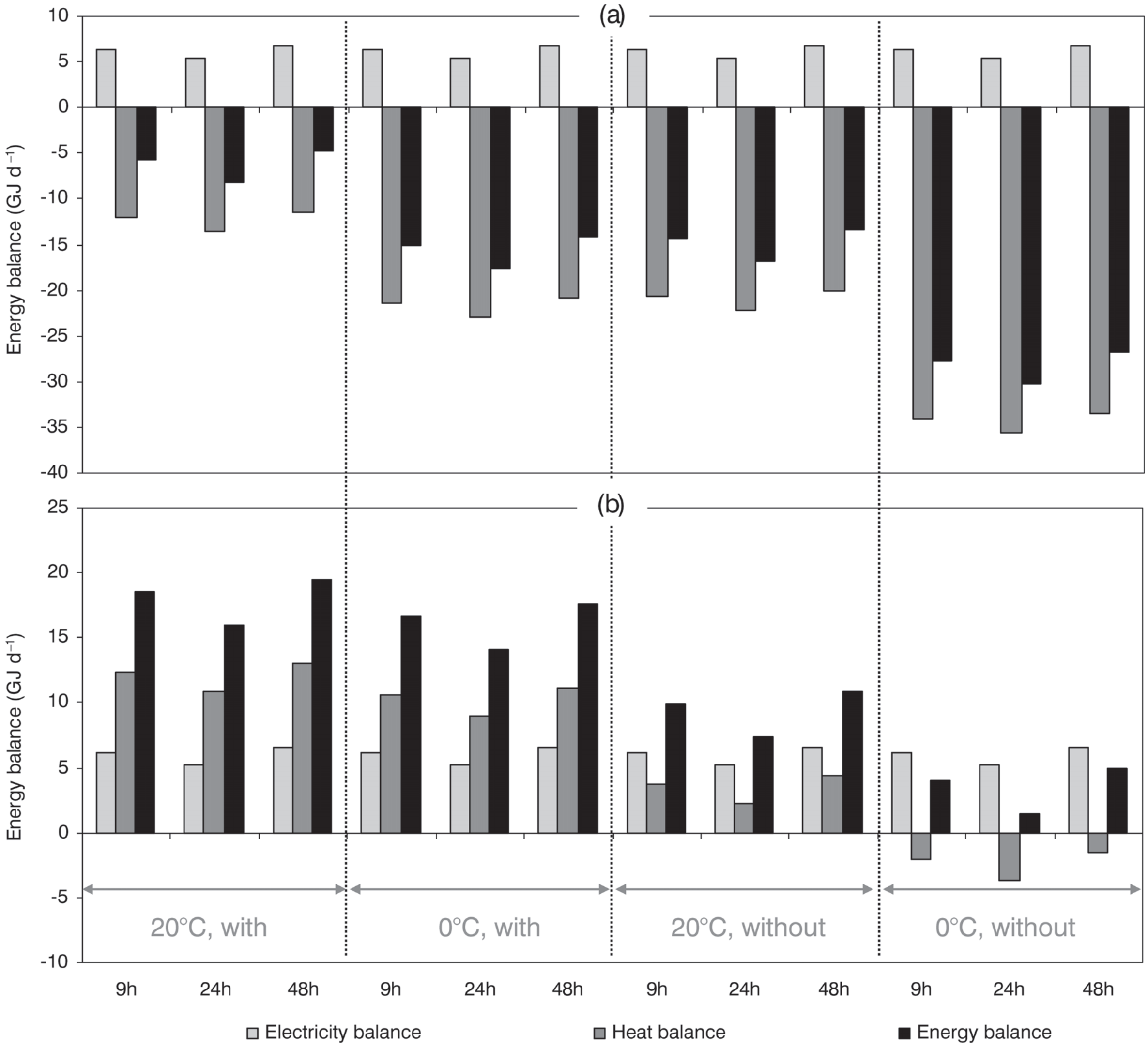

Figure 2. *Theoretical Electricity, heat and total energy balance (kJ d^{-1}) as a function of 70°C pre-treatment time, in two-stage (70°C/55°C) anaerobic digesters treating 100 $m^3_{sludge\ d}{}^{-1}$; with energy recoveries from biogas (a) and from biogas and the effluent sludge (b). Environmental temperature is either 20 or 0°C, for digesters with and without wall insulation.*

spond to the lowest SRT for the first and second stage. Apparently, similar energy production would be expected from thermophilic digesters at SRT of 10–20 days and mesophilic digesters at SRT of 20 days. This is a matter of concern, since lowering the SRT enables to reduce the reactor volume, hence its capital cost, and consequently the costs of sludge and wastewater treatment. Throughout this work it has been shown that thermophilic sludge treatment at SRT of 10 days results in stable and efficient performance.

CONCLUSIONS

The thermophilic anaerobic digestion of sewage sludge, with and without a 70ºC pre-treatment step, was assessed from an energy perspective, by calculating theoretical energy balances using experimental data. The main conclusions of this study are summarised as follows:

1. Sludge solubilization after 70ºC pre-treatment was shown by the increase in VDS and VDS/VS ratio (from 5 to 50%), already after the shorter pre-treatment assayed (9–24 h). However, VFA generation was only enhanced after 24 h, which might be the threshold for the so-called predigestion step. From this moment, VFA concentration increased up to almost 5 g VFA L^{-1} after 72 h.
2. During thermophilic batch tests, initial biogas production rate was similar for raw and 9–48 h

pre-treatments; but accumulated biogas production at day 10 was 50% higher for 9–48 h pre-treatments.

3. Sludge pre-treatment at 70ºC enhanced biogas and methane production through thermophilic digestion at 10 days SRT. Biogas yield was some 30% higher (0.28–0.30 vs. 0.22 L gVS_{fed}^{-1}). Methane content in biogas ranged between 60–70% in all cases.
4. Thermophilic sludge digestion in insulated digesters, with energy recovery from biogas and effluent sludge, would result in net energy production regardless of environmental temperature (0–20ºC). Additional surplus energy production would be expected by incorporating a 70ºC pre-treatment step.
5. According to the results, a short period (9 h) low temperature pre-treatment should be enough to improve methane and energy production through thermophilic anaerobic digestion of sludge.

Bearing in mind that the best results were obtained for the 9 h pre-treatment; the evaluation of shorter pre-treatments at 70ºC should be of interest for future work. Furthermore, the results would be improved using experimental data from pilot-scale reactors, leading to a more accurate energy assessment.

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Activated Sludge Properties After Ultrasonic and Thermal Treatments and Their Potential Influence on Dewaterability

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ABSTRACT: Two excess sludge reduction processes (ultrasounds and thermal) were studied with specific attention to some physico-chemical characteristics of treated sludge. Several parameters were monitored and discussed in respect to process efficiency and implications to dewaterability of excess sludge generated. Release of biopolymers, floc size reduction, transfer of ionizable functional groups in the liquid fraction and decrease of relative hydrophobicity were observed. According to the applied treatment, these modifications may improve or worsen the sludge dewaterability properties.

INTRODUCTION

WASTEWATER TREATMENT with activated sludge processes (ASP) generates large quantities of excess sludge which must be eliminated. This disposal is subject to various social and economic problems. Thus, interest in solutions allowing sludge volume and mass reduction is growing up. Ultrasonic and thermal treatments are among the most promising recent technologies for reducing sludge production in wastewater treatment plants [1]. Among the different strategies for excess sludge production reduction, thermal and ultrasonic treatments belong to the lysis-cryptic growth processes [2]. There are two stages in these processes: the first one is the lysis and is achieved by thermal or ultrasonic treatment itself. The second stage is the biodegradation of the solubilized products by recirculation in the aeration tank or anaerobic digestion.

Previous works already focused on the effectiveness of sludge reduction by ultrasounds and thermal treatment during activated sludge process [3, 4]. However, few data is available concerning the quality of sludge produced by these systems. Results concerning dewaterability of treated sludge are contradictory: Some authors noticed that dewaterability was decreasing after ultrasonic pre-treatment [5, 6] whereas others authors observed that capillary suction time (CST) of digested sludge was decreased by ultrasounds [7]. Concerning thermal treatment, the dewatering properties have been found to be highly dependant on the treatment temperature [8].

The aim of this article is to give a comprehensive insight into physico-chemical properties of activated sludges subjected to thermal and ultrasound treatments as lysis processes. The further biodegradation step was not considered. Therefore, results concerning the amount of sludge reduction are presented immediately after the treatment stage. This may not be representative of the total reduction of sludge mass after the global process including the biodegradation stage. Mixed liquor biochemical composition, sludge volume index (SVI), image analysis, relative hydrophobicity and total number of ionizable functional groups were assessed. Results were discussed in respect with dewaterability of excess sludge produced.

METHODS

Ultrasonic and Thermal Treatments

Ultrasounds and thermal treatments were carried out in batch mode on sludge collected from the aeration tank of the Limoges wastewater treatment plant (France) and stored at 4°C before use. Total solids (TS)

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concentration varied between 3.5 and 4 g/L and the ratio of volatile solids was 68%.

The ultrasonic device used throughout this study was an ultrasonic homogenizer (Sonopuls, Bandelin). The operating frequency was 20 kHz. The power delivered by the apparatus was 100W. Experiments were carried out in a 1L beaker without temperature regulation. The volume of the treated sample was 900 mL. The specific energy (Es) supplied ranged from 0 (untreated sample) to 163,300 kJ/kg TS and was defined by Equation (1) :

$$E_S = \frac{P * t}{V * TS_0} \tag{1}$$

Where,

E_S = specific energy supplied (kJ/kg TS)
P = ultrasonic power (W)
t = ultrasonic treatment time (s)
TS_0 = total solids concentration before sonication
V = sample volume (L)

Thermal treatment was carried out at temperatures ranging from 45°C to 120°C. Sludge was conditioned in 100 mL Pyrex flasks. Caps were tightly screwed to avoid evaporation. A water bath (Lauda A106T) and an oil bath (Memmert ONE 7-45) were used for temperatures lower than 100°C and higher than 100°C respectively. Several flasks were introduced in the bath at ambient temperature. Once the bath reached the desired temperature, the flasks were keeped inside for 2h. In table or figure presentations, untreated sludge was associated to 20°C temperature.

Table 1 presents the amount of sludge mass reduction achieved immediately after the treatments in terms of both total suspended and volatile suspended solids (TSS and VSS) reduction).

Table 1. TSS and VSS Reduction After Ultrasonic and Thermal Treatments.

Treatment		TSS Reduction (%)	VSS Reduction (%)
Ultrasound (kJ/kg TS)	24,700	11.2	12.1
	49,400	18.8	21.6
	98,900	32.4	39.5
	163,300	39.2	49.2
Thermal (°C)	45	8.7	10.2
	75	18.4	22.5
	95	20.7	25.0
	105	22.3	26.7
	120	24.2	28.8

Mixed Liquor Physico-chemical Properties

Sludge characteristics measurements were done in triplicate. Polysaccharides were determined using the colorimetric method of Dubois *et al.*, [9]. Proteins and humic acids were determined using the method of Lowry *et al.*, [10] modified by Frølund *et al.*, [11]. The soluble fraction is defined here as the fraction resulting from the filtration of the samples through a cellulose nitrate membrane (0.45 µm pore size). For all colorimetric methods used in this study, the standard deviation for triplicate samples was 1–8% and 5–20% for soluble and total fractions respectively.

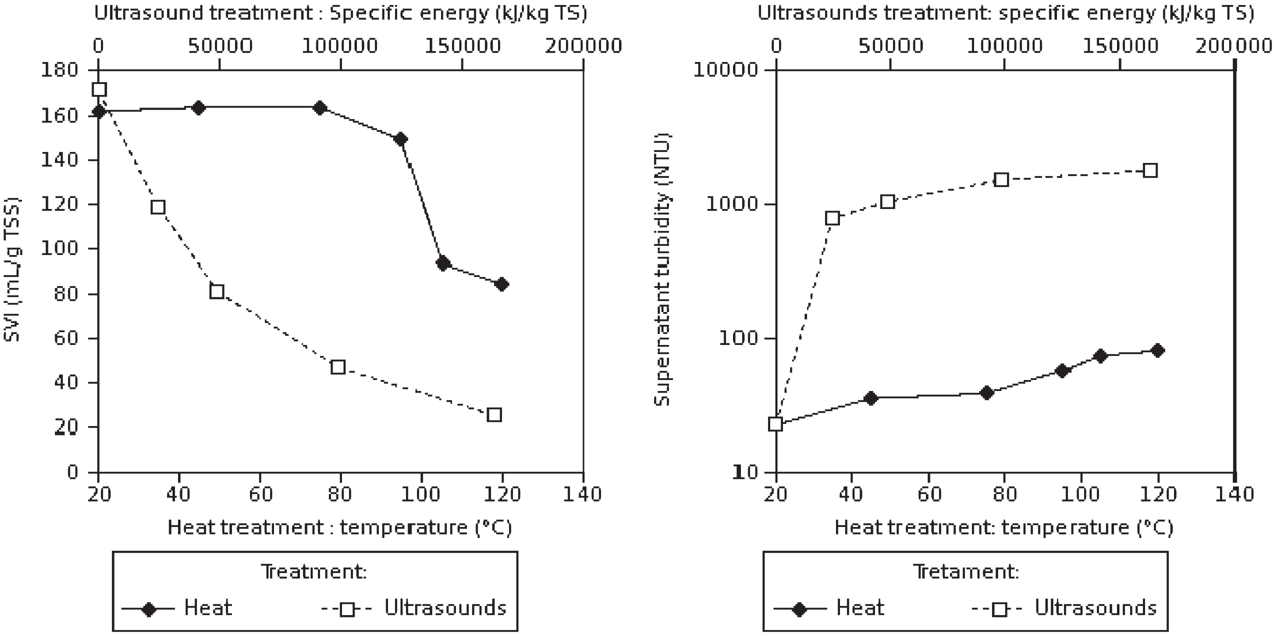
Sludge settleability was evaluated by the sludge volume index (SVI), which is defined as the sludge volume per gram of total suspended solids (TSS) after 30 min sedimentation. An initial volume of 100 mL was used. Sedimentation was carried out in an Imhoff cone. Turbidity was measured on the sedimentation supernatant with a Hach Ratio 18000 turbidimeter.

Flocs Granulometry

Captures were made using an optical microscope (Olympus CX 31) equipped with a CCD video camera (Resolution: 768 × 574 pixels) connected to a PC via a grabbing card. Measurements were done 24h after the treatment. Sludge was stored at 4°C. This period allowed the stabilization of the particle size: potential reflocculation due to the release of organic compounds was finished [12].

A drop of mixed liquor was carefully deposited and covered with a cover slip. Neither staining nor fixation was done. At least 100 images (magnification 100×) were grabbed. Pixel size calibration was done with a stage micrometer (160 pixels = 100 µm).

Average floc size was assessed by automated image analysis. A new procedure deriving from [13] has been developed with the software Visilog® 6 (Noesis, Saint Aubin, France). Sludge particles appeared both lighter and darker than the background. The grey-level histogram mode of each picture (768 × 576 pixels on 256 grey levels) was determined. This mode gave the average grey level of the background. Then, pictures were segmented by considering as belonging to the background the pixels whose grey level was this mode ± 20. All the other pixels were considered as belonging to objects. On the resulting binary images, the size of each object was determined by its projected surface area. Size distribution was finally calculated over the full set



(a) (b)

Figure 1. *Evolutions of settling properties of activated sludge during thermal and ultrasounds treatments: (a) Sludge Volume Index (SVI), (b) supernatant turbidity (error bars not showed as experimental errors were not significant).*

of images. Knowing the image calibration (160 pixels = 100 micrometers), it was possible to calculate the average floc size.

Surface Properties

The mixed liquor relative hydrophobicity (RH) was measured as adherence to hydrocarbons with a protocol deriving from Wilén *et al.*, [14] and previously described by Laurent *et al.*, [15]. The standard deviation for triplicate samples was 1–6%.

The total number of ionizable functional groups was determined on both floc surface and soluble fraction by potentiometric titration. Mixed liquor was centrifuged (6000 g for 20 min at 4°C). Supernatant was used for titration of the soluble fraction. Pellet was resuspended in 0.01 M $NaNO_3$ and re-centrifuged. Supernatant was discarded. This procedure was done twice and the final floc-$NaNO_3$ suspension was used for titration. An automatic titrator (Metrohm) was used for titration in dynamic mode with 0.01 M NaOH as base and 0.01 M HNO_3 as acid. Titrations were always carried out in a sealed thermostated (25°C) titration vessel with constant N_2 bubbling. Titration data were fitted to a non electrostatic surface complexation model with PROTOFIT [16] in order to obtain the total number of ionizable functional groups.

EFFECTS OF THERMAL AND ULTRASONIC TREATMENTS ON SLUDGE PHYSICO-CHEMICAL PROPERTIES

Sludge Settleability

Sludge settleability is a key parameter in the wastewater treatment plant quality control: good settling properties and low turbidity are generally required. Settleability of treated sludge has been assessed by measuring its sludge volume index (SVI) (Figure 1). Results showed that both treatments leaded to the enhancement of settleability as SVI decreased. This increase rapidly occurred for ultrasound treatment and SVI ranged from 171 to 25 mL/g TSS when specific energy was increasing from 0 to 163,300 kJ/kg TS. However, this settleability enhancement was concomitant with an increase of the decantation supernatant turbidity from 22 to 1790 NTU. For thermal treatment, the SVI remained almost constant at 163 ± 1 mL/g TSS from 20 to 75°C. It seemed that 95°C was a temperature threshold as SVI drastically decreased from 149 to 84 mL/g TSS when temperature was increasing from 95 to 120°C. This temperature threshold has already been observed at a temperature of 150°C [8]. The difference is probably due to the fact that these authors used a more concentrated sludge in their study. This threshold could be explained by the release of interstitial water from the flocs occurring at high temperature leading to better floc compressibility.

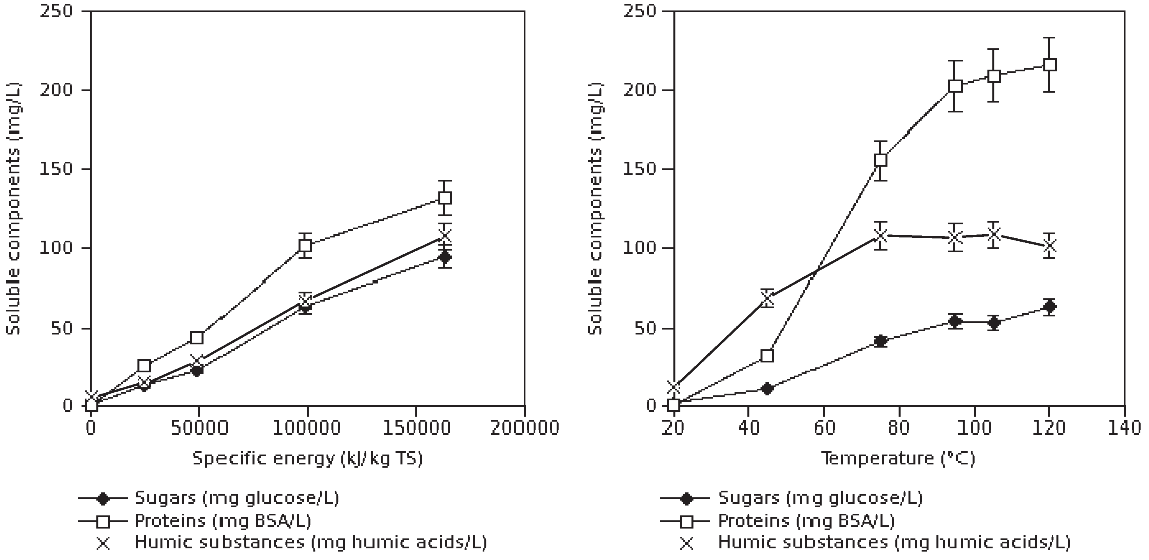
Solubilization of Organic Compounds

Sludge settleability is greatly modified by thermal and ultrasounds treatments. They are supposed to induce floc and/or bacterial cells breakage, thus leading to organic matter solubilization. Process efficiency and modifications of the mixed liquor soluble fraction composition were assessed: concentrations of soluble sugars, proteins and humic substances were measured. Figure 2 shows the increase of these compounds concentrations as the temperature/specific energy raised.

When the temperature increased from 25°C (untreated) to 75°C, activated sludge flocs were easily disintegrated, leading to the release of organic compounds: concentrations of soluble sugars, proteins and humic substances increased fast from 2.4 ± 0.2 to 41 ± 3, 1 ± 0.1 to 156 ± 12 and 12 ± 1 to 108 ± 9 mg/L respectively. For temperatures > 75°C, both concentrations of humic substances and sugars remained almost unchanged (from 108 ± 9 to 101 ± 8 and from 41 ± 3 to 63 ± 5 mg/L respectively) whereas protein concentration rose from 156 ± 12 to 215 ± 17 mg BSA /L. On the one hand, lower temperatures (< 75°C) seemed to induce disruption of the extracellular polymer matrix as the concentrations of soluble humic substances and sugars increased fast. On the other hand, the continuous increase of protein concentration for temperatures > 75°C suggested a cellular lysis occurring at higher temperatures. This assumption has already been made by Bougrier *et al.*, [8] and was confirmed by measurements carried out by flow cytometry by Prorot *et al.*, [17]. During ultrasound treatment, soluble concentrations of studied compounds increased rapidly and almost linearly. This increase was similar for all compounds. Concentration of soluble compounds ranged from 1.1 to 95, 0.5 to 132 and 5.6 to 108 mg/L for sugars, proteins and humic substances respectively. Therefore, ultrasound treatment seemed to act on the extracellular polymer matrix but no hypotheses could be drawn concerning any potential cellular lysis.

The increase of the organic matter content of the soluble fraction underlines that both treatments are efficient to disintegrate flocs. Moreover, organic matter solubilization was concomitant with both SVI decrease and supernatant turbidity increase.

Release of extracellular/intracellular biopolymers induced by the treatment could affect both effluent and sludge quality. Indeed, as previously showed [12], organic matter released during ultrasonic treatment could act as a good flocculent and thus improve settleability / dewaterability of the excess sludge. It was also noticed that increasing relatively low levels of sludge extracellular polymeric substances (EPS) can improve dewaterability by increasing flocculation [18]. An increase of the heavy metal concentration in the liquid



(a) (b)

Figure 2. Increase of soluble biochemical components during: (a) ultrasonic treatment, (b) thermal treatment.

fraction (i.e. effluent) could be expected: indeed, complexation of heavy metals with the negatively charged functional groups of these biopolymers should occur as EPS have a high affinity for the binding of heavy metals [15; 19].

Concerning thermal treatment, the threshold temperature observed in this study for settleability improvement was also observed concerning filterability: capillary suction time (CST) was increasing for temperatures ranging from 20 to 150°C and dropped at higher temperatures [8]. This phenomenon was attributed to the release of EPS which are highly hydrated during the treatment.

Floc Size Variations

Above results showed an important organic matter release probably due to floc breakage by thermal and ultrasonic treatments. Floc size study is of great interest as it constitutes a key parameter of sludge settleability, dewaterability [5] and could affect the fate of heavy metals during the treatment[15]. Average floc size was measured by automated image analysis.

Floc disintegration was effective for both thermal and ultrasound treatments as floc size decreased drastically for the two treatments (Figure 3).

For thermal treatment, the decrease occurred in a two steps sequence: average floc size dropped from 1044 to 285 μm when temperature increased to 45°C. For higher temperatures, the decrease was less important and average floc size ranged from 285 to 137 μm when temperature varied from 45 to 120°C.

During ultrasound treatment, the floc size decrease was more important: it changed from 775 to 73 μm when sludge was treated at 24,700 kJ/kg TS. Higher specific energies led to a less important decrease: from 73 to 24 μm when specific energy ranged from 24,700 to 98,900 kJ/kg TS. Surprisingly, average floc size seemed to increase to 42 μm at the highest studied specific energy (163,300 kJ/kg TS): the number of small size flocs was so high that several objects were joined on the picture and considered as a single one by the procedure.

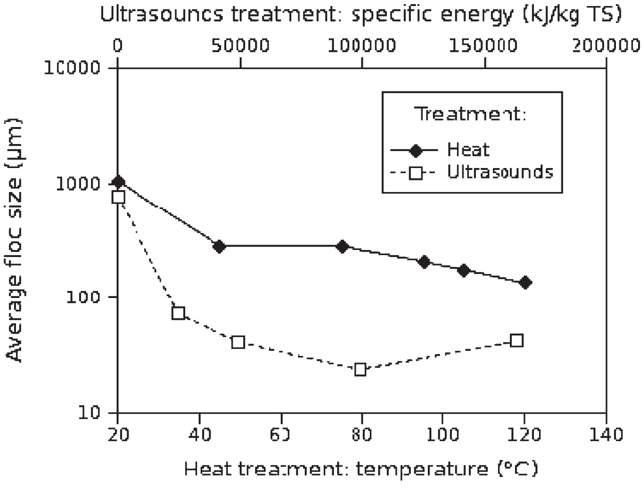


Figure 3. *Average floc size during thermal and ultrasounds treatments.*

The floc size decrease observed after sonication is concomitant with previous results obtained in the literature [12] and illustrates floc mechanical disruption due to ultrasonic cavitation. Thermal treatment effects are more complex to explain: it was observed that sludge origin seemed to have a significant effect on floc size after treatment [20]. Several phenomena may be involved and have antagonistic effects on floc size: solubilization, reflocculation, chemical reactions occurring at high temperature between macromolecules (i.e. Maillard reactions between reducing sugars and amine functional groups), mineral matter precipitation.

Depending on the ultrasonic power level, sludge CST can be significantly decreased by ultrasound treatment [21]. It was also noticed that specific resistance to filtration and CST were increasing after ultrasound treatment of waste activated sludge [6]. These authors proposed several hypotheses to explain this behavior: sludge biopolymers released during the treatment had a high affinity to water and thus improved viscous properties of the sludge. The decrease of floc size after sonication provides a greater surface area for adsorbing water: free water was “transformed” into interstitial water.

The dewaterability of sonicated sludge is the result of two counteractive mechanisms [5]: on the one hand, the disruption of the EPS matrix can lead to improved dewaterability as a substantial amount of water is bound onto its structure. On the other hand, floc size reduction could cause clogging of the sludge cake during mechanical dewatering (filtration). These authors observed a decreased dewaterability after ultrasound treatment in terms of both filter cake dryness and CST.

EFFECTS OF THERMAL AND ULTRASONIC TREATMENTS ON SLUDGE SURFACE PROPERTIES

Ultrasound and thermal treatments leaded to floc breakage and organic matter solubilization. Floc surface properties, and thus ionizable functional groups, might be affected, influencing sludge settling and dewatering properties. The fate of micropollutants during the treatment could also be affected. The functional groups present at the floc surface and in the soluble fraction were monitored by measuring the number of ionizable functional groups by potentiometric titration of both fractions and the relative hydrophobicity of the mixed liquor.

It was observed that the number of ionizable functional groups present in the soluble phase was increasing as the temperature / specific energy was increasing (Figure 4). This transfer of functionality could be linked to the release of soluble biopolymers previously shown. Therefore, functional groups corresponding to the solubilized molecules were more present in the soluble fraction: carboxyl (proteins, humic substances), amine (proteins), hydroxyl (polysaccharides, humic substances).

The relative hydrophobicity (RH) measured in this study is an average value of both hydrophobic and hydrophilic groups in both floc surface and liquid fraction. Generally, hydrophilic molecules are polar or charged while hydrophobic molecules are non-polar [22]. Therefore, the decrease of RH observed for both treatments (Figure 5) could be the result of two phenomena:

- The release of biopolymers in mixed liquor liquid fraction during the treatments.
- The greater availability of functional groups at the floc surface due to floc disruption [15].

RH decrease was less important during thermal treatment. Indeed, floc size reduction was less pronounced during this treatment.

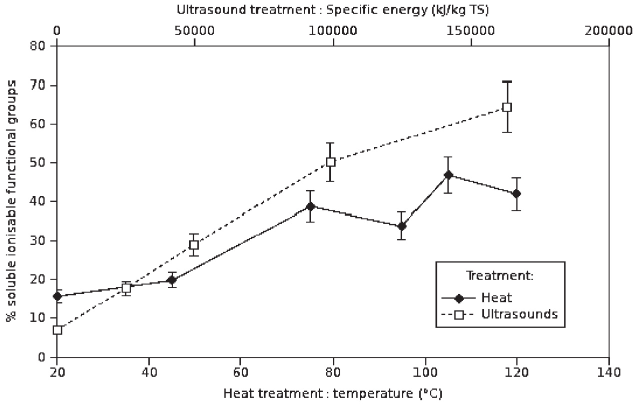


Figure 4. Increase of the number of ionizable functional groups in the soluble fraction during thermal and ultrasounds treatments.

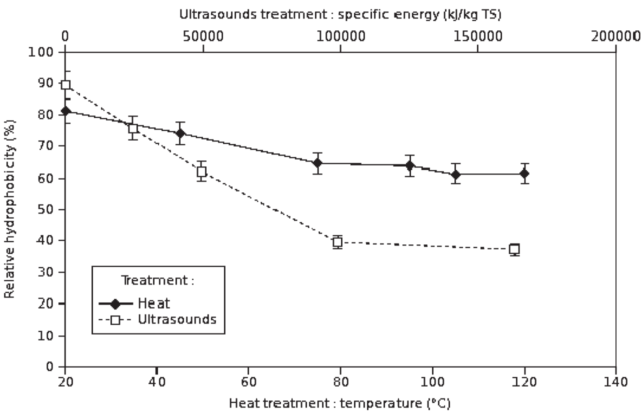


Figure 5. Evolution of mixed liquor relative hydrophobicity during thermal and ultrasounds treatments.

Since non-polar molecules mix relatively less readily in water compared to polar molecules, they should contribute to the aggregation of the sludge flocs [22]. As previously mentioned, the decrease of relative hydrophobicity observed for both treatments underlined the greater availability of polar/charged molecules in mixed liquor. Therefore, the increased relative hydrophobicity observed for both treatments underlines the weakest floc structure after treatment, especially after sonication. In fact, the RH decrease was more pronounced for ultrasound treatment illustrating that mechanical floc disruption caused by ultrasound cavitation generated a great amount of small diameter particles (< 1 μm) unable to sediment as showed by supernatant turbidity correlation with RH.

Morgan Sagastume *et al.*, [23] noticed a net increase of negative surface charge suggesting a less hydrophobic sludge during temperature up shifts from 30 to 45°C in pilot scale sequencing batch reactors. They also observed that more negatively charged floc surfaces lead to electrostatic repulsion among floc particles, decreasing bioflocculation. They proposed several hypotheses to explain this behavior: adsorption of previously released EPS onto remaining flocs, floc disruption increasing the specific surface area, bacterial physiological stress responses.

SYMBOLS

TSS = total suspended solids concentration (g/L)
TS = total solids concentration (g/L)
E_s = ultrasounds specific energy (kJ/kg TS)
SVI = sludge volume index (mL/g TSS)
CST = capillary suction time (s)
RH = sludge relative hydrophobicity (%)

CONCLUSION

Ultrasounds and thermal treatments provided a means to significantly modify the chemical and physical properties of activated sludge. Biopolymers of extracellular or intracellular origin were released in the liquid phase leading to the transfer of ionizable functional groups in this phase. Flocs were disrupted and their size was considerably reduced by both treatments. These evolutions could affect further sludge disposal as they are likely to worsen or improve dewaterability of the excess sludge generated. According to the different studies available in the literature, several mechanisms can be invoked to explain the dewaterability properties of sludge subjected to thermal or ultrasound treatment: on the one hand, biopolymers release in the soluble fraction tends to improve dewaterability by inducing biofloculation and the release of interstitial water. On the other hand, the floc size decrease tends to decrease dewaterability by increasing sludge viscosity and clogging of the filters. Hydrophobic and electrostatic interactions should also be considered.

In the case of ultrasounds treatment, it seems that the floc size decrease was the main mechanism explaining filterability decrease observed in the literature. Concerning thermal treatment, settleability and dewaterability seems to be highly dependent on temperature.

Particular consideration should be taken to the fate of heavy metal as biopolymer released during the treatment are expected to complex heavy metals and retain them in the liquid phase.

This study constitutes a first approach of properties of sludge generated by systems incorporating an excess sludge reduction process. A pilot-scale study is required in order to provide a complete characterization of excess sludge reduction and properties in a long term period.

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Evaluation of Different Sludge Mechanical Dewatering Technologies

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ABSTRACT: The two most dominant technologies in sludge dewatering are belt filter presses and centrifuges. The objective of this work is to evaluate the two technologies in parallel operation, using full scale data from two wastewater treatment plants of different size. According to the data obtained, centrifuges produced a drier cake and exhibited slightly lower polymer requirements compared to belt filter presses. Based on a cost analysis performed, the annual sludge dewatering and disposal cost for a small to medium size and a medium to large size WWTP was higher for the belt filter press and ranged from 106–147 €/ton DS versus 82–114 €/ton DS for the centrifuge dewatering system.

INTRODUCTION

General Overview

TREATMENT of liquid wastes results in the production of large quantities of sludge, which constitute a high polluting load that requires environmentally safe disposal or reuse. Within the European Union the enforcement of the 91/271/EC Directive concerning municipal wastewater treatment has led to a steep increase in the quantities of the produced sludge. Sludge dewatering is a crucial element in all efficient sludge management schemes and aims at reducing the volume of the sludge. Improving sludge dewatering results in a cake that is less expensive to dispose of or apply to land. It can also optimize further processing of the sludge by composting, thermal drying or incineration. Finally improving sludge dewatering may lead to a reduction in the pollution loading originating from centrate or filtrate recycling.

The two dominant technologies involved in sewage sludge dewatering are based on belt filter presses and centrifuges. Both are well established technologies, which through continuous development and improvement, are capable of meeting current sludge dewatering requirements. The choice between the two depends on many parameters such as sludge characteristics, dewatering efficiency, operating and capital costs, odours potential, ease of operation, etc.

Belt filter presses consist of two or in some cases three filtering belts that move towards each other forming a closed shape envelope. Flocculated sludge is initially dewatered under gravity and then squeezed between the two belts. Dewatering is achieved in two steps: filtration and expression. Filtration occurs at the initial gravity drainage zone where no pressure is exerted to sludge. Following water drainage the sludge solids content is not more than 6–10% [1]. Thereafter, due to the progressively increasing pressure, trapped water within and between sludge particles is removed. Typically belt presses can achieve a dewatered sludge solids content between 15–25% when feeding solids content varies from 2–5% [2].

Decanter centrifuges employ a high speed rotational process to achieve dewatering by applying high forces of 2000–4000 g directly to the feed solids. Centrifuges compared to belt filter presses offer some advantages such as smaller footprint, more efficient odour and aerosol control during the dewatering process, fewer and less frequent cleaning requirements, lower water consumption and often a higher cake solids content. However these advantages over belt filter presses come at a higher capital cost and a higher power consumption. In addition belt filter presses operation is quieter and has lower maintenance skill requirements. There-

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fore making a choice between the two is not easy and should be done on a case by case basis, taking into account many factors such as plant size, sludge characteristics, sludge disposal and energy costs, labour cost, additional sludge treatment, etc.

The objective of this work is to evaluate the two technologies in parallel operation, using laboratory and full scale data from two wastewater treatment plants (WWTP) in Greece. Both WWTPs at the time of the experiments employed belt filter presses for sludge dewatering. The paper presents a technical and economic evaluation of the two dewatering systems that was based on the following parameters: capital cost, cake dryness, solids capture efficiency, polymer consumption, energy consumption, labour requirements, maintenance cost, sludge disposal cost, water consumption and centrate or filtrate treatment cost.

EXPERIMENTAL MATERIALS AND METHODS

Laboratory and full scale experiments were conducted using aerobically and anaerobically stabilized sludge samples obtained from two municipal Wastewater Treatment Plants (WWTPs) in Lavrio and Volos, Greece. Lavrio WWTP, an extended aeration activated sludge system with a treatment capacity of approximately 10000 p.e., was selected as a representative of small to medium size sewage treatment plants in Greece. Volos WWTP, a conventional activated sludge treatment with anaerobic treatment of the primary and secondary sludge and a treatment capacity of approximately 130000 p.e., was selected as a representative of medium to large sewage treatment plants in Greece that employ anaerobic digestion for sludge stabilization.

Laboratory Scale Experiments

Sludge conditioning laboratory scale experiments were conducted using aerobically and anaerobically stabilized sludge samples obtained from the two municipal WWTPs. The objective of these lab-scale experiments was to evaluate the performance of various cationic polymers and to determine the optimum polymer dose for sludge dewatering. Capillary suction time (CST) was employed to evaluate the effect of polymer addition on sludge dewaterability.

Five different dry cationic polymers supplied by SNF Ltd and Kemira Water Solutions Inc., were evaluated with aerobically and anaerobically stabilized sludge samples. Polymer properties are listed in Table 1. All polymer stock solutions were prepared daily, at a 0.25% concentration. All sludge conditioning experiments for the aerobically and the anaerobically stabilized sludges were conducted at 24°C with the same sludge sample and were completed within a week from sludge sampling. The characteristics of the two thickened sludges employed in the CST tests are shown in Table 2.

In order to achieve the desired polymer dose for each experiment, different measured volumes of the polymer stock solution were added to 500 ml of thickened stabilized sludge. In order to simulate full scale polymer dosing, where dosage changes are achieved by adjusting the polymer flow rate, the volume of added polymer was varied rather than the polymer solution strength. Rapid mixing was performed for 30 seconds with an electric hand mixer. After that a jar test apparatus, set at 30 rpm was used to mix sludge samples for five minutes. CST values were determined in duplicates and the average was recorded in order to evaluate the dewaterability of conditioned sludge samples. CST measurements were performed using a Triton 304B model with a Whatman no. 17 paper filter, according to Standard Methods [3]. Sludge total and volatile solids concentrations were measured prior to polymer addition according to Standard Methods.

Table 1. Characteristics of Polymers Employed during Laboratory Scale Experiments.

Polymer Name	Supplier	Cationic Charge	Molecular Weight
43–50	SNF	25%	10×10^6
44-90	SNF	40%	10×10^6
46-98	SNF	50%	10×10^6
DF–552	Kemira	35%	9×10^6
45-50	SNF	45%	10×10^6

Table 2. Characteristics of Thickened Stabilized Sludge Samples Obtained from Lavrio and Volos WWTPs.

Sludge Type	Initial pH	Total Solids (%)	Volatile Solids (%TS)
Aerobically stabilized thickened sludge from Lavrio WWTP	7.20	3.4	67
Anaerobically digested thickened sludge from Volos WWTP	7.60	2.4	58

Table 3. Technical Characteristics of the Full Scale Belt Filter Presses and Centrifuge Employed in this Study.

Parameter	Centrifuge	Belt Filter Press of Volos WWTP	Belt Filter Press of Lavrio WWTP
Supplier	Pieralisi FP600 2RS	Sernagioto BPF 2000 WRU	Krüger
Maximum capacity, m^3/hr	9 m^3/hr	40 m^3/hr	16 m^3/hr
Years in operation	4	10	11
Power requirements, kW	11	9.1	7.1

Full Scale Experiments

Full scale trials were conducted at the two municipal WWTPs of Lavrio and Volos, that both employ belt filter presses for sludge dewatering. In order to compare the dewatering performance of belt filter presses and centrifuges under the same conditions a Pieralisi FP600 2RS decanter centrifuge was installed and operated in parallel with the existing belt filter presses receiving the same thickened sludge. The technical characteristics of the three dewatering devices are shown in Table 3. Full scale trials lasted for approximately 3–4 days in each WWTP. During the trials the feed thickened sludge flow was set in all units at approximately 60%–70% of the maximum capacity of each unit.

RESULTS AND DISCUSSION

Laboratory Scale Experiments

CST tests were conducted in order to determine the optimum polymer doses for the two thickened sludges from Lavrio and Volos WWTPs. Results of CST tests conducted with thickened sludge samples from Lavrio and Volos WWTPs are shown in Figures 1 and 2, respectively. A similar pattern was observed for both sludges and all polymers added. At low dose levels (up to 2–4 g polymer/ kg DS) a significant improvement in sludge dewaterability was observed by increasing the polymer dose. Further increment of the dose showed that over a wide range of polymer doses dewaterability does not appear to improve significantly as indicated by fairly constant CST values that range from 10–20 sec. Finally, high polymer doses (over 8 g polymer/ kg DS) appear to cause deterioration of sludge dewaterability as indicated by the higher CST values obtained. As reported by many researchers ([4], [5] and [6]) the increase in CST values at higher polymer doses is due to the increase in sludge viscosity and does not reflect the inability of sludge to further agglomerate. It has been argued, [6], that the increase in CST values obtained in the overdose region reflects the increase in the total dissolved solids concentration due to the fact that a significant portion of polymer remains in solution. Therefore the overdose effect obtained through the CST test should correlate well with an increase in filtrate or centrate total solids concentration and not with cake solids content. These findings are supported by the full scale results, presented in the next section, that show the correlation between CST values and centrate quality as well as total solids cake content.

As shown in Figure 1, for Lavrio CST experiments, the optimal total polymer doses for all the cationic polymers tested were in the range 5–8 g polymer/ kg DS

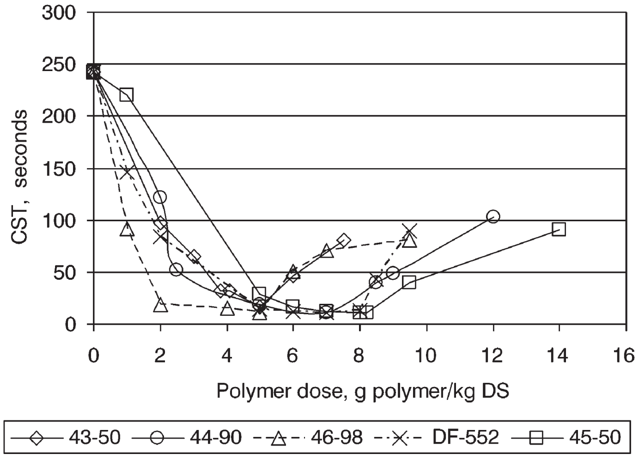

Figure 1. *CST as a function of polymer dose using aerobically stabilized thickened sludge sample obtained from Lavrio WWTP.*

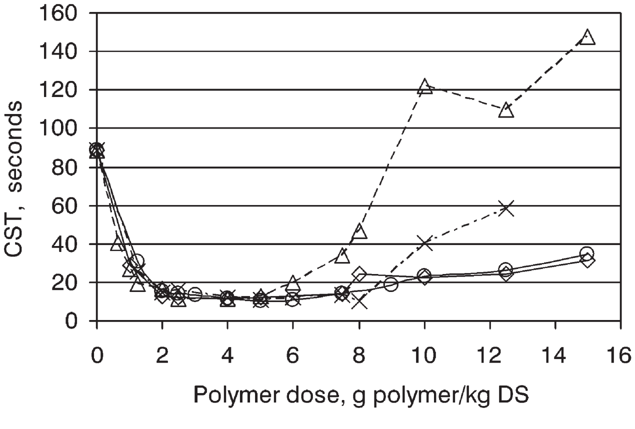

Figure 2. *CST as a function of polymer dose using anaerobically stabilized thickened sludge sample obtained from Volos WWTP.*

with corresponding minimum CST values in the 11–17 seconds range. Similarly for the sludge sample obtained from Volos WWTP the optimal polymer doses for all polymers were between 4–8 g polymer/ kg DS with corresponding minimum CST values in the 10–11 seconds range. Therefore the anaerobically digested sludge from Volos WWTP exhibited slightly better dewaterability compared to the aerobically stabilized sludge from Lavrio extended aeration activated sludge system. Optimum results were obtained for both sludges with cationic polymer 44–90 and DF-552 supplied by SNF Ltd and Kemira Water Solutions Inc., respectively.

Full Scale Experiments

In order to compare the dewatering performance of belt filter presses and centrifuges under the same conditions Pieralisi FP600 2RS decanter centrifuge was installed and operated in parallel with the existing belt filter presses of Lavrio and Volos WWTPs. The only difference between the sludge fed to the belt filter presses and the centrifuge was the type of cationic polymer employed. Belt filter presses received cationic polymer type 45–50 supplied by SNF Ltd, that was selected by WWTP operators through years of operation and trials, whereas thickened sludge fed to the centrifuge was conditioned by addition of polymer type 44–90 supplied by SNF Ltd.

The possibility of employing the same type of polymer for both dewatering devices was explored through full scale experiments conducted at Lavrio WWTP. A series of centrifuge experimental runs was carried out in order to evaluate the performance of the two polymer types. Results shown in Table 4, illustrate that the polymer type 45–50, selected for filter press operation, could not achieve effective sludge conditioning for centrifuge dewatering. It should be stressed that CST tests failed to identify the different conditioning efficiency of the two polymers. Similar findings regarding the link between chemical conditioning and type of dewatering equipment has been reported in the literature ([5], [6] and [7]). According to these reports some dewatering methods such as centrifugation create high shear conditions that tend to break up flocs that result from application of conventional polymers. For these high shear dewatering devices, polymer types with controlled degrees of cross-linkage that provide high molecular weights paired with a network type structure are more suitable because they can tolerate the shear stress associated with centrifuge operation. Based on these findings, it was decided to use different type of polymers for the operation of the belt filter presses and the centrifuge.

During the initial phase of the full scale experiments conducted at the Volos WWTP the optimum polymer dose determined by the CST tests was verified through operation of the full scale centrifuge. As shown in Table 5 the results from the CST tests and the full scale trials are in good agreement. According to both laboratory and full scale experiments optimum polymer dose was observed at polymer doses in the 6–8 gr/kg DS range. At higher doses CST values tend to increase indicating deterioration of sludge dewaterability. As reported previously this deterioration is associated to an increase in sludge viscosity and centrate total solids and not to a lower cake total solids content. These results tend to support the findings reported in the literature [8] that CST values are a function of centrate solids and viscosity.

The results of the parallel operation of the belt filter press and the centrifuge conducted at Volos WWTP are shown in Table 6. Thickened anaerobically digested sludge fed to the two systems had an average total solids concentration of approximately 2.8% and a volatile sol-

Table 4. Results of Full Scale Centrifuge Experiments Employing Polymer Types 45–50 and 44–90 (mean values ± standard deviation).

Polymer dose, gr/kg DS	Polymer Type	Feed Thickened Sludge TS, %	Cake TS, %	Centrate TSS, mg/l
7.4	45–50	2.8 ± 0.1	15.4 ± 0.1	128 ± 6
11.3	45–50	2.4 ± 0.1	15.2 ± 0.1	148 ± 6
12.5	45–50	2.9 ± 0.1	14.5 ± 0.1	91 ± 5
8.5	45–50	2.5 ± 0.1	12.9 ± 0.1	242 ± 5
10.7	45–50	2.5 ± 0.1	15.0 ± 0.1	61 ± 3
14.2	45–50	2.5 ± 0.1	19.9 ± 0.1	72 ± 4
6.8	44–90	3.4 ± 0.1	18.5 ± 0.1	119 ± 6
8.6	44–90	3.4 ± 0.1	21.4 ± 0.1	131 ± 6
10.0	44–90	2.4 ± 0.1	21.8 ± 0.1	131 ± 6

Table 5. Results of CST Tests and Full Scale Centrifuge Experiments (mean values ± standard deviation).

		Full Scale Experiments		
Polymer 44–90 Dose, gr/kg	**SCST Tests, seconds**	**Feed Thickened Sludge TS, %**	**Cake TS, %**	**Centrate TSS, mg/l**
0	88.6 ± 11	3.4 ± 0.1	14.3 ± 0.1	19890
4	11.5 ± 1.3	3.4 ± 0.1	20± 0.1	1457
6.2	10.8 ± 0.9	3.3± 0.1	22± 0.1	362
7.8	14.5 ± 1.1	3.5± 0.1	21.8± 0.1	310
12	26.1 ± 2.1	3.4± 0.1	22.5± 0.1	3900

ids content of 59% of TS. The belt filter press and the centrifuge produced dewatered sludge with an average cake solids content of approximately 21.8 % and 22.4%, respectively. More distinct differences were obtained in the quality characteristics of the filtrate and centrate and in polymer consumption. Centrifuge exhibited a higher solids capture with an average centrate total solids concentration of 214 mg/l versus 535 mg/l obtained with the belt filter press. Additionally belt filter press polymer consumption was approximately 25% higher than the centrifuge.

The results of the parallel operation of the belt filter press and the centrifuge conducted at Lavrio WWTP are shown in Table 7. Thickened aerobically stabilized sludge from the extended aeration WWTP of Lavrio fed to the two systems had an average total solids concentration of approximately 2.6% and a volatile solids content of 67% of TS. The attainable cake solids level by the centrifuge was between 21.5%–22.2%, substantially higher than the one achieved by the belt filter press that ranged between 16.6%–17.8%. It should be stressed that the higher centrifuge dewatering performance was obtained at polymer dosages 25% lower than the ones applied during belt filter press operation. Both dewatering devices achieved high solids capture with filtate and centrate solids concentration that did not exceed 200 mg/l.

In the past, several studies have reported ([9], [10]) that anaerobic digestion leads to poorer dewatering properties. However, the results of the dewatering performance of the centrifuge obtained at the two WWTPs, showed no significant correlation between sludge type and sludge dewatering characteristics. Aerobically and anaerobically stabilized sludge samples appear to have similar dewatering properties. The most important parameters that are reported to affect sludge dewatering characteristics are particle size distribution, extracellular polymeric substances (EPS), bound water and organic solids content ([11], [12]). As reported by Mikkelsen and Keiding [11], EPS exert a twofold effect on sludge dewaterability. On the one hand, EPS has a positive effect on floc stability and filterability and on the other hand EPS increase the water bound within flocs by polymers. Therefore the comparable dewatering properties of aerobically and anaerobically stabilized sludge samples observed within this study may be attributed to the lower EPS and organic content of anaerobically digested sludge.

Table 6. Dewatering Performance of the Belt Filter Press and the Centrifuge at Volos WWTP (mean values ± standard deviation).

	Belt Filter Press			Centrifuge		
Thickened Sludge TS, %	**Polymer Dose, g/kg DS**	**Cake TS %**	**Filtrate TSS, mg/l**	**Polymer Dose, g/kg DS**	**Cake TS %**	**Filtrate TSS, mg/l**
2.4 ± 0.1	**11.7**	21.3 ± 0.1	556 ± 11	10.2	21.7 ± 0.1	238 ± 5
3.4 ± 0.1	**11.7**	21.5 ± 0.1	804 ± 16	7.1	23.3 ± 0.1	126 ± 5
3 ± 0.1	**11.7**	21.7 ± 0.1	432 ± 9	8	22.9 ± 0.1	242 ± 5
2.9 ± 0.1	**11.7**	22.7 ± 0.1	284 ± 6	8.3	23.3 ± 0.1	151 ± 6
2.4 ± 0.1	**11.5**	21.7 ± 0.1	666 ± 12	10	23.1 ± 0.1	193 ± 5
3.4 ± 0.1	**11.5**	20.4 ± 0.1	516 ± 10	7.1	21.8 ± 0.1	326 ± 7
2.7 ± 0.1	**11.5**	22.2 ± 0.1	378 ± 7	8.9	23.1 ± 0.1	221 ± 6
2.4 ± 0.1	**11.5**	22.6 ± 0.1	610 ± 11	10	21.9 ± 0.1	221 ± 6
2.2 ± 0.1	**11.5**	22.5 ± 0.1	568 ± 10	10.9	20.3 ± 0.1	206 ± 5
Average	**11.6**	**21.8**	**535**	**8.9**	**22.7**	**214**

Table 7. Dewatering Performance of the Belt Filter Press and the Centrifuge at Lavrio WWTP (mean values ± standard deviation).

	Belt Filter Press		Centrifuge	
Thickened Sludge TS, %	**Polymer Dose, g/kg DS**	**Cake TS %**	**Polymer Dose, g/kg DS**	**Cake TS %**
2.9 ± 0.1	12.2	16.7 ± 0.1	8.3	21.9 ± 0.1
2.7 ± 0.1	12.2	16.8 ± 0.1	8.9	22.1 ± 0.1
2.5 ± 0.1	12.2	17.2 ± 0.1	9.6	21.5 ± 0.1
2.7 ± 0.1	12.2	16.6 ± 0.1	8.9	21.9 ± 0.1
2.4 ± 0.1	12.2	16.6 ± 0.1	10	21.8 ± 0.1
2.5 ± 0.1	12.2	17.8 ± 0.1	9.6	2.2.2 ± 0.1
Average	**12.2**	**17.0**	**9.2**	**21.9**

Economic Evaluation of Belt Filter Presses and Centrifuges

The total cost of the two dewatering technologies was evaluated and compared for two different plant sizes that corresponded to the two WWTPs examined in this study: a small to medium size WWTP with a sludge production of approximately 1560 kg DS/day and a medium to large WWTP with a sludge production of 12000 kg DS/day. Capital cost of belt filter presses and centrifuges required for each plant was estimated according to information provided by several vendors and the literature. Operation and maintenance costs (O&M) were determined based on the findings of the full scale experiments, information provided by suppliers, the literature and expert judgement. For each case the total cost (capital and O&M costs) was determined on an annual basis assuming an interest rate of 6% and a 15 year depreciation period for both dewatering devices.

O&M costs estimated within the context of this study comprised of the following elements: chemical consumption, labour requirements, power, water consumption, maintenance and spare parts, centrate and filtrate treatment cost and sludge disposal cost. Power consumption costs were determined at 0.06 €/kwh, sludge disposal cost at 5 €/ton of wet sludge and cost of manpower at 18 €/hr. Centrate and filtrate cost for a small and a medium size WWTP was estimated according to operating data from Lavrio and Volos WWTP to be approximately 0.35 €/kg COD and 0.22 €/kg COD, respectively. Chemical costs for all the polymers used in the belt filter presses and the centrifuge were calculated based on a polymer cost of 5 €/kg of polymer. Labour requirements for the centrifuges and the belt filter presses were approximately two staff hours and four staff hours per 8 hours of unit operation, respectively. In order to minimize labour costs two different operating scenarios were evaluated for the medium to large plant. The first scenario involved operation of two belt filter presses or two centrifuges for a total of 50 hours/ week and the second operation of one filter press and one centrifuge for a total of 100 hours/week.

The technical and operating characteristics of the equipment required to meet the dewatering needs of the two different sizes WWTPs as well as their capital cost are shown in Table 8. The total cost (capital and O&M costs) of the two dewatering technologies estimated on a yearly basis is presented in Table 9. According to the

Table 8. Operating Characteristics and Capital Cost of the Dewatering Equipment Employed in this Study.

Operating Time of Dewatering Equipment (hrs/week)	Technical Characteristics	Capital Cost (€)
	Medium—Large WWTP	
100 hrs/week	1 belt filter press, 2 m width with a maximum capacity of 30m^3/h	112.500
100 hrs/week	1 decanter centrifuge, with a maximum capacity of 37 m^3/h	155.000
50 hrs/week	2 belt filter presses, 2 m width, each with a maximum capacity of 30m^3/h	225.000
50 hrs/week	2 decanter centrifuges, each with a maximum capacity of 37 m^3/h^3	310.000
	Small—Medium WWTP	
30 hrs/week	1 belt filter press, 1.5 m width with a maximum capacity of 15 m^3/h	53.000
30 hrs/week	1 decanter centrifuge, with a maximum capacity of 15 m^3/h	108.00

Table 9. Annual Sludge Dewatering Total Costs (capital and O&M costs) in €.

	Medium—Large Size WWTP				**Small—Medium size WWTP**	
	Belt Filter Press		**Decanter Centrifuge**		**Belt Filter Press**	**Decanter Centrifuge**
Annual Costs	**50 hrs/week**	**100 hrs/week**	**50 hrs/week**	**100 hrs/week**	**30 hrs/week**	**30 hrs/week**
Capital cost, €	11583	23167	15959	31918	5457	11120
Chemicals, €	257242	257242	195149	195149	35171	26522
Water consumption, €	22176	22176	53	53	4752	53
Power, €	2883	2883	14256	14256	675	2851
Labour, €	47520	23760	23760	11880	14256	7128
Maintenance, €	4500	7700	3100	6200	1060	2500
Centrate/fitrate treatment, €	23319	23319	6088	6088	5366	1378
Sludge disposal, €	105600	100800	105600	100800	16958	13104
Total Cost, €	**474823**	**465846**	**359165**	**366403**	**83695**	**64657**
Total Cost, €**/ton**	**108**	**106**	**82**	**84**	**147**	**114**

cost analysis conducted sludge conditioning represents the major cost component of sludge management often exceeding 50% of the total cost for sludge dewatering and disposal. Based on the data of the full scale experiments the annual sludge dewatering and disposal cost for a small to medium size and a medium to large size WWTP was significantly higher for the belt filter press and ranged from 106–147 €/ton DS versus 82–114 €/ton DS for the centrifuge dewatering system. Therefore it appears that although the centrifuges based option has a significant higher capital cost compared to the belt filter presses option the long term operations and maintenance costs of the centrifuges were significantly lower resulting in a lower overall life cycle cost compared to the belt filter presses option. In fact when all elements are taken into consideration the capital cost appears to be a small fraction of the total annual cost of each solution ranging between 2–17% for all dewatering technologies and WWTP sizes studied.

A sensitivity analysis was performed in order to determine the effect of the assumptions made regarding manpower and sludge disposal costs. As shown in Figure 3 varying labour requirements from 20–100% of the operational time of the two dewatering devices caused an increase in total costs but it did not change the conclusions in favour of the belt filter presses option. As shown in Figure 4 for a small to medium size WWTP, increasing sludge disposal cost was significantly in fa-

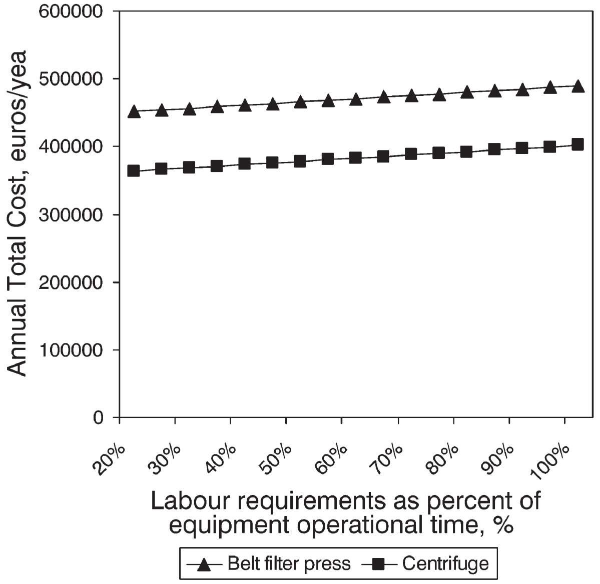

Figure 3. *Annual total cost for belt filter press and centrifuge for a medium to large WWTP, assuming dewatering unit operational time of 10 hr/d.*

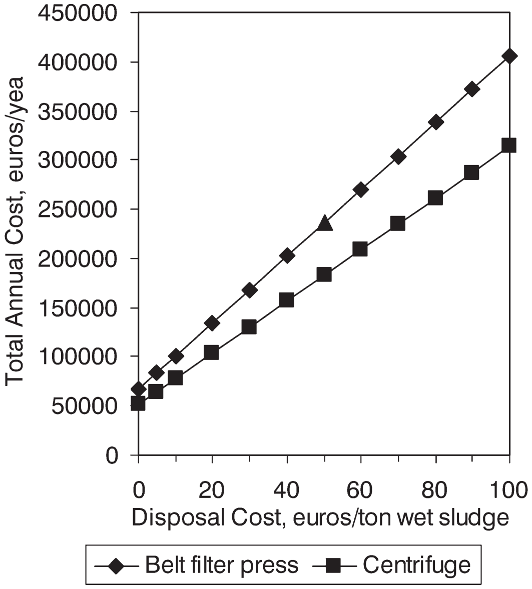

Figure 4. *The effect of sludge disposal cost on the total annual cost of belt filter press and centrifuge options for a small to medium size WWTP.*

vour of the centrifuge option as centrifuges tend to produce a drier cake.

CONCLUSIONS

Based on laboratory and full scale data collected in this study it is hypothesized that the rapid decrease in CST values with polymer addition, obtained at low polymer dose levels, corresponds to a significant improvement in sludge dewaterability. Minimum CST values obtained, are mostly related to minimum centrate solids content. The increase in CST values obtained in the overdose region, is attributed to the increase in sludge viscocity and centrate solids and does not reflect a decrease in cake solids content. Finally CST test did not appear to provide an accurate assessment of the ability of conditioned sludge to tolerate high shear stress conditions created by centrifuges.

Full scale data from the parallel operation of centrifuge and belt filter press units appear to indicate that centrifuges tend to yield drier solids and higher quality recycling waters at a lower polymer consumption rate. Although the centrifuge based option has a significant higher capital cost compared to the belt filter press option the long term operations and maintenance costs of the centrifuges were estimated, for the WWTPs studied, to be significantly lower resulting in a lower overall total cost compared to the belt filter press option. Based on the data of the full scale experiments the annual sludge dewatering and disposal cost for a small to medium size and a medium to large size WWTP was significantly higher for the belt filter press and ranged from 106–147 €/ton DS versus 82–114 €/ton DS for the centrifuge unit.

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Bio-Fuels and Bio-Char Production from Pyrolysis of Sewage Sludge

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ABSTRACT: The limited reserves of fossil fuels along with the environmental concern about green-house gases have led to the search for new energy sources. Biomass offers a sustainable and renewable energy system. Sewage sludge, a residue generated in wastewater treatment plants, is one of the environmental problems in industrialized countries. Its contents of volatile matter represents a valuable resource, a possible reuse is the conversion into fuels by means of pyrolysis that yields gas, bio-oil and biochar. The composition and heating value of the gas makes it suitable for use as a fuel. The bio-oil may be evaluated as an environmentally-friendly green biofuel. The biochar product is carbon-rich and a potential solid biofuel. Other ways it might be used as a C and N source in soil amendment.

INTRODUCTION

THE increase in the production of sludge, an inevitable by-product of the treatment of waste water, is causing more and more concern owing to the risks to health and the environment. Production, estimated at around 40–50g of dry matter per person per day, is increasing as more new plants are set up [1]. Sludge has traditionally been dealt with in three different ways: application to the soil to recycle nutrients and organic matter, energy production and dumping. Here we concentrate on its energy potential and consider the possibilities that the thermochemical processes offer. Sewage sludge like most organic wastes is rich in volatile matter and can therefore be converted into a usable energy source. The recovery of energy from sewage sludge and solid wastes has focused on thermochemical processes such as direct combustion [2], gasification [3,4] and pyrolysis [5,6,7,8,9]. Of these processes, pyrolysis has been receiving increasing attention in recent years as an acceptable route for waste disposal. The main reason for this is that in the pyrolysis process, which entails heating material in an inert atmosphere, the conditions can be optimised to maximize the production of either chars, oils or gases depending on the product required [10,11,12]. In this study, the proposed semi-pilot pyrolysis plant yields bio-oil, gas and biochar. Bio-oil is a complex mixture, highly-oxygenated with a great number of large size molecules, which include almost all species of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids and alcohols [13]. Biochar is a soil amendment that has very specific and unique properties that make it stand out among the opportunities for sustainable soil management. The benefits of biochar rest on two pillars: the extremely high affinity of nutrients to biochar and the extremely high persistence of biochar. These two properties can be used effectively to address some of the most urgent environmental problems of our time: soil degradation and food insecurity, water pollution from agro-chemicals and climate change. The key for securing environmental benefits is the production of a biochar by-product during pyrolysis which can be applied to soil [14]. The main components of the gas samples are H_2, CO, CO_2, and CH_4. In the pyrolysis process the heavier hydrocarbons are cracked giving rise to lighter ones; these are the greatest interest as their heating values are higher [15].

The aim of this work is the characterization and valorization of the gas, liquid and solid fractions obtained in the pyrolysis process of sewage sludge.

EXPERIMENTAL

Material

A representative sample of anaerobically stabilised

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sewage sludge from an urban wastewater treatment plant from León (Spain) was used in this work. It goes through a dehydration and thermal drying in the wastewater treatment plant of origin. Table 1 summarizes the main chemical characteristics of the sludge. It is carbon and oxygen rich feedstock, containing hydrogen and nitrogen at a low ratio and trace amounts of sulphur. The volatile matter content was 59.2 wt.%, making it a valuable source of organic compounds when it is pyrolysed, while the amount of ashes was 32.4%. The moisture content was around 6.8%. And the lower heating value was 15.3 MJ/kg.

Table 1. Chemical Analyses (%) and Heating Values of Original Sewage Sludge.

	Sludge
Moisture	6.8
Volatile Matter[a]	59.2
Ash[a]	32.4
Fixed Carbon [a,c]	8.4
Carbon[b]	55.3
Hydrogen[b]	7.8
Nitrogen[b]	9.8
Sulphur[b]	1.4
Oxygen[b,c]	25.7
L.H.V. (MJ Kg^{-1})	15.3

[a] Results expressed as a percentage of dry matter.
[b] Results expressed as a percentage of dry matter free of ashes.
[c] Calculated by difference.

Experimental Set-up in the Laboratory

The experimental design used in the laboratory pyrolysis tests is shown in Figure 1. Pyrolysis was carried out in a reactor consisting of a quartz tube 40 cm long with a diameter of 7 cm placed in an electrically heated horizontal oven [16].

A 30 g sample was pyrolized. Helium was fed into the front of the reactor, and, before heating began, it was fed through at a flow rate of 200 mL min^{-1} for 60 minutes to remove the air from the system. Pyrolysis conditions were a maximum heating ramp of 30ºC/min, starting from room temperature to a final temperature of 550ºC and at a He flow rate of 100 mL min^{-1}. When the reactor reached 550ºC, this temperature was maintained for approximately 1 minute and then the process was stopped. As for the heating ramp, the maximum allowed by the oven was used, and no tests were made with other gradients, as the bibliographical references showed that within the range 5–30°C/min no variation in the heating gradient significantly affected product formation [17]. The final temperature was chosen from a previous thermogravimetric study, as the heating gradient was within the range studied [18]. It was observed that the range of temperatures over which devolatilization of the residue occurs was quite large, running from 200ºC to 550ºC, with devolatilization in the thermobalance being almost complete. The gases produced in the pyrolysis process were carried by the He through the lower part of the reactor, where they passed through a number of "traps", where the oils (condensable gas fraction) were collected. The traps comprised a balloon and two U-shaped glass tubes packed in ice and filled with Raschig rings. Finally, the gases were fed into a methyl methacrylate container

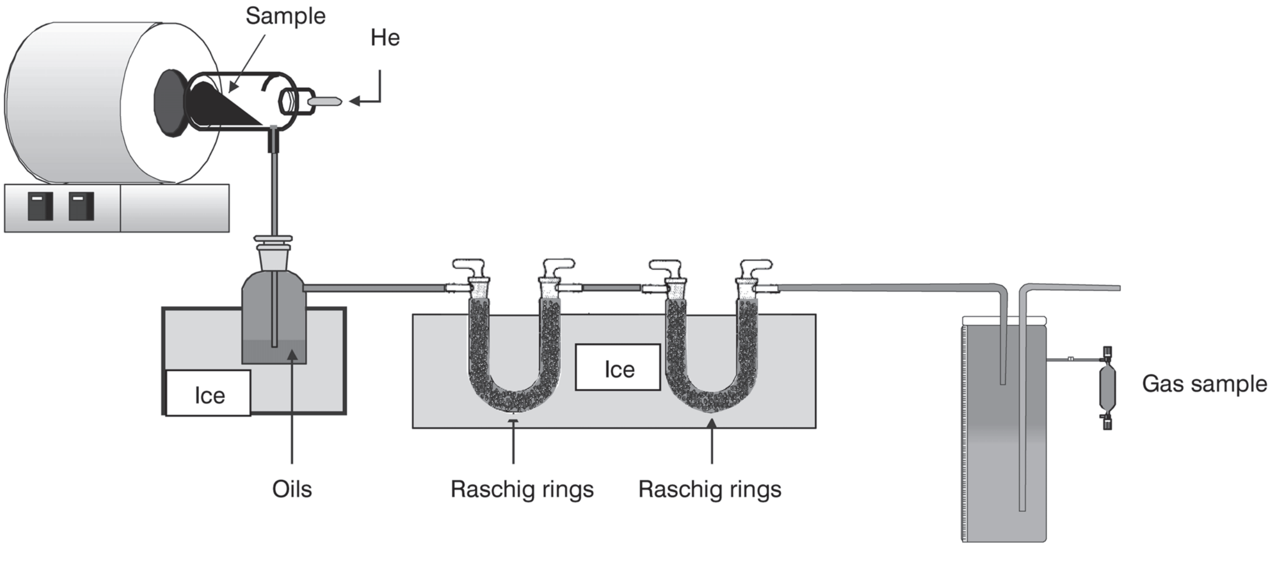

Figure 1. *Laboratory Experimental Set-up.*

with water inside, which was displaced, and a sample taken for gas analysis. The gas yield was checked by directly measurement of the volume of gas produced in the pyrolysis process.

Characterization of Gas

The gas fraction was analysed by GC with an HP-5890 series II with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Different pyrolysis experiments established that the relative values of gas composition do not deviate more than 5%. To analyse hydrocarbons (C_xH_y), an HP-AL/S semi-capillary column with a length of 50 m and an internal diameter of 0.53 mm was used, with He as carrier gas and the FID detector. H_2, O_2, N_2, CH_4 and CO were analysed in a 5 Å molecular exclusion packed column of 1/8″ outer diameter, 6 feet long, with a mesh of 60/80 and He as carrier gas and the TCD detector. CO_2 was analysed in a Chromosob 102 packed column specific for this substance with an outer diameter of 1/8″ and a length of 6 feet, with a mesh of 80/100 and He as carrier gas, the TCD also being used. For the identification and quantification of the gaseous species, three SUPELCO gas reference standards were used.

Characterization of Bio-oil

Elemental analysis of the bio-oil was performed according to ASTM D 5373. The heating value was determined according to ASTM D 3286-91a. These analyses were repeated at least three times for good accuracy, the results differing by ± 0.1 wt%.

The bio-oil was analysed by GC-MS, a Hewlett-Packard HP 6890 gas chromatograph coupled to an HP 5973 mass spectrometer quadrupole detector. A 60 m × 0.25 mm capillary column coated with a 0.25 µm thick film of 5% phenylmethylpolysiloxane (HP-5) was used and helium was employed as a carrier gas at a constant flow of 0.9 mL min^{-1}. The initial oven temperature of 40 ºC was held for 5 min and then programmed from 40 to 300ºC at 5ºC/min with an isotherm held for 30 min. The split ratio was 20:1 and the injection was carried out at 300ºC. The ion source and transfer line temperatures were 230 and 325ºC, respectively. Data were collected in the full-scan mode between m/z 25–533 and a solvent delay of 6 min was used. The chromatographic peaks were identified with the help of the NIST mass spectral data library.

Characterization of Biochar

In the characterization of the solid materials, both the original biomass and biochar, a proximate analysis was run. Moisture was determined in a SELECTA THREOVEN with forced ventilation. Volatile matter and ash were analysed with a THERMOLYNE 48000 muffle furnace with automatic temperature control. Regulations UNE 32 002, 32 019 and 32 004 were followed respectively for moisture, volatile matter and ash respectively. Fixed carbon was determined by difference.

An elemental analysis was also run to determine the main chemical elements present in the sample: carbon, hydrogen, nitrogen, sulphur, and oxygen, the last by subtraction. For the first three elements, a LECO CHN-600 apparatus was used and ASTM standard D-5373 was followed. Total sulphur was determined with a LECO SC-132 according to ASTM standard D-4239.

Heating value was determined with a LECO AC-300 using the adiabatic method in accordance with regulation UNE 32 006.

These analyses were repeated at least three times for good accuracy, the results differing by ± 0.1 wt %.

The carbonized solid fraction was subjected to combustion at a programmed temperature and thermogravimetric analysis in an STD 2960 thermobalance. The initial sample mass was 5 mg, this being distributed uniformly over the base of the sample holder so as to facilitate the transfer of heat and of material. The atmosphere used was air with a flow rate of 100 mL min^{-1} . The heating rate was the 50ºC min^{-1} from room temperature up to a final temperature of 800ºC. TG runs were repeated at least three times, the average relative error being ± 5%.

RESULTS AND DISCUSSION

Pyrolysis Product Yields

The bio-fuels and biochar yields (% weight) under the process conditions fixed in the reactor were: 27% gas, 28% bio-oil and 45% bio-char.

Characterization of the Gases

The main components of the gas samples are H_2, CO, CO_2 and CH_4 (Table 2).

Table 2. Composition (% vol) and Heating Value (MJ m^{-3}) of the Gases.

	(% vol)
Methane	23.38
Ethane	4.11
Ethylene	4.50
Propane	1.43
Propylene	2.69
i-butane	0.12
n-Butane	0.16
Acetylene	< 0.01
t-2-Butene	0.13
1-Butene	0.31
Isobutylene	0.42
c-2-Butene	0.10
Isopentane	0.03
n-Pentane	0.04
1,3-Butadiene	0.31
C5 Rest	0.24
C6	0.34
H_2	25.76
N_2	6.83
CO	14.03
CO_2	14.15
Others	0.90
L.H.V. (MJ m^{-3})	24.40

In the pyrolysis process the heavier hydrocarbons are cracked, giving rise to lighter ones, methane and hydrogen. Those of greatest interest are the light hydrocarbons, as their heating values are higher than the other gas components. The CO and CO_2 contents of the gaseous fraction are indicators of the oxygen present in the sample [19]. This oxygen derives from the pyrolytic decomposition of partially oxygenated organic compounds (cellulose, lignin, lipids and carbohydrates).The high H_2 content of the pyrolysis gas may be due to the cracking of hydrocarbons, processes favoured by high temperatures, apart from the contribution of the H in the elemental composition of the sludge itself.

The net calorific value that could be theoretically recovered through stoichiometric combustion of the evolved pyrolytic volatiles at 550ºC is calculated accounting for the amounts of measured combustible volatiles at 550ºC and using the corresponding heat of combustion for each volatile. The heating value obtained (24.4 MJ m^{-3}) is higher than those recorded in studies by other authors also performed in electric ovens, where the heating value was within the range 13–14 MJ m^{-3} [11], the different conditions under which the process is carried out must be considered, which imply a change in the composition of the gases obtained and therefore in the heating value.

Characterization of the Bio-oil

Bio-oil is one of the desirable products of pyrolysis, and is usually mixed with condensed water. Bio-oil is a carbon rich oxy-fuel containing a small proportion of nitrogen and trace amounts of sulphur (Table 3). Bio-oil can be an alternative for heating fuel. The low sulphur content of bio-oil is a very important advantage [1].

Figure 2 shows a GC-MS chromatogram of the pyrolysis oils. These are complex mixtures of organic compounds: n-alkanes and 1-alkenes (C11-C31); monoaromatic hydrocarbons (benzene, toluene (6), styrene (15), phenol (22), 1H-indene and their alkyl derivatives), aromatic compounds bearing nitrogen and oxygen such as pyridine, alkylpyridines, 1H-pyrrole (5), 1H-indole (41), isoquinoline, methylquinolines, 9H-carbazole and benzofurane; aliphatic and aromatic nitriles; carboxylic acids (RCOOH) (72), where R represents long aliphatic chains with 14, 15, 16 and 18 carbon atoms; long chain aliphatic amides and steroids (cholestene (93), cholestadiene or formyl cholestene), and polycyclic aromatic hydrocarbons (PAHs) were also detected in these bio-oils. Different pyrolysis experiments established that the relative values of bio-oil composition do not deviate more than 5%.

Bio-oil may be used as a raw material in a fractioning process for obtaining fuels. By its distillation, gasoline, diesel fuel or alternative fractional products to fuel-oils are obtained. These fractions may either be used directly or mixed with other conventional fuels. By the application of various processes (such as Fischer-Tropsch synthesis, cracking, hydrogenation, etc.) fuel characteristics may be improved and oil under these circumstances may either be used directly or its

Table 3. Elemental Analysis (%) and Heating Value (MJ/kg) of Bio-oil.

C(a)	H$^{(a)}$	N$^{(a)}$	S$^{(a)}$	Cl$^{(a)}$	O$^{(a),(b)}$	L.H.V.
59.4	7.5	6.2	0.71	< 0.02	17.8	29.01

$^{(a)}$Results expressed as a percentage of dry matter.
$^{(b)}$Calculated by difference.

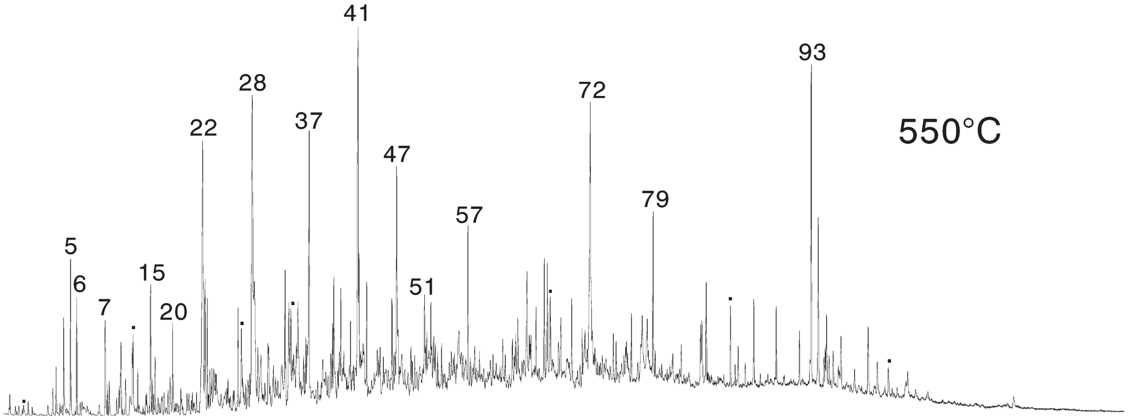

Figure 2. *GC-MS chromatogram of the pyrolysis oils.*

fractions may be evaluated as an alternative gasoline, diesel fuel and fuel-oil [20].

Characterization of the Bio-char

Table 4 shows the chemical characterization of the biochar. As a consequence of pyrolysis, the carbon content of the carbonized residue increased with regard to the original sludge, along with a deoxygenation as a consequence of the loss of functional groups during the process. There was also a noticeable decrease in the hydrogen content, due to initial polymerization reactions which involve the loss of hydrogen because can often be accomplished though internal hydrogen transfer [21]. There was a concentration of sulphur in the solid fraction, which caused emissions of sulphur dioxide compounds during combustion so a gas cleaning treatment for the combustion gases being necessary.

Reactivity of the carbonized solid in air was studied by means of thermogravimetric analysis. The evolution of the mass loss (TG) and mass loss rate (DTG) against temperature is shown in Figure 3.

Table 4. Chemical Analyses (%) and Heating Values of Carbonized Sewage Sludge.

	Sludge
Moisture	2.3
Volatile Matter[a]	8.1
Ash[a]	70.2
Fixed Carbon [a,c]	8
Carbon[b]	88.0
Hydrogen[b]	1.8
Nitrogen[b]	8.0
Sulphur[b]	1.8
Oxygen[b,c]	0.4
L.H.V. (MJ Kg^{-1})	9.42

[a] Results expressed as a percentage of dry matter.
[b] Results expressed as a percentage of dry matter free of ashes.
[c] Calculated by difference.

First appears to be moisture lost from the sample with a small DTG response loss in the 40–100ºC region. Then a main mass loss peak is to be observed over a wide temperature range (350–600ºC), owing to reactive material remaining in the carbonized solid. At low temperatures, it is attributed to a volatile material that had remained in the carbonized solid being driven off and to the presence of structures more reactive in air, capable of reacting at low temperatures. At high temperatures, the reaction of more condensed structures occurs. TG profile shows a solid residue at temperatures above 600ºC (combustion ashes) similar to the percentage obtained from the chemical analyses (70%). The heating value of the pyrolysed residue was quite low in comparison with that of other fuels [11], lower even than that of the sludge before pyrolysis, the high ash content (70%) might explain the low heating value of the char. Co-combustion of this pyrolysed residue and coal may provide an attractive option for the disposal and utilization of a renewable waste resource such as sewage sludges in an economic and environmentally safe manner [22].

Other ways it may be employed include use as a source of C and N. During the conversion of sewage sludge to biochar the original carbon is retained in the biochar, which offers a significant opportunity for creating a carbon sink. The long persistence of biochar in soil makes it a prime candidate for the mitigation of climate change as a potential sink for atmospheric carbon dioxide [10]. The success of effective reduction of greenhouse gases depends on the associated net emission reductions through biochar sequestration. All or-

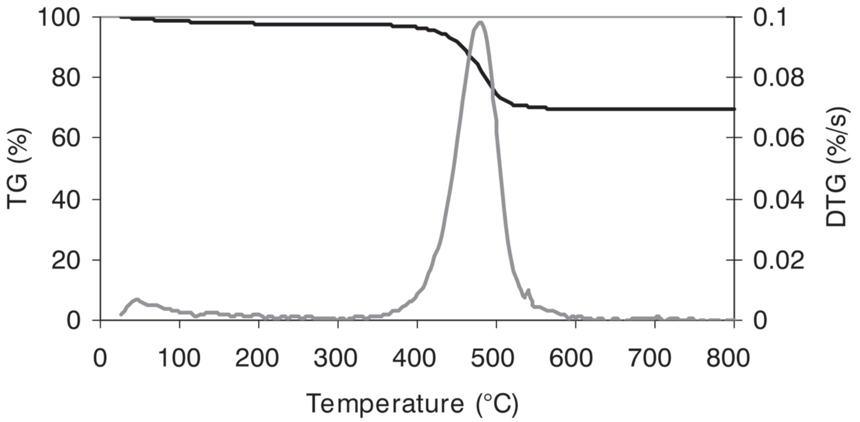

Figure 3. *TG and DTG profiles of the programmed-temperature combustion of the biochar.*

ganic matter added to soil significantly improves soil functions, not the least the retention of several nutrients that are essential to plant growth. The biochar from sludge contains 0.86% N, 0.91% P_2O_5 and 1.52% K_2O. The biochar persistence in soil is also important related with any other form of organic matter applied to the land. It is undisputed that biochar is much more persistent in soil than any other form of organic matter that is commonly applied to the land [14].

What is special about biochar is that it is much more effective in retaining most nutrients and keeping them available to plants than other organic matter for example compost or manures. Therefore, all associated benefits with respect to nutrient retention and soil fertility are longer lasting than with alternative management.

CONCLUSIONS

The composition of the pyrolysis gas makes it suitable for use as a fuel, given the concentration of light hydrocarbons and hydrogen, and its heating value.

Bio-oil, with its very low sulphur content, may be considered from the point of view of the environment as a potential alternative to fuel-oil. After some improving applications it can also be used as an alternative for heating fuel.

Biochar may be evaluated as an amendment to improve soil fertility and nutrient retention, but on this point it would be necessary to undertake a more complete study. Combustion at a programmed temperature of the biochar revealed its good combustibility, but its applicability as a fuel will depend on the use of techniques for the treatment of combustion gases, as it concentrates much of the sulphur of the original waste.

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Influence of Source and Treatment Method on the Properties of Activated Carbons Produced from Sewage Sludge

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ABSTRACT: This paper reports an investigation into the effects of the geographical origins of sludge and the treatment methods applied to it on its properties as a feedstock for producing activated carbons. The approach taken firstly utilises a response surface methodology (RSM) to model the relationship between the activation conditions and the textural characteristics of the carbons produced from two different UK sludges. Subsequently, the optimal conditions obtained were employed to prepare activated carbons from a range of French and Polish sludges. The activated carbons generated have been characterised in terms of their textural characteristics, chemical composition and their surface chemistry.

INTRODUCTION

THE increasingly stringent legislation governing the use of sewage sludge as a fertiliser, coupled with the decline in the viability of existing sludge disposal routes such as landfill and incineration, have created a drive for more sustainable alternatives [1]. The conversion of sludge into activated carbon by the combined processes of pyrolysis and partial gasification (steam activation) is one option that, due to its valorisation of the sludge, is particularly attractive [2,3].

Activated carbon is a high surface area adsorbent used to clean gases and liquids. Its retail price is up to £2000 pounds per tonne. It can be produced by two main methods, physical and chemical activation. This paper focuses on physical activation using steam as it is far more commercially viable, as well as being more environmentally friendly. Steam activated sludges and sludges mixed with other material have been examined before by many groups [4–6].

The adsorption properties of activated carbon are mainly dependent on two parameters: their physical and chemical properties. Physical property tests include nitrogen gas adsorption analysis and chemical property tests including elemental analysis, ash content and Fourier Transform Infrared Spectroscopy (FTIR).

EXPERIMENTAL METHODOLOGY

Precursors: Sewage Sludge Types and Locations

Sewage sludges of six types and from five sources were collected from municipal wastewater treatment plants throughout Europe. The type, location and treatment method are shown in Table 1. After collection, sewage sludges were dried at 105–110°C. They were crushed to below 10 mm using a cross beater mill (Glen Creston, London, UK) and stored in air tight containers prior to further use.

Response Surface Methodology (RSM) and Sludge Based Adsorbent Production

RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimising processes [7]. In this research, a RSM was employed to identify the relationship between the activation temperature and dwell time, and the key properties for Sludge Based Adsorbent (SBA) production from DRAW or DMAD sludges. RSM models have been used elsewhere to optimise activated carbon production experiments [6,8,9]. To design the model, two independent variables; activation time and temperature, were coded into a matrix of two factorial design [7,10,11]. The particular design used is a "central composite design", which are widely used for fitting sec-

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Table 1. Types of Sewage Sludge.

Type Abbreviation	Type of Sewage Sludge	Location	Country
DRAW	Dewatered, RAW filter cake	London	UK
DMAD	Dewatered, Mesophilic Anaerobically Digested	Kent	UK
DSBS	Dewatered, Secondary Biological Sludge#	Nantes	France
KAN	digested*	Kalisz	Poland
KAW	digested*, with lime	Kalisz	Poland
GOS	Mesophilic Anaerobically Digested	Lodz	Poland

#DSBS-aerobically digested, residual from 2nd biological treatment stage with added organic polymer coagulant.

*KAN-comprises a mixture of primary sludge stabilised by anaerobic fermentation and excess sludge stabilised by aerobic digestion and KAW is produced by the liming of KAN.

ond-order response surfaces. Note that the design consists of four runs at the corners of a square, plus four runs at the center of this square plus four axial runs or "star points" [7]. The star points allow for an estimation of the curvature of the response surface. The equations used for the design are shown below [Equations (1)–(3)]. In equation 1, X_1 represents temperature. In Equation 2, X_2 represents time. Equation (3) is in the form of a second order polynomial with Y_j representing either the SBA yield, ash or BET surface area, depending on the response being monitored. The midpoint offsets of X_1 and X_2 used in this experiment were 825°C and 60 min, respectively.

$$X_1 = \frac{temperature - 825^\circ\text{C}}{75} \quad (1)$$

$$X_2 = \frac{time - 60\text{ min}}{40} \quad (2)$$

$$Y_j = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2 \quad (3)$$

where a_0 is the intercept term, a_1 represents the influence of the activation temperature, a_2 represents the influence of the activation time, a_{12} represents the interaction effect between the activation temperature and activation time and a_{11} and a_{22} are curve shape parameters [8].

The given responses of each particular variable at different activation temperatures or dwell times were tested and evaluated through an iterative process using an algorithm written in MatLab (R2006a).

SBA Preparation

A Carbolite 11/150 laboratory scale rotary furnace (Carbolite, UK) was employed for a single step process of carbonisation and steam activation of sewage sludge. For each run, 210 g of sewage sludge was loaded in a quartz reactor, which was set to rotate at 10 rpm, and heated at a rate of 10°C/min up to the desired temperature, under an inert nitrogen atmosphere of 500 ml/min. At the desired maximum temperature, water was directly injected into the reactor using a peristaltic pump at a flow rate of 0.7 ml/min. The flow was maintained throughout the required dwell time. Subsequently, the furnace was automatically cooled down to room temperature. The SBAs were crushed and sieved to a particle size below 150 μm prior to other characterisation tests.

The optimised conditions from steam activation of DRAW and/or DMAD were then applied to the other types of sewage sludge. Steam activation at the optimal conditions for each type of sewage sludge are identified by Sewage Sludge type abbreviation_S, for example DRAW_S.

Textural Characterisation by Nitrogen Gas Adsorption

The SBAs were subjected to surface area and porosity characterisation by a Coulter Omnisorp® 100 (Beckman-Coulter, UK). Prior to analysis, the SBAs were degassed at 150°C for 7–8 hours until a pressure below 10^{-5} Torr was reached [12,13]. From this analysis, the adsorption isotherms, desorption isotherms, BET surface area [14] and t-plot (which indicates the amount of meso and macropores in the activated carbon) [15] can be determined.

Chemical Tests

Elemental (CHNS) analysis was performed in order to evaluate the carbon, hydrogen and nitrogen content of the sample. This analysis was carried out using a Carlo-Erba EA1108-CHNS analyser by MEDAC Ltd, UK, Ash contents of SS and SBA samples were determined following the methods described in ASTM 2866-94 [16].

Surface Chemistry Tests

Fourier Transform Infrared (FTIR) Spectroscopy was performed on sludges and SBAs. Samples were dried at 150°C, mixed and crushed with KBr (Spectrograde, Fisher Scientific Ltd, UK) using an agate pestle and mortar at a ratio of approximately 1:100

Table 2. SBA Yield, Ash and Surface Area of Steam Activated DRAW and DMAD Sludges.

		DRAW Sludge			**DMAD Sludge**		
Temp/Time (°C/min)	**Code**	**Solid (SBA) (%)***	**Ash (%)**	**BET Surface Area (m^2/g)**	**Solid (SBA) (%)***	**Ash (%)**	**BET Surface Area (m^2/g)**
X_1/X_2	X_1/X_2	Y_{R1}	Y_{R2}	Y_{R3}	Y_{A1}	Y_{A2}	Y_{A3}
750/20	–1/–1	30.3	54.6	155.7	50.7	76.5	128.4
900/20	1/–1	26.3	61.5	227.2	47.4	80.5	157.3
750/100	–1/1	26.0	61.0	231.4	47.7	80.5	145.9
900/100	1/1	18.8	80.0	222.6	41.8	88.7	144.3
825/60	0/0	25.0	63.5	262.6	47.2	81.0	165.4
825/60	0/0	24.8	63.2	269.7	47.0	81.5	164.5
719/60	–√2/0	28.5	56.1	180.6	49.9	78.3	124.7
931/60	√2/0	21.0	73.9	233.5	42.2	87.8	143.4
825/3	0/–√2	29.2	55.7	137.4	50.0	79.2	126.5
825/117	0/√2	22.0	70.5	267.5	45.4	84.0	161.5
825/60	0/0	25.1	62.8	252.6	47.3	81.1	164.9
825/60	0/0	25.1	63.3	260.1	47.3	81.1	165.8

*% calculated from the original mass of sewage sludge (210 g).

(w/w). A solid disc with a diameter of 10 mm and a thickness of about 1 mm was formed by pressing the mixed sample at 10 metric tonnes of pressure for a period of 10 mins with a pneumatic die press (Specac, UK). The disc was then analyzed in a MAGNA 560 IR Spectrometer (Nicolet, USA). Measurements were performed in the 4000–400 cm^{-1} region at a spectral resolution of 4 cm^{-1}. Background measurement was made of the air within the sample chamber. The sample spectrum was then corrected for the background IR measurements using the FTIR software. The positions of the absorbance peaks from the samples were automatically identified by the FTIR software.

RESULTS AND DISCUSSION

Product Yield, Textural Characterisation and Ash Content of DRAW and DMAD on RSM Models

SBA yield, surface area and ash content results from the design RSM are reported in Table 2 with all experimental errors being less than 2%. The results of the coefficient estimation for the fitted model equation are shown in Table 3. The correlation coefficient values (R^2) were all higher than 0.89. This indicated that the results gained from the experiments and the predicted results from the model were in good agreement. The graphs for the response results of SBA yield of DRAW and DMAD and surface area of DMAD are shown in Figure 1(a) and 1(b) respectively.

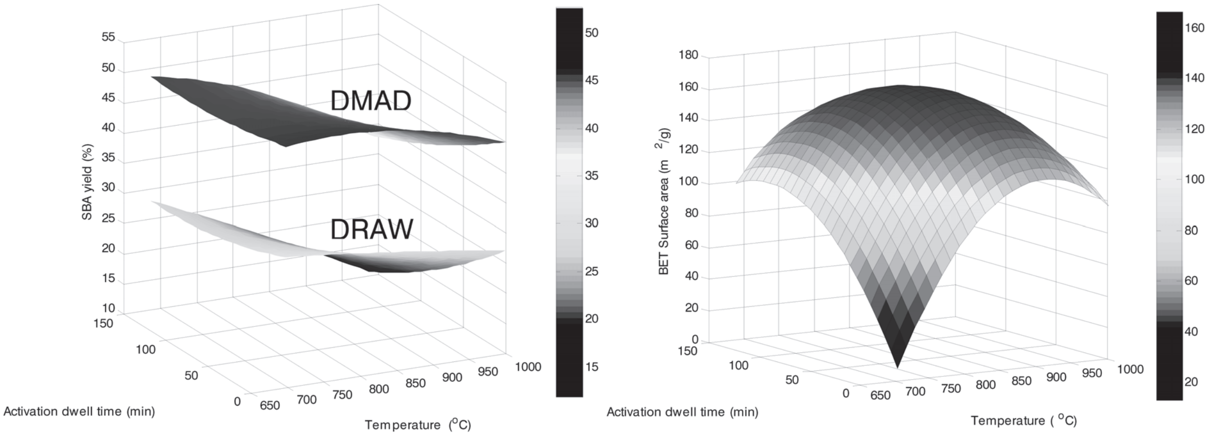
From Figure 1(a), it is generally clear for the SBA yield that the higher the temperature and dwell time, the lower the carbon yield. This can be explained quite simply by noting that as the temperature increases, a larger variety of gasification reactions can occur more quickly, thus a higher amount of carbon will be removed, opening blocked pores (indicative of the endothermic steam reaction). This observation was in good agreement with work carried out by Rio *et al.* [6].

Correspondingly, ash content responses showed an

Table 3. Coefficient Estimation for the Fitted Model Equation.

Regressive Coefficients	Y_{R1}	Y_{R2}	Y_{R3}	Y_{A1}	Y_{A2}	Y_{A3}
a_1	25.00	63.20	261.25	47.20	81.18	165.15
a_2	–2.73	6.38	17.19	–2.51	3.20	6.72
a_3	–2.75	5.73	31.89	–1.89	2.37	6.75
a_{12}	–0.80	3.03	–20.08	–0.65	1.05	–7.63
a_{11}	–0.08	0.96	–25.98	–0.57	0.74	–14.31
a_{22}	0.34	0.01	–28.28	0.26	0.02	–9.34
R_2	0.996	0.996	0.917	0.989	0.963	0.894

Fitted equation example: $Y_{R1} = 25.00 - 2.73X_1 - 2.75X_2 - 0.80X_1X_2 - 0.81X_1^2 + 0.34X_2^2$.



(a) (b)

Figure 1. (a) Mesh response of SBAs yield (%) for steam activated DRAW and DMAD sludges, (b) Mesh response of DMAD sludge.

opposite response to the SBA yield, in that increases in either maximum temperature or dwell time results in increased ash content. The carbon yields of DRAW and DMAD sludges differ by approximately 20%, which has been attributed to the fact that the DMAD sludge has already been digested, and thus fewer volatiles are produced. Therefore, it can be said that steam activation affects both types of sewage sludge in a similar manner.

The mesh response for the BET surface area of DMAD sludge is show in Figure 1(b). DRAW and DMAD sludges both responded in the same manner. The BET surface area of DRAW sludge was optimised at 838°C and at a dwell time of 80 min, which yielded a BET surface area of 270.6 m^2/g. The optimal activation temperature for DMAD sludge was also 838°C and the optimum dwell time was, at 73 min, only slightly less; these conditions yielded a BET surface area of 166.7 m^2/g. Essentially, the BET surface area of DRAW and DMAD sludges was maximised under the same activation conditions. Comparing DRAW and DMAD sludges, it can be seen that excessive temperatures and/or dwell times resulted in an excessive carbon burn-off, which destroyed the pores and lowered the surface area. From a BET surface area point of view, DRAW sludge is more suitable for producing SBA. However, considering the SBA yield per batch and multiplying by the surface area, it can be said that DMAD sludge can yield a slightly greater BET than DRAW sludge by input weight.

SBA Yield, Textural Characterisation and Chemical Tests on Different Types and Source of Sewage Sludge

The optimal conditions of temperature and dwell time for BET surface area were applied to different types and sources of sewage sludge. The SBAs' yield, surface areas, CHN and ash contents are shown in Table 4. Note that the DRAW and DMAD sludges come from different sample batches than those used to initially determine the optimal conditions and therefore, a small variation in the results are to be expected and were within acceptable errors as stated earlier.

The SBA yield of DRAW sludge is approximately

Table 4. SBA, Surface Area Yields, CHN and Ash Content at the 838°C and 73 Minutes of Six Sludges.

		Surface Area (m^2/g)			*CHN (%)*			
Sample	**SBA Yield (%)**	***BET***	**Meso & Macropore***	**Micropore****	**C**	**H**	**N**	**Ash (%)**
DRAW_S	22.7	253.1	173.2	79.9	29.0	0.6	1.0	69.4
DMAD_S	40.4	179.3	107.7	71.6	22.6	0.6	< 0.1	78.2
DSBS_S	35.9	206.2	77.6	128.6	34.6	0.7	1.8	61.0
KAN_S	37.4	158.1	76.9	81.3	19.0	0.4	< 0.1	82.7
KAW_S	31.4	12.3	12.3	0.0	0.3	0.6	< 0.1	100.0
GOS_S	42.4	146	106.3	39.7	17.6	0.4	< 0.1	82.4

*t-plot surface area (Meso and Macro pore surface area, pore width > 2 nm).
**Calculated by different between t-plot and BET (Micropore surface area, pore width < 2 nm).

20%, whereas the SBA yield of all other sludges is approximately 30–40%. This was explained earlier by noting that DRAW sludge loses more weight (i.e., exhibits more thermal decomposition) before reaching the activation temperature, whereas the other type of sludges had already decomposed during the digestion processes. KAW_S has the lowest yield among the treated sludges, which is probably due to the high $Ca(OH)_2$ content being converted into CaO and water [17]; all the other digested sludges have a similar yield.

For textural characterisation, all types of steam activated sludges except KAW_S exhibit Micro, Meso and Macropore surface area. DRAW_S yields the highest BET surface area, mainly from its Meso and Macropore surface area. Most of the steam activated sludges show mainly Meso and Macropore surface area except for DSBS_S and KAN_S, which exhibit a higher Micropore than Meso and Macropore surface area. This may be explained by two factors: Firstly, the activation method may not be optimised for these sludges. Secondly, differences in the carbonaceous components arising from different sources and treatment methods may affect the texture of the steam activated sludges themselves.

Before steam activation, the carbon contents of DRAW, DMAD, DSBS, KAN, KAW and GOS were 41.0, 32.1, 40.3, 33.7, 24.7 and 33.8% respectively. These values agree well with the finding that DRAW, as the most carbonaceous material, yielded the SBA with the highest surface area. However, the SBA produced from the DSBS sludge, which has nearly the same amount of carbon content as DRAW sludge produced a 50 m^2/g lower surface area, while the carbon content of DSBS_S yielded a 5% higher carbon content than DRAW_S. From these results, it helps to confirm previous assumptions that the Micro, Meso and Macropore surface area development of DSBS_S is affected by a difference in carbonaceous composition even though it gives the same carbon content. The difference in the carbon content before and after steam activation for all sludge types vary from approximately 6–16% except for KAW sludge, which has a carbon content difference of 25%. This suggests that during the steam activation reaction, the high amount of lime (which is predominantly calcium) significantly accelerated the gasification reaction. Calcium is known to be a catalyst for gasification, thus resulting in a much higher burn-off of carbon [18].

The ash content of the sludges before steam activation for DRAW, DMAD, DSBS, KAN, KAW and GOS were 20.4, 39.6, 23.6, 37.3, 48.6 and 38.4%. The ash content of DSBS_S sludge was 8% lower after activation than DRAW_S, whereas the DRAW sludge had a lower ash content and thus should have been expected to present a lower ash content in its final state if it reacted with the steam reaction in the same manner. This may be further confirmation that the DSBS sludge could exhibit a greater degree of activation, perhaps through an increase in the dwell time, which would enhance the porosity, with a higher level of carbon removal and thus resulting in a higher ash content.

Surface Chemistry Tests

In addition to the physical properties of an adsorbent, the surface chemistry is important in influencing its adsorption behaviour [19, 20]. Therefore, FTIR analysis was performed in order to determine the surface functional groups that were present on the SBAs.

Figure 2 shows the FTIR spectra of various SBAs. All FTIR spectra were very similar except for the KAW_S. A sharp peak at 3642 cm^{-1} of KAW_S could be assigned to the O-H free functional group, which may be attributed to the formation of $Ca(OH)_2$. Any CaO present in the sludge will readily react with any moisture in the air thus changing to $Ca(OH)_2$. The peak at 3407–3445 cm^{-1} for all types of the sludge could be due to the O–H with H bonding, which can be attributed to some moisture content within the sample. Except KAW_S, the peaks at 1615–1617cm^{-1} can be assigned to C=O functional groups [3]. KAW_S presents peaks at 1637 cm^{-1} and 1456 cm^{-1} , which are outside the region for this functional group, and may be assigned to some oxygen functional groups that bond with the mineral content within the sludges since CHN analysis gave values that were near zero for this sludge (see Table 3) and thus, functional groups containing CHN should not be formed. All the SBAs produce peaks at 1040–1060 cm^{-1} which indicate the presence of Si–O–C and Si–O–Si functional groups [3,21,22]. For KAW_S, the presence of a peak at 916 cm^{-1} may due to the formation of micas [21], which may bond with Ca. The other bands below this wave number (for all SBAs) are mainly contributions from mineral content, which include whitelockite, feldspars and calcite [21,23].

Even though the surface functional groups of SBAs are very similar, the absorbance intensity of the surface functional groups, especially at 1040–1060 cm^{-1} , is obviously different. For example, DMAD, KAN and GOS have different peak to peak height ratios. Despite the ash content and CHN analyses being similar, the

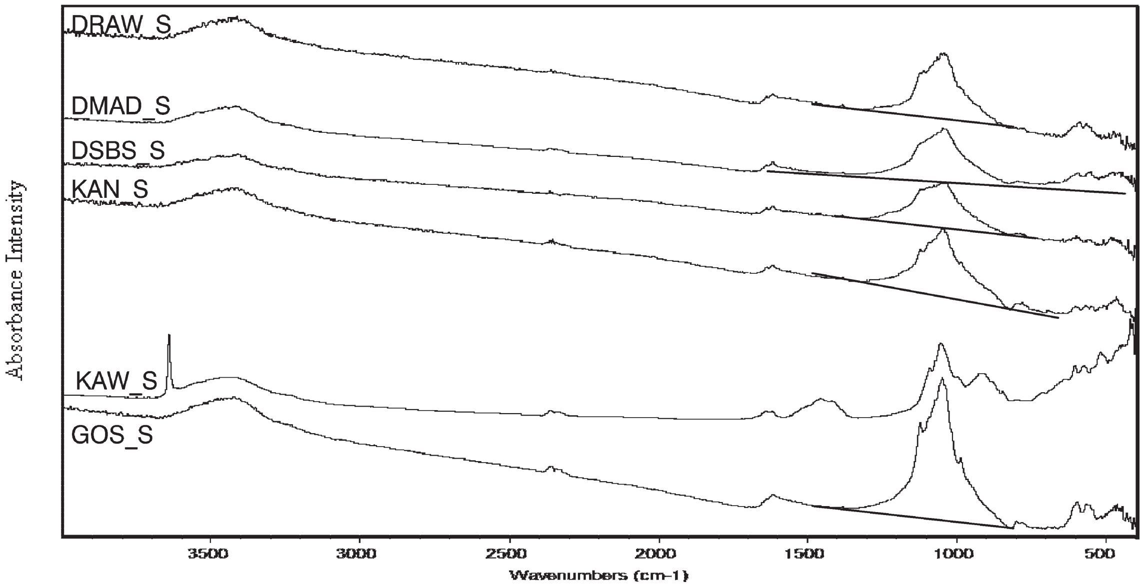


Figure 2. *FTIR of sludges and sludge based adsorbents.*

Si–O–Si content varies. This also indicated that after the digestion treatment, the sludges from different locations and origins yield a different ratio of mineral content within the ash.

CONCLUSIONS

In general, it can be said that sludges from different sources and treatment methods produce a range of activated carbons in terms of both their physical and chemical characteristics. Anaerobically digested sludges (without lime addition) yield the same physical properties (surface area), carbon and mineral content irrespective of source and treatment method after steam activation. The reason for these similarities may be attributed to the fact that the digestion process removes the same components from the carbonaceous content of the sludge. It can be said that the differences in carbonaceous content before digestion may be due to carbohydrates, fats and proteins which can vary among sources due to the different socio-economic conditions of the catchment areas connected to the wastewater treatment facility. The only significant difference between the digested sludges from different sources is the relative amount of minerals within the ash, which make a negligible contribution to the surface area of the SBA. However, the differing mineral content between sludges may have an effect on the adsorption properties of the SBA.

The RSM model has been shown to be a useful tool for identifying the optimal physical conditions for processing precursor carbon feedstock. However, each type of sludge used in this study whether it is anaerobically digested (with or without lime addition) aerobically digested or raw sludge, displays slight differences in their activation behaviour and thus, for true optimisation a unique RSM model is required for each sludge type.

Further, results suggest that sludges with lime added are least suitable for producing activated carbon due to their low carbon content and the acceleration of gasification reactions, which is attributable to their high calcium content.

Except for sludges with lime added, it can generally be said that sludges are a good potential precursor for adsorbents and can produce surface areas up to 270 m^2/g by steam activation. The best surface area obtained was from raw sludge.

The practical adsorption applications of these carbons are under investigation using endocrine disrupting chemicals, specifically Bisphenol A, which is a model EDC.

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Improved Dewatering by Hydrothermal Conversion of Sludge

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ABSTRACT: A growing demand for renewable energy resources, together with increasing criticism on the competition with food crop production caused by current production methods, has stimulated new interest for fuel production from sewage sludge. One of the processes to recover fuel from sludge is hydrothermal conversion (HTC), whereby the wet sludge undergoes a high temperature/high pressure treatment, with the possible addition of catalysts. In this study, the influence of subcritical HTC treatment with regard to sludge dewaterability was investigated. A range of different temperatures (150–240°C), pH values (3–11), and peroxide additions (0–150% of COD) were studied. It was shown that after hydrothermal treatment of sludge or predewatered sludge cake and subsequent mechanical dewatering, dry matter contents of up to 60% could be obtained, and that the cake mass after HTC decreased by a factor of 5 on average, compared to the untreated sludge. The HTC process also resulted in an enrichment of the inorganic matter in the final cakes, by solubilisation of the organic matter into an easily biodegradable form. The energy demand of the HTC process was low compared to drying by evaporation and might be partially provided by biofuels generated in the process, according to energetic calculations.

INTRODUCTION

DUE to the large-scale wastewater treatment operation launched in Europe in the last decades, increasing amounts of sewage sludge are being produced. This sludge is characterized by a troublesome dewaterability, due to its high content in organic matter,, as a result of which the amounts of sludge cake that are being disposed of are a multiple of the amount of produced dry matter. At the same time, concerns about climate change and increasing fossil fuel prices favor the exploitation of renewable energy resources. Increasing criticism on the competition of energy crops with food crop production is causing the industry to focus on other renewable energy supplies than agricultural crops. Considering these two issues, energy recovery from sewage sludge has a bright future. Such energy recovery is already being realised to some extent by anaerobic sludge digestion, an operation that decreases the sludge amount, thereby producing biogas with a high calorific value. Yet, even after sludge digestion, the sludge may contain a substantial amount of organic matter and exhibit limited dewaterability. In an ideal situation, all the organic material from the sludge would be transformed into usable energy forms (e.g. biogas, bio-oil or bio-coal), so that the final sludge only consists of well dewaterable inorganic solids. Many treatment techniques have been described in literature to reduce sludge volumes or increase dewaterability. These can be either biochemical (anaerobic digestion, fermentation), chemical (e.g. Kemicond process [1], or Fenton peroxidation [2]), thermal (e.g. pyrolysis, gasification, . . .) or thermochemical, a combination of the latter two techniques. Hydrothermal conversion (HTC)—also called thermolysis or hydrothermolysis—is a technique whereby wet organic matter is heated and pressurized to subcritical or supercritical conditions [3–8]. Chemicals can be added to enhance the process, making it a thermochemical operation. The present study aims to investigate the technical and economical feasibility of hydrothermal conversion (HTC) to convert the organic material in sludge into a soluble and biodegradable fraction and to assess the dewatering properties of the remaining sludge after HTC.

MATERIALS AND METHODS

Thickened municipal sewage sludge was sampled from the Ossemeersen wastewater treatment plant

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(Gent, Belgium) and stored in a fridge (4°C) for a maximum of 4 days prior to use. Sludge samples of 200g were subjected to hydrothermal conversion in a closed Parr 4651 high pressure reactor, connected to a Parr 4842 temperature controller, for one hour. Selected temperatures were 150°C, 195°C and 240°C. pH modifications were obtained by adding H_2SO_4 or NaOH. For some experiments, the sludge was treated with H_2O_2 as an oxidizing agent, dosed at 150% of the chemical oxygen demand.

Prior to dewatering, sludge samples were conditioned with the cationic polymer Zetag 7878FS40 (Ciba Specialty Chemicals) in a dose of 8 g/kg original dry matter. Dewatering was performed in a specially designed miniature piston filter press (30 ml volume), at 400 kPa pressure for 1000 seconds. The filter press contained a Nordifa Lainyl MC4/S5/6 piece of filter cloth. Determination of the dry matter content was performed by drying a sample at 105°C during 24h, whereas the volatile solids content was determined from calcining a sample at 600°C for 1h.

The electrophoretic mobility was measured with a Malvern Zetasizer IIc sample on a partially centrifuged sample. Chemical oxygen demand was determined by the classical potassium dichromate titration method and biological oxygen demand was determined by the oxytop method ([9]).

Calorimetric measurements on the sludge and sludge extracted phases was done on an IKA C7000 calorimeter after calibration with benzoic acid tablets.

RESULTS AND DISCUSSION

Influence of Temperature on Sludge Dewaterability and Cake Composition

Figure 1 shows the dry matter content obtained after dewatering the sludge treated in the HTC process, as well as the dry matter content of the untreated sludge after dewatering the control samples. It is clear that the HTC process enhances the dewaterability of the sludge remarkably. Whereas values of 20% dry matter content and less are encountered for untreated sludge, HTC delivers dry matter contents of 50% and up, especially at the higher HTC treatment temperatures (195°C and 240°C).

Even more important than the dewaterability is the final sludge mass obtained after dewatering the HTC treated sludge sample, as the latter will determine the ultimate disposal costs for the wastewater treatment plant. Figure 2 shows the relative cake mass after HTC followed by dewatering compared to the mass of sludge cake after dewatering the control sludge. On average, a 5-fold reduction is seen in the sludge cake mass, which confirms the benefits of the HTC treatment with regard to sludge dewaterability.

In order to explain these results, an analysis was made of the sludge and filtrate composition after HTC. Figure 3 shows the fraction of volatile solids in the cake obtained after HTC treatment, as well as the volatile solids fraction of cake obtained from the control sludge. Whereas the control sludge had a high volatile solids content of 60 to more than 70%, the HTC treatment delivered cakes with a volatile solids content as low as 30%, at the highest temperature of 240°C.

This indicates that a considerable amount of organic matter has been converted into a more soluble form. The resulting relative increase of non-volatiles or

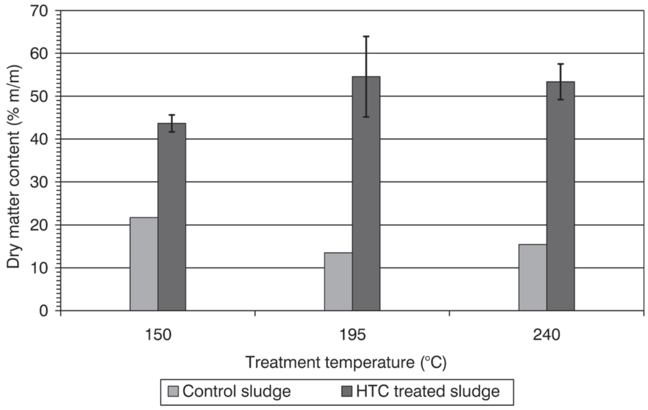

Figure 1. Dry matter content of sludge cakes obtained from pressure dewatering after HTC treatment or for untreated samples. The error bars represent standard deviations from three measurements.

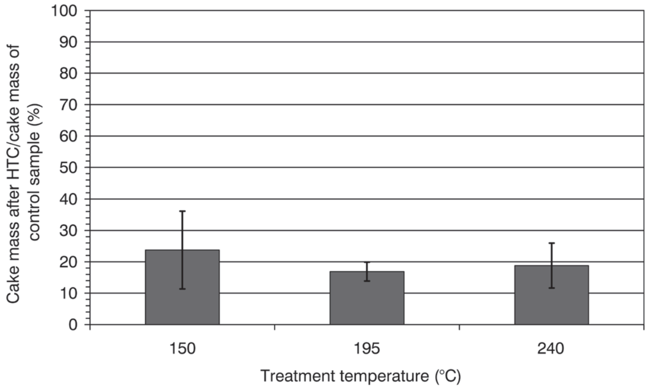

Figure 2. Relative cake mass after HTC followed by dewatering compared to the mass of sludge cake after dewatering the control sludge. The error bars represent standard deviations from four to six measurements.

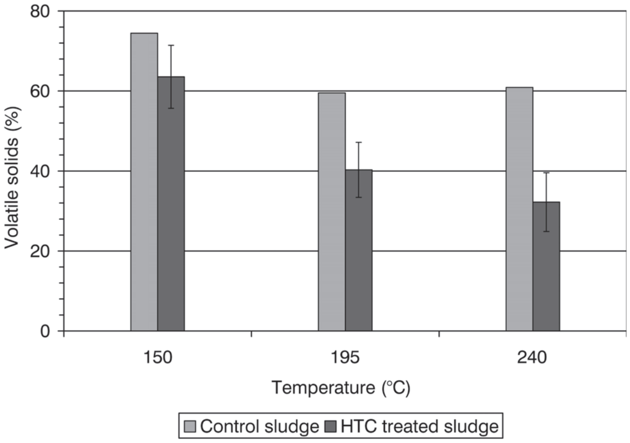

Figure 3. *Fraction of organic matter in the cake obtained after HTC treatment, as well as the organic matter fraction of cake obtained from the control sludge. The error bars represent standard deviations from three measurements.*

inorganics in the solid fraction can explain the improved dewaterability, thanks to a firmer structure and hence reduced compressibility of the material. Furthermore, extracellular polymeric substances (EPS), which are known to make up to 70% of the organic matter in sludge are considered to be responsible for the sludge's poor dewaterability due to their high water retention capacity ([10]). The improved dewaterability could therefore likely be explained as well by a reduction of these EPS.

This conversion of organic matter from a solid state to a soluble or dispersable state is confirmed by analyzing the chemical oxygen demand (COD) of the filtrate before and after HTC. Figure 4 shows the COD levels of the filtrate obtained after dewatering untreated and HTC treated sludge. The data, expressed as percentage of the original COD content of the sludge sample show that there is an important shift of the COD from the cake to the liquid phase.

The HTC process does not only convert compounds from the solid phase into the liquid phase, but an enhanced breakdown or conversion can also lead to the formation of volatile compounds, that end up in the gas phase. It was noted that in the case of HTC treatment, 21% of the dry matter had moved to the gas phase during the treatment at 195°C and even 30% at 240°C. Furthermore, the conversion process might have enhanced the biodegradability of the organic phase in some cases. The ratio of biological oxygen demand to chemical oxygen demand measured for the filtrate after HTC treatment at various temperatures in this study was 84 ± 15 % (average ± standard deviation), compared to 73% for the filtrate from the original sludge. This opens possibilities for an advanced biological treatment of the filtrate, e.g. by anaerobic digestion, allowing a further harvesting of energy through the production of biogas.

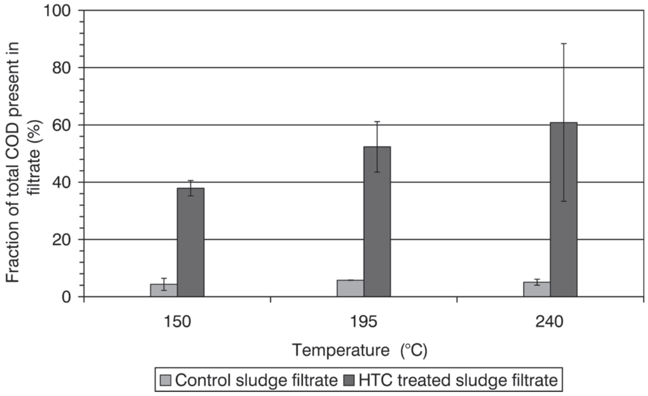

Figure 4. *Chemical oxygen demand of filtrate expressed as percentage of chemical oxygen demand present in sludge. The error bars represent standard deviations from two measurements.*

The Influence of Chemical Parameters on the Sludge Composition

Referring to the results described above, it was seen that the highest temperature (240°C) was the most effective in improving the sludge dewaterability and reducing the cake mass. This temperature was therefore selected as a starting point to investigate the beneficial effect of chemical pre-treatment of the sludge.

Figure 5 displays the cake dry matter contents from dewatered sludge after HTC at different pH values (a), as well as the final relative cake mass (b). It is noticed that the acid treatment causes the highest dry matter contents, and the lowest final cake masses.

One of the reasons why the acid treatment shows an increased dewaterability might be the change in surface charge, which allows for better coagulation of the individual particles. Figure 6, which depicts the electrophoretic mobility of the sludge particles as a function of pH after HTC treatment, clearly demonstrates that the particles are neutralized when the pH is decreased. In this case, the interparticulate repulsive forces are reduced and filtration is improved by an improved porosity of the system. From measurements of pH before and after HTC treatment, it was also noticed that neither the temperature of the HTC treatment, nor the addition of H_2O_2 did have an important effect on the pH that was obtained after HTC treatment. In general, it was noted that the pH after HTC treatment tended to have shifted to neutral or

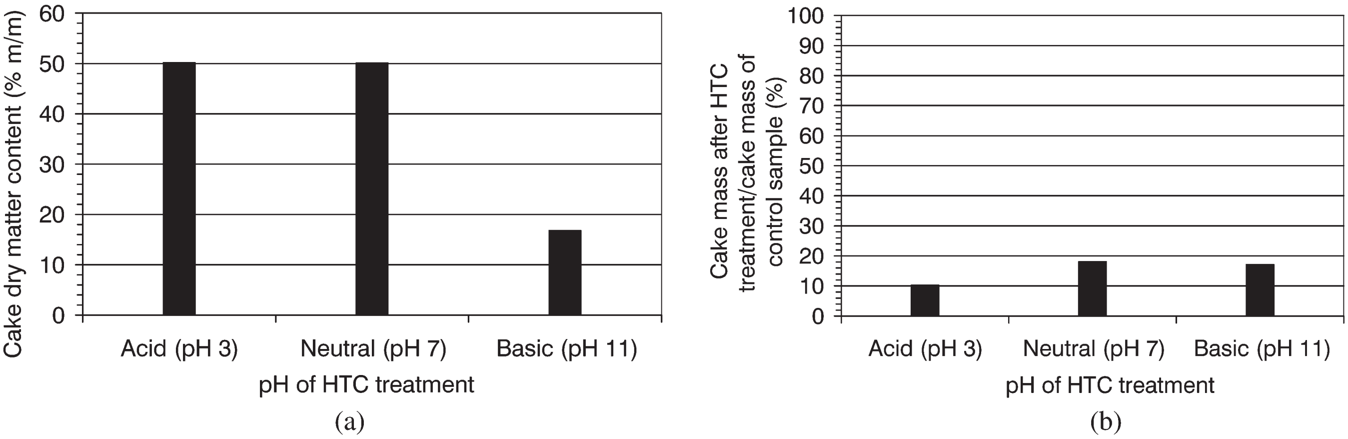

Figure 5. *(a) Cake dry matter content and (b) remaining cake mass (relative to control) for HTC treatments at different pH conditions.*

slightly acidic conditions. Therefore, it can be hypothesized that the final pH is the determining factor for the electrophoretic mobility.

In an attempt to further reduce the organic content of the sludge, hydrogen peroxide (H_2O_2) was added as an oxidant, in a dose of 150% of the chemical oxygen demand. It was observed that in some cases the final cake weight could be further reduced in this way, although the results were not always consistent. This might be due to the limited oxidation capacities of hydrogen peroxide when used as sole reagent. It is known that hydrogen peroxide combined with other reagents, e.g. iron ions (denoted as Fenton's reagent), is a much more powerful oxidant [2]. Also the cost of hydrogen peroxide used at the levels in the present study could not be justified by the additional reduction in cake mass.

Energetic Considerations

Energy studies of thermal processes like the one depicted in this work are difficult to perform without full scale reactor data. Yet, an approximate assessment of the energy requirements can help in judging the technical and economical feasibility of the process, and is therefore given below.

The amount of energy required to bring water as a saturated liquid to a temperature of 240°C is about 1000 kJ/kg, which is roughly 40% of the amount of energy required for evaporation. With a current natural gas price of about 0.03 € per kWh, and assuming that sludge mainly consists of water, this implies an energy cost of about 10 Euro per ton of water. It is clear that the final cost for sludge HTC treatment will be determined by its initial water content, and therefore a

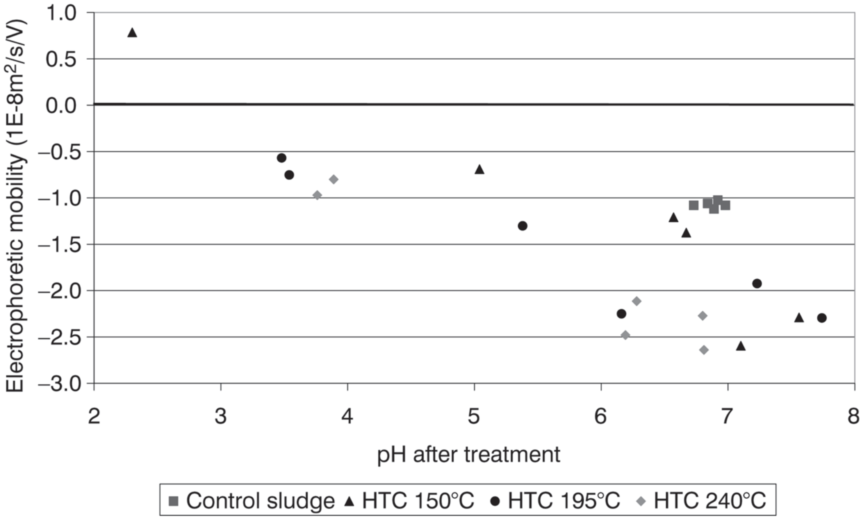

Figure 6. *Electrophoretic mobility of a series of HTC treated sludge samples at different pH values indicating neutralization of the surface charge under acidic conditions.*

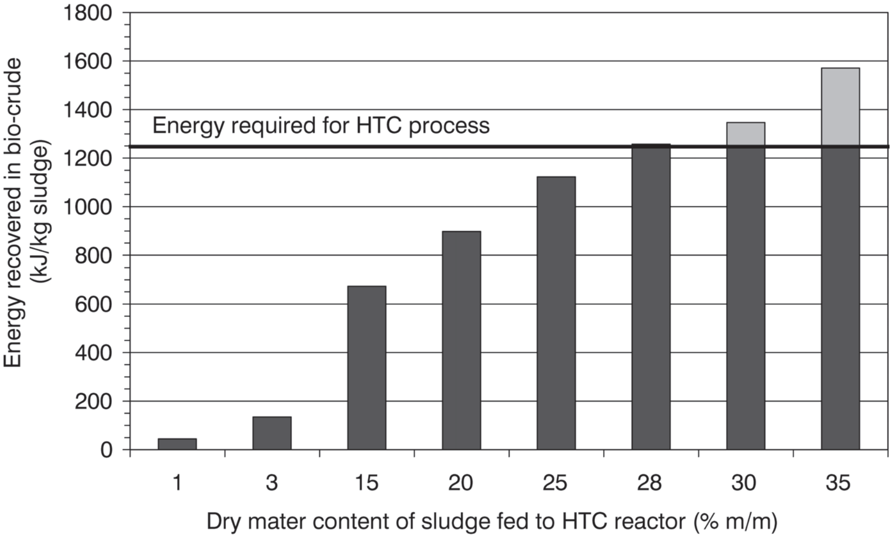

Figure 7. *Calculated energy recovery for the HTC process from transformation of sludge dry matter into crude oil as function of initial sludge dry matter content. The horizontal blue line represents the energy requirements of the HTC process (1250 KJ/kg sludge).*

pre-thickening and/or dewatering of the sludge prior to hydrothermal conversion is desirable. Yet the energy requirements for the HTC treatment can be partially or even fully provided by the process itself. The hydrothermal conversion showed to generate a crude oily phase, which was readily extracted by means of dichloromethane. Calorimetric measurements showed that the original sludge had an energy density of 14.3 MJ/kg dry matter, whereas the retrieved crude oil had an energy density of 31.1 MJ/kg. The energy recovery to the oil was optimized by analyzing the results of a series of treatments and it was found that by adding a catalyst to the process (Na_2CO_3, dosed at 8% of dry matter), increasing the temperature to 300°C and increasing the dry matter content to 14% by prethickening, an energy recovery of 31.4% could be realized into the oily phase. This means that 31.4% of the calorific value of the sludge was converted into the crude oil. When considering these energetic values (14.3 MJ/kg dry matter; energy conversion into oil at 31.4% efficiency) and further assuming that the specific heat capacity of sludge equals that of water, and that heating sludge as a saturated liquid to 300°C requires 1250 kJ/kg of water, the energy balance of the HTC process can be estimated for sludges with different initial dry matter contents (Figure 7).

From these results, it can be shown that when sludge is predewatered to about 28% dry matter, a typical dewatering result for a wastewater treatment plant, the crude oil produced by the HTC treatment provides enough energy to sustain the process. It should be noted that the tests in this study were performed in a closed batch reactor. In full scale processes, which run continuously, energy conversion and usage can further be optimized by using heat exchangers for energy recovery. In addition to this, the gases formed during HTC might have some calorific value as well, although this has not been tested.

As an alternative to producing oil, anaerobic digestion of the filtrate might be considered in order to produce a combustible biogas. It is known that after anaerobic digestion of activated sludge, a considerable fraction of organic matter is still not degraded and ends up in the sludge cake after dewatering [11]. This is often due to the biochemical composition of the sludge, which contains large amounts of poorly biodegradable biopolymers like EPS, lignin, etc. The 'cracking' action produced by HTC might enable the biological breakdown of these recalcitrant products in a second anaerobic digestion process. The good biodegradability of the filtrate, as mentioned above, offers the possibility of coupling HTC to anaerobic digestion.

In addition to the energy requirements, investment and operation costs will also arise for the HTC installation and the second dewatering operation. These will ultimately determine the economical feasibility of the process.

CONCLUSIONS

Hydrothermal conversion of sewage sludge was studied under a variety of experimental conditions, with a special focus on the dewatering properties of the treated sludge. It was shown that the dissolution of organic matter into the liquid phase markedly increased the dewaterability of the remaining sludge. Furthermore, the reduction in organic matter content and improved dewaterability, caused the final sludge cake mass to decrease with a factor of five to ten, compared to the cake mass obtained from dewatering the control sludge. The conversion process also caused a shift of dry matter from the solid phase to the liquid and gas phase. Initial results suggest that acidification improves the sludge dewatering properties, whereas hydrogen peroxide has limited effects. Finally, energy calculations showed that a crude oil produced by the process, can be used to provide for the energy requirements of the conversion reaction, when the initial water content of the sludge is reduced by mechanical dewatering.

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Sludge Drying Reed Beds: A Case Study

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ABSTRACT: Sludge drying reed beds stand as a suitable technology for sludge management in certain situations. This work examines two full-scale sludge drying reed beds systems located in a Mediterranean region. Samples of influent sludge and sludge accumulated in the reed beds were analysed for total solids (TS), volatile solids (VS), chemical oxygen demand, nutrients, heavy metals and faecal bacteria indicators. The results show a high dewatering degree (from 1–3 to 20–22%TS), progressive organic matter removal (10–30% VS/TS) and sludge mineralization during sludge storage. The concentration of nutrients, heavy metals and faecal bacteria indicators suggest a good quality of the sludge for land application.

INTRODUCTION

SLUDGE drying reed beds consist of concrete basins or land excavations, which are filled with a gravel layer and planted with emergent rooted wetland vegetation such as *Phragmites australis* (common reed). They have been used for sewage sludge treatment since the end of 1980's [1].

In these systems the sludge water content flows vertically through the gravel filter leaving a concentrated solid sludge on the surface. The sludge treated in such systems is dewatered by water percolation and plants evapotranspiration. Moreover, reed beds allow for a certain degree of sludge stabilization. The final product of the treatment, resulting from both dewatering and biodegradation processes, may be suitable for land application [2], favouring sludge reuse instead of sludge disposal in landfill or sludge incineration.

Most studies on sludge drying reed beds have been carried out in Northern Europe [3], showing excellent results. This technology is by far less common in the Mediterranean region. The purpose of this study was to evaluate the efficiency of two full-scale drying reed beds from a Mediterranean region in terms of sludge dewatering, mineralization and hyginenisation. To this end, the operation of the systems was characterized and the composition of untreated and treated sludge compared.

MATERIALS AND METHODS

The studied systems are located in the wastewater treatment plants (WWTP) of Alpens (800 person equivalent (PE), 3 drying reed beds) and Sant Boi de Lluçanès (1500 PE, 6 drying reed beds), in the province of Barcelona (Catalonia, Spain). Both facilities are operated by the company Depuradores d'Osona S.L. since 2006 (process start-up).

The reed beds in Alpens have a total surface area of 198 m^2, with a total nominal volume of 109 m^3 for sludge accumulation. The total surface area in Sant Boi de Lluçanès is 324 m^2, and the total nominal volume is 178 m^3. The draining layer (55 cm height) consists of gravel and sand, which is planted with *Phragmites australis.*

The beds are fed with waste activated sludge from the activated sludge—extended aeration unit in the WWTP. The surface sludge loading rates (around 50 kg TS/m^2·year) are within the range suggested in the literature [2].

Sludge characterization was carried out during two sampling campaigns. In each facility, influent sludge and sludge stored in a representative drying reed bed were analysed. Sludge thickness inside of this bed was also measured. Sample cores were collected from three locations along a central transect of the bed. In each sample Total and Volatile Solids (TS and VS), Chemical Oxygen Demand (COD), Total Kjehldahl Nitrogen (TKN), Total Phosphorus (TP), heavy metals and faecal bacteria indicators (*Salmonella sp.* and *Escherichia*

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coli) were analysed in triplicate using Standard Methods [4].

RESULTS AND DISCUSSION

One of the most important parameters in this type of systems is the sludge thickness increasing rate, which determines the annual volume reduction for sludge accumulation and dictates the lifespan of the system. According to the sludge height measured and considering the period between both campaigns, the annual increase of the sludge layer thickness is around 7 cm/year in Alpens and 30 cm/year in Sant Boi de Lluçanès. The first value is in accordance with the maximum increase (10 cm/year) recommended by Nielsen (2003) [2]. The second one, considerably higher, might be attributed to an excessive loading of the beds during the start-up period, due to operation problems in the feeding system.

Sludge dewatering is successfully achieved in both facilities, as shown by the TS results in Table 1. A systematic rise in TS concentration from the influent sludge (0.7–2.9%) to the sludge stored in the beds (16–29%) was observed. This actually means that sludge moisture decreases from 97–99% to 70–75% within the beds, with subsequent decrease in the sludge volume to be disposed of at the end of the treatment. Initially, part of the water content in the sludge percolates through the gravel filter (i.e. lixiviates), while another part is progressively evapotranspirated by the plants during sludge storage. Moreover, at the end of each operating cycle (up to 10 years), there is a resting period that lasts around 1 year (without sludge feeding), in which the solids content is further increased up to 30% [2]. In this way, the solids concentration obtained in the final product of drying reed beds systems is similar to that of conventional treatments such as centrifuges, vacuum filters and belt presses [5, 6].

Table 1. Total Solids (TS), Volatile Solids (VS) and Chemical Oxygen Demand (COD) Concentration in Sludge Samples from Both Drying Reed Beds.

		Alpens	Sant Boi de Lluçanès
TS (%)	Influent	1.09 ± 0.42	2.86 ± 0.05
	Bed	24 ± 5.27	20.46 ± 4.61
VS (% TS)	Influent	59.74 ± 8.5	52.21 ± 1.09
	Bed	39.45 ± 8.3	38.51 ± 5.3
COD (g/Kg TS)	Influent	915 ± 32	—
	Bed	534 ± 110	506 ± 100

The results show a certain degree of sludge stabilization during sludge storage, as indicated by the decrease in VS content (Table 1) from the influent (52–67% VS/TS) to the sludge accumulated in the beds (32–47% VS/TS). The same pattern was observed in terms of COD. Similar trends are reported by Hardej and Ozimek (2002) [1]. It should be noticed that VS concentration in the influent (52–67% VS/TS) is relatively low compared to other sludges (60–80% VS/TS)[5, 6], since it consists of waste activated sludge from an extended aeration unit (i.e. it is partially stabilized). For this reason, VS removal (10–30%) is lower than typical values for other stabilization processes, such as anaerobic digestion [5,6]. Nevertheless, the VS content in the sludge from the reed beds is in the range of anaerobic digested sludge [5,6].

In general, the concentration of nutrients for influent sludge samples (5.7–4.7% TKN/TS and 0.72% TP/TS) was higher than the one found in the reed bed's sludge (3.4–2.6% TKN/TS and 0.08% TP/TS) (Table 2). Regarding TKN, the results suggest that some of the organic nitrogen content is transformed into mineral forms, such as nitrates, which are found in lixiviates

Table 2. Concentration of Nutrients, Heavy Metals and Faecal Bacteria Indicators in Sludge Samples for Both Drying Reed Beds.

			Alpens	Sant Boi de Lluçanès
TKN (% TS)		Influent	5.75 ± 0.18	4.66 ± 0.05
		Bed	3.39 ± 0.23	2.62 ± 0.51
TP (% TS)*		Influent	0.72 ± 0.01	—
		Bed	0.08 ± 0.07	0.08 ± 0.07
Heavy Metals (ppm)	Cr	Influent	35.8	36.4
		Bed	55.4	48.8
	Ni	Influent	27.9	50.2
		Bed	29.4	36.3
	Cu	Influent	227	183
		Bed	392	161.7
	Zn	Influent	348	609
		Bed	551	533.5
	Cd	Influent	0.41	0.66
		Bed	0.63	0.69
	Hg	Influent	4.29	1.99
		Bed	5.27	3.54
	Pb	Influent	30.3	51.0
		Bed	51.8	42.8
Salmonella sp. (presence-absence /25 g)		Influent	Absence	Absence
		Bed	Absence	Presence
E. coli (MPN/g)		Influent	1100	1100
		Bed	460	1100

(data not shown). Similarly, a certain amount of TP in lixiviates was also found (data not shown).

With respect to heavy metals (Table 2), the concentration of all the heavy metals analysed in the reed bed was high compared to the influent sludge from Alpens facility (the results are not so clear for Sant Boi de Lluçanès). In practice, heavy metals tend to accumulate in the system and their concentration increases together with the TS increase. It is worthwhile mentioning that the results in Table 2 are well below the limit concentrations of heavy metals in sludge to be used on land, regulated by the Council Directive 86/278/CEE [7], and those proposed in the 3rd Draft EU Working Document on Sludge [8]. However, these are only preliminary results on the quality of the final product for land application. The accumulation of heavy metals during the treatment makes it necessary to determine the quality of the final product (at the end of each operating cycle).

Although it is not yet regulated, faecal bacteria indicators were also analysed according to the 3rd Draft EU Working Document on Sludge [8]. While *E. coli* was always present, *Salmonella sp.* was only detected in the bed of Sant Boi de Lluçanès. Further analyses would be required to evaluate hygienisation aspects of this technology in the long term.

CONCLUSIONS

This work studied the performance of full-scale sludge drying reed beds from a Mediterranean region, by analysing and comparing the characteristics of influent sludge and sludge stored in the reed beds. In terms of sludge dewatering, the systems are as efficient as conventional technologies (such as centrifuges), as indicated by the TS increase (from 1–3 to 16–29% TS). Furthermore, progressive sludge stabilization is suggested by the decrease in VS concentration (from 52–67 to 32–47% VS/TS), reaching values similar to those of traditional stabilization treatments (such as anaerobic digestion). In general, the sludge composition suggests its suitability for land application, fulfilling the regulated heavy metals limit concentrations. On the whole, the studied systems demonstrate the efficiency of drying reed beds technology and its potential use in the context of small and remote WWTP in Mediterranean regions.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	**Core Temp. (DSC peak)**	**T_E**	**Char Yield, %**
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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