Comparison of the impact of three drying processes on the characteristics of Wastewater sludge

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Abstract

Sewage sludge constitute an important by-product of municipal wastewater treatment plants. Their production has grown exponentially during the last decade and was estimated at more than 9 million tons of dry matter in Europe in 2013. Sustainable valorization or disposal options involve direct amendment for crop production or composting. A step of drying is commonly used before, which aims at sanitizing and at reducing the volume of sludge thus lowering the transportation cost. Drying pretreatment processes includes thermal drying, Advanced Oxidation Processes (AOP) or methanation which has the supplementary advantage to produce energy.

The objective of this study was to compare the influence of three different processes: thermal drying, electron beam (e-beam) irradiation and anaerobic digestion on the organic matter (OM) characteristics of wastewater sludge (WWS). Indeed the knowledge of the characteristics of this residual biomass is essential to improve their valorization. WWSs OM were investigated at the global scale using elemental analysis, attenuated total reflectance Fourier transform infrared spectroscopy, thermogravimetric analysis and OM fractionation. Double-shot thermochemolysis coupled with gas chromatography and mass spectrometry (GCMS) which has been demonstrated to be an accurate and efficient method for characterizing WWS, was used to compare the diversity and distribution of the molecular contents.

A strong influence of thermal drying on lipid and humic-like substances contents was observed through OM fractionation, which traduced a weakening of the OM. The anaerobic digestion induced an increase in lipids for the hydrolysis phase followed by a decrease which correlates with the volume reduction of sludge by about 30%. E-beam induced change in the distribution of the different pools of organic matter depending on the irradiation dose.

At the molecular scale, fatty acids, steroids and aromatics were the main thermochemolysis products in all the samples. The thermal drying induced an increase in fatty acids and steroids, probably released from the refractory OM. The anaerobic digestion modified exclusively the amount and distribution of fatty acids while e-beam induced a decrease in all the identified compounds including aromatics. Finally double-shot thermochemolysis-GCMS demonstrated the impact of 3 drying processes on the molecular contents of WWS, which can have consequences on its valorisation.

Introduction

Sludge management into a wastewater treatment plant (WWTP) represents major capital and operating expenditures and is an important technical challenge. The main limitation in sludge handling is dewatering operations consequently several advanced sludge treatments (AST) including thermal hydrolysis, chemical oxidation and biological digestion have been developed [1,2]. In WWS, microorganisms are embedded and protected into a strongly hydrated matrix of extracellular polymeric substances (EPS). EPS mainly consisted of different classes of organic compounds such as proteins, polysaccharides, lipids and humic like substances [3-5]. It has been demonstrated that proteins and saccharides represent up to 80% of the total EPS and the remaining

20% might be attributed to humic compounds, uronic acid, nucleic and lipids [6,2]. The main technical strategy to improve WWS dewatering operation is the degradation of EPS.

Compared to other AST techniques, advanced oxidation process seems the most promising results with reduced operating cost [7]. The most common radical species generated during the AOPs is the hydroxyl radical ($HO^{\bullet}$). Several AOPs were studied in the literature in order to improve sludge dewatering: Wet oxidation process, Ozonation, Fenton's like reaction, etc… For example, Yin et al. 2007 found that an Ozone/hydrogen peroxide/microwave process could release more than 30% of total phosphor and 20% of the total kjeldahl nitrogen into the water phase of the sludge. In addition up to 37% of the total organic carbon was solubilized from the sludge matrix [8].

Among all existing AOPs, the electron beam (e-beam) irradiation process presents important advantages due to its high-flow rate treatment capacity and its small footprint [9]. E-beam irradiation might interact with the whole sludge matrix inducing strong modification into bacteria, organic compounds and micropollutants. It is commonly observed that an irradiation dose lower than 1 kGy (i.e: 1 kJ/m^3) is sufficient to reach a high degree of disinfection [10]. Changqing et al. (2012) observed that the soluble chemical oxygen demand, soluble nitrogen and UV absorption intensity of the water phase of the sludge strongly increased while the mixed liquor suspended solids content considerably decreased with an increasing doses up to 20 kGy [11]. However, according to authors' best knowledge no study was reported on the characterization at molecular scale of bulk organic of WWS. Such work might improve the understanding of organic matter modification occurring during e-beam irradiation in order to optimize AST.

Anaerobic digestion process transforms organic matter into biogas. The latter consists mainly of methane (CH_4) and carbon dioxide (CO_2) gazes. The primary interest of anaerobic digestion of the sewage sludge is to reduce its volume and to value produced energy. The studies and projects dedicated to biogas are multiplying, thanks to the will of European states to support the production sectors of "*green*" energy through several new legislations. In France, the trend in the development of anaerobic digestion of sludge from sewage treatment plants comes from the development of biowaste co-digestion (from the food industry, the separate collection of household waste, organic waste from kitchens, etc.). The biogas from WWTP sector would be a positive development in the number of facilities, increasing to 130 installations in 2020 [12]. Anaerobic digestion allows 40 to 50% reduction of the sludge organic matter (SOM) [13]. Biogas production is in the order of 0.8 to 1.2 Nm^3 / $kg_{\text{consumed SOM}}$. However, it remains as a result of the process a significant amount of organic material to dispose of or to recover in agriculture through soil amendment. A better knowledge of this organic matter (OM) is essential to (i) estimate its interaction with micro-pollutants and soil OM as part of the amendment but also (ii) consider other recovery methods. Many researches were done to evaluate the impact of operating conditions on the quality and quantity of the biogas [14-16], but there is to author's knowledge no study on molecular evolution of organic matter in the anaerobic digestion process of sewage sludge.

There are many factors affecting the biodigestion and the generation of gas, the pH, the temperature and the loading rate. A deviation from normal operating temperature and pH could induce a drop of digester performance due to an inhibition of mesophilic bacteria. The appropriate temperature and pH are usually set at 35°C and 6.5 to 7.5, respectively. The loading rate of most municipal digester is ranged between 0.5 and 1.6 kg volatile solid per m^3 of sludge per day. In addition, the carbon to nitrogen ratio (C/N) is often recommended to high values ranged from 20/1 to 30/1. Indeed, high concentration of nitrogen could decrease the methanogen activity, inhibiting the aerobic digestion process. Methanation is often divided into three stages - the acidogenesis, acetogenesis and methanogenesis - although actually, they tend to occur simultaneously.

The objective of this study was to compare the influence of three different processes: thermal drying, electron beam (e-beam) irradiation and anaerobic digestion on the organic matter (OM) characteristics of wastewater sludge (WWS). Indeed the knowledge of the characteristics of this residual biomass is essential to improve their valorization. WWSs OM were investigated at the global scale using elemental analysis, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA-DSC) and OM fractionation. Double-shot thermochemolysis coupled with gas chromatography and mass spectrometry (GCMS) was used to compare the diversity and distribution of the molecular contents.

2. Materials and methods

2.1. Wastewater treatment plants and sludge line

Floated sludge samples (LF-0) were collected from the wastewater treatment plant of Poitiers (semi-separative urban network, 152,200 population equivalent, sludge residence time: 48 hours, sludge production: 1,794 t dry matter a year) on April 2015.

The WWT plant of Poitiers is based on an activated sludge process with an advanced dephosphatation treatment step. The secondary effluent (treated wastewater) is separated from the solid compounds (sludge) via a settling tank ($FeCl_3$ is added to improve settling velocity). While secondary effluent is directly rejected to the environment (if regulation limits are reached) sludge are subjected to further processes.

2.2. Thermal drying

Dried sludge (LF-85) was produced at the WWT plant of Poitiers thanks to a thin film conductive drier working at 85°C. The 6 mm pellets (LF-120) are produced using a dryer-pelletizer working at 120°C. The sludge pellets are then stored at ambient temperature before agricultural recycling or incineration. The total sludge production is equal to 1,357 tons of DS/year. Before drying the concentrated sludge is mixed with a cationic polymer (ZETAG, BASF France) at a concentration of 15 kg per ton of DS. 68 % of the total WWS amount is used in co-composting and 32 % is transformed into pellets.

2.3. Electron beam oxidation

Sludge irradiation was performed on fresh sampled sludge, thanks to an electron accelerator (Van de Graaff 3 MeV, VIVIRAD, France). The electron beam was produced by a heated and high voltage tungsten filament. Two radiation doses were investigated : 1.25 kGy (B1) and 50 kGy (B50).

An irradiation dose of 50 kGy corresponds to 43.1s exposure time according to the equation: ($T_{expo} = \frac{irradiation\ dose}{DDm}$). The number of passes under the electron beam was set at 21.

After irradiation, the samples were frozen at -20°C and lyophilised to enable their characterisation.

2.4. Digestion

Methanogenic bacteria were provided by the biogas plant of Thouars (Tiper-Methaneo, Deux-Sèvres, France). Methanogenic bacterias are kept under anaerobic conditions at 37°C before the pilot startup to maintain their capacity and ensure their methanogenic activity.

The bioreactor used was a BioFlo Fermentors & CelliGen® Bioreactors 115 with a capacity of 7L purchased from New Brunswick® from Eppendorf. The heating is controlled thanks to an external jacket around the feed glass tank. The feed tank is sealed with a steel lid equipped with nozzles for all accessories. The ventilation and evacuation tubing gas are equipped with sterile membrane filters to avoid any contamination. Four perilstatic pumps could be used to purge or feed the biological mixed. Finally, several Electrodes and sensors might be used to control the temperature, pH.

Once the biological mix (sludge + inoculum) was introduced into the bioreactor, the mixture was aerated one hour with nitrogen to remove oxygen and to operate into anaerobic conditions. The mixture was kept under constant blade stirring at 200 rpm. The reactor temperature was maintained at 37 °C. The biogaz production was measured using a graduated cylinder filled with tap water. The glassware was connected to the bioreactor and to a separation funnel. The amount of biogaz produced was measured every 24 hours according to the variation of the water level in the graduated cylinder. Every 7 days, 200 ml of digest were removed from the pilot via peristaltic pumps to maintain anaerobic conditions. The samples (D1, D2, D3, D4) were frozen (-20 °C) and lyophilized (-50 °C; 0.034 mbar) and then stored at -20 ° C until analysis.

2.5. pH measurement

The sludge were separated by centrifugation into a supernatant and a pellet. The pH of the supernatant was measured directly. The pellet was diluted in ultra- pure water 5/1 in order to measure the pH of the suspension.

2.6. Elemental Analysis

The OM content (i.e: mixed liquor volatile suspended solids) of WWS was determined from 3g sample, by combustion at 500°C for 4 h. Elemental analysis (C, H, N) was carried out on 1 mg sample using an elemental analyser (Thermo Electron Corporation Flash EA 1112 series) by catalytic combustion under oxygen at 970°C. To determine the sulfur percentage, 1 mg of vanadium oxide was added to 1 mg of the raw sludge.

2.7 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra were recorded on a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with a diamond crystal. Spectra were taken between 4000 and 650 cm^{-1} with a resolution of 4 cm^{-1}. 16 Scans were collected per spectrum. In an aim of consistency and to allow comparison, the spectra are normalized to the C-H band (2960 cm^{-1}).

2.8 Chemical fractionation

The OM was fractionated according to the following protocol. Lipids were extracted from 10 g WWSP with 3 x 240 mL dichloromethane/methanol (2/1) using a Speed Extractor (Buchi). The extraction temperature was set to 80°C, nitrogen pressure was 50 bars, and the solvent contact time with the pellets was 5 min. The solid remaining after extraction was the residue.

“Humic” and “fulvic acids” were extracted from the residue by 0.1 M NaOH (10 mL per g) under a nitrogen atmosphere in order to prevent OM oxydation. “Humic acids” were separated from “fulvic acids” by acidification to pH 1 (1 M HCl solution) and centrifugation (20 min, 8000 g). The alkaline-insoluble residue corresponded to “humin”.

2.9. DSC/ATG

DSC and TGA were carried out on a TA Instruments SDT Q600. WWSP was analyzed without any pre-treatment. The analysis was performed using platinum crucibles in air (combustion) atmosphere. The following conditions were employed: heating rate of 5°C min^{-1} from 25 to 900°C and an isotherm of 5 min at 900°C. A flow-rate of 100 $cm^3.min^{-1}$ of air was maintained during the analysis.

2.10. Thermochemolysis (THM-GC/MS)

Thermochemolysis was done using tetramethyl ammonium hydroxide (TMAH) as alkylating agent using a temperature ramp from 100 °C to 350 °C with a temperature increase of 500 $°C.min^{-1}$. The pyrolyzer was a Frontier Lab EGA 2020 pyrolyzer equipped with an AS-1020E auto-shot sampler coupled with GCMS (Shimadzu QP 2010 Ultra). 0.5 mg of lipids were mixed with 5 µL of TMAH methanolic solution 50/50 (v/v) in methanol and then placed in an inox cup. GC separations were done using a capillary column (30 m long, 0.25 mm i.d., 0.25 µm phase thickness). The injector temperature was set at 250°C. Column temperature was programmed from 50 to 300 °C at a rate of 5 $°C.min^{-1}$ and then kept at 300 °C for 9 min. The detector was a quadrupolar mass spectrometer. The ionization mode was electron impact (70 eV) and the source temperature was 220 °C.

The organic compounds were identified on the basis of their GC retention times and by comparison of their mass spectra with those of standards and library data (NIST).

Quantification was done using calibration standards (hexadecanoic acid, coprostanol and styrene) as describe by Collard et al. (2015) [17].

3. Results and discussion

3.1. Bulk properties

The elemental composition (table 1) and ash content (table 2) are in agreement with those previously determined for activated sludge [1].

Table 1: pH and elemental analysis of sludge

	pH +/- 0.2	C (%) +/- 1.2	H (%) +/- 0.3	N (%) +/- 0.2
LF-0	6.6	35.3	5.4	6.0
LF-85	6.7	36.5	5.6	6.4
LF-120	6.6	38.5	5.8	6.8
B-1	6.4	37.6	5.0	6.8
B-50	6.0	39.7	5.5	7.0
D-1	6.2	37.2	5.3	6.8
D-2	7.4	36.6	5.5	6.6
D-3	7.2	36.5	5.4	6.7
D-4	7.2	37.1	5.6	6.8

Table 2: chemical fractionation and ash content (%)

	Lipids	Fulvic acids	Humic acids	Humin	ash
LF-0	12	20	7	38	23
LF-85	13	17	9	39	22
LF-120	22	32	12	9	25
B-1	8	10	5	43	34
B-50	5	25	7	41	23
D-1	15	18	7	38	22
D-2	10	17	6	40	27
D-3	7	18	6	39	30
D-4	6	18	7	37	32

ATR and diffuse reflectance FTIR spectroscopy have been used to characterize or monitor the transformations of different fractions of OM of environmental samples such as composts or sewage sludge [18]. ATR-FTIR spectra exhibited the following peaks wave numbers: 3270 cm^{-1} (OH stretch), 3180 cm^{-1} (NH_2 stretch of amides) [19], 2925 cm^{-1} and 2855 cm^{-1} (aliphatic C-H stretch), 1630 cm^{-1} (O-H bond), 1540 cm^{-1} (C=O of amides) [20], 1250 cm^{-1} (C-O of carboxylic acids or C-N of amides), 1030 cm^{-1} (C-O stretch of polysaccharides) [17, 21].

The DSC curves show two exothermic phenomena corresponding respectively to volatilization of light compounds such as aliphatic molecules or carbohydrates and to oxidation of high molecular weight components [22]. The endotherm observed between 25 and 150 °C is mainly related to dehydration reactions. The two exothermic phenomena corresponding to the OM decomposition are observed in the 200–600 °C range. The first one, associated with desorption of aliphatic compounds, is observed between 200 and 350 °C. The second one, associated with the degradation of more complex aromatic structures, is observed between 400 and 550 °C.

The chemical fractionation according to the IHSS protocol was used to monitor transformation such as complexification or weakening of the organic matter. Four fractions of OM are obtained according to their solubility [23]. The relative abundances of each fraction are reported table 2.

3.1 Thermal drying

The LF-0 sludge was dried at 85°C (LF-85) to reduce water content then pelletised at 120 °C (LF-120). The O/C and C/N ratios which are respectively linked with oxidation and biodegradability remained stable (table 1) during the thermal drying process [24].

The C-O/C-H ratio determined from ATR-FTIR spectra decreased with increasing drying temperatures which traduces the predominance for the reduction of OM.

The total OM content of WWS remained constant during the process. However the fractionation of OM after thermal drying showed a clear increase in lipids, fulvic acids and humic acids (table 2). In parallel, a strong decrease in humin fraction is observed. These changes are probably due to a weakening of OM. Lipidic compounds which were bound to the macromolecular network via ester, or ether bonds were probably released during this period thus increasing the extractable fractions [25]. Such a desorption has already been observed in soil as the equilibrium was perturbed [26].

The molecular analysis was performed by THM-GC/MS. The same molecules were detected all along the process with stanols, sterols and fatty acids as main compounds (table 3). An increase of respectively 27% and 73% for acids and steroids is observed for LF-85 followed by a decrease of respectively 29% and 50% for acids and steroids for LF-120. As observed by Gobé et al. 2000, it is highly probable that polycyclic alcohols (stanols and sterols) and fatty acids were linked to the macromolecular network of polar lipids by ether and ester bonds. In the first stage of thermal drying (LF-85) these bonds could have been broken leading to an increase in stanols, sterols and fatty acids. These released compounds were degraded in the second stage of drying (LF-120).

Table 3 : amount mg/g

	FaMe	Sterols	aromatics
LF-0	47.1	8.1	3.8
LF-85	58.2	36.1	3.2
LF-120	42.3	18.4	3.1
B-1	26.1	3.2	< LOQ
B-50	13.7	2.6	< LOQ
D-1	54.9	7.7	3.9
D-2	35.1	11.3	3.8
D-3	36.9	9.5	3.9
D-4	36.5	14.4	3.8

The branched (iso+anteiso) to linear fatty acids ratio (table 4) decreased along the process demonstrating that the drying process has an inhibiting effect on bacterial activity [27]. Moreover the relative increase in stanols versus sterol traduces reducing conditions which are not favourable to bacterial activity.

Table 4 : stanols to sterols and branched to linear fatty acids ratios

	Stanols/sterols	Branched/linear
LF-0	4.26	2.43
LF-85	4.82	2.30
LF-120	4.95	2.12

3.2. e-beam irradiation

e-Beam process principle consists on the acceleration of electrons emitted from a cathod in a vacuum tube due to an electric field. In aqueous solutions, high energy electrons (up to 3 MeV) induce the ionisation of water molecules (called water radiolysis) leading to the formation of ions and radicals as described by the following equation :

Initiation : $H_2O + e^- \rightarrow H_2O^{+\bullet} + 2\,e^-_{aq}$

Propagation : $H_2O^{+\bullet} \rightarrow HO^\bullet + H^+$

$H^+ + H_2O \rightarrow H_3O^+$

$H_3O^+ + e^-_{aq} \rightarrow H^\bullet + H_2O$

Termination : $H^\bullet + H^\bullet \rightarrow H_2$

$HO^\bullet + HO^\bullet \rightarrow H_2O_2$

The aqueous solution irradiation with an electron beam is the most effective technique among AOPs. When the OM in suspension is irradiated with highly energetic electrons, the electron energy is absorbed by the molecules of water [28]. The active species produced through the use of an electron accelerator for treating aqueous solutions are hydroxyl radicals ($HO^\bullet$), which have very high reactivity in an aqueous solution and hydrated electrons (e^-_{aq}). These two species are the most reactive with the solutes present in the solution to be treated.

The raw floated sludge pellet exhibited a pH equals to 8.0 (table 5) while its supernatant was equal to 6.6. The pH of the 1.25 kGy irradiated sludge (B-1) is 6.4 whereas the pH of the supernatant is 7.3. The irradiation of the organic material, as described in equations 1 and 2 therefore induced an acidification. The pH of the sludge irradiated to 50 kGy (B-50) is 6.0 and that of the supernatant is 6.7. The acidification is related to the increase in concentration of the ion [H_3O^+] produced by radiolysis of water increased with the irradiation dose.

The decrease in pH which is higher in the supernatant than in the pellet confirms that irradiation has a greater impact on water (radiolysis) than on the organic matter [28].

Table 5: pH +/- 0.2 after centrifugation of sludge

	pH	pH

	supernatant +/- 0.2	pellets +/- 0.2
LF-0	8.0	6.6
B-1	7.3	6.4
B-50	6.7	6.0

The evolution of the weight loss associated with exotherm 2 to exotherm 1 ratio (R_{TGA}), is presented in table 6. The irradiation at low dose (B-1) induces an increase in the R_{TGA} ratio associated with a stable OM content which demonstrates a complexification of the OM. The irradiation at 50 kGy (B-50) causes a slight decrease in the R_{TGA} ratio compared to the LF-0. This decrease is significant in comparison to the R_{TGA} ratio observed for B-1. Thus contrary to the first dose, 50 kGy irradiation induced a weakening of OM.

The stable organic matter content correlates with the total organic carbon measurements (TOC) measured on secondary effluents before and after irradiation [28].

A gradual increase of the relative abundances of C=C bonds (R_{IR1}) is observed as a result of radiation (table 6). This aromatization phenomenon can be correlated to the complexification of organic matter demonstrated by thermal analysis. The relative intensity of the signal associated to the C-O bonds (R_{IR2}) reflecting the oxidation of organic matter also increases for both radiation doses received by the samples. But the oxidation does not induce a change in C-O to C=O bonds ratio (R_{IR3}).

Table 6: Thermogravimetric and infrared ratios

	R_{TGA}	$\mathbf{R_{IR1}}$	$\mathbf{R_{IR2}}$	$\mathbf{R_{IR3}}$
LF-0	0.68	1.57	2.31	0.27
B-1	1.06	1.76	2.96	0.28
B-50	0.65	1.89	3.20	0.30

Independently of the irradiation dose, the humin fraction does not vary significantly (table 2). For a dose of 1.25 kGy, the relative amounts of humic acid increase while those of lipids and fulvic acids were reduced. This means that the relative amount of the less complex organic matter decreased in favor of the most complex organic matter.

The irradiation at 50 kGy causes an evolution of the different fractions of OM. Indeed, the relative amounts of lipids and humic acids decreased while the relative amount of fulvic acids increased. The relative amount of humin does not vary (table 2), which means that the relative amount of less complex organic matter decreases without changing that of humin. These results tend to demonstrate a slight complexification of organic matter with high irradiation dose.

3.3 Anaerobic Digestion

Centralized biogas plant uses an innovative process that converts various types of agricultural by-products and food (liquid manure, manure, slaughterhouse waste or food processing ...) to produce electrical and thermal energy. This process also provides a natural fertilizer deodorized, spreadable directly into the fields for local farmers. As an example, the installation of Thouars (Vienne, France) enables the production of renewable energy equivalent to the consumption of around 12,000 inhabitants, which will save 4 million liters of fuel a year and prevent the emission of 7,000 tons of CO_2. From the agricultural point of view, the resulting fertilizer with high agronomic value and deodorized, avoids the spreading of 220,000 kg of pure nitrogen is 660,000 kg of fertilizer each year.

Anaerobic digestion is constituted with three biological and chemical stages: hydrolysis, acidogenesis (including acetogenesis), and methanogenesis. The DOM content and composition in the biogas reactor are influenced by these three stages. For example, insoluble organic polymers (insoluble in solvent), such as carbohydrates, are broken down to solvent soluble derivatives like sugar in the hydrolysis stage, which causes the increase in the DOM content. Meanwhile, methanogenesis converts the dissolved intermediate products to biogas (methane, carbon dioxide), decreasing DOM content [29].

In order to observe the evolution of organic matter in the digestate, the study was conducted in batch mode, without the addition of sludge in the pilot. There is a cessation of gas production in the 25th day, the study was stopped on the 35th day. In order to validate the study and to confirm the production of methane, the produced gas was analysed by gas chromatography and methane accounts for 42 % of the produced gas.

According to elemental analysis, there is no change induced by anaerobic digestion on bulk parameters (1).The C/N ratio is much lower than recommended in several studies, which can explain the amount of produced gas. OM content slightly decreased during anaerobic digestion, from 66.7% to 52.3%.

The amount of lipids (table 2) increased by 30 % the first two weeks and then declined. The final amount represented 62% of the initial amount. The lipid fraction is the biodegradable fraction that is digested by methanogens bacteria. The increase in lipid content in a first phase, can be attributed to hydrolysis. Then acetogenesis and methanogenesis cannot be distinguished during the second phase where lipids content decrease.

The characterization of the digestate was performed by double-shot pyrolysis. Fatty acids and steroids were the main identified products from the first shot (table 3). The relative abundance of fatty acids decreases during the digestion from 91% to 77%. On the contrary, there is a relative increase (3% to 12 %) in the amount of steroids. The second shot allows the identification of aromatic compounds resulting from the degradation of proteins, polysaccharides and lignin. Predominantly present molecules are toluene, styrene and ethylbenzene. There is no significant change in the abundance of these compounds during digestion.

The branched to linear fatty acids ratio increased (table 7), which was characteristic of a high bacterial activity and then fall from the 2nd week of methanation. This indication of bacterial activity correlates with the strong production of biogas in the first weeks and a stop of this production at the 5th week. Quantities of short chained fatty acids increased during hydrolysis and then level off (table 7): they are produced during sludge digestion by methanogenic bacteria.

During the process, fatty acids increased first and then decreased until the end of the experiment, as lipid content do. At the contrary, the opposite phenomenon is observed for steroids (table 3).

Methanogenic bacteria stop the process before the total consumption of nutrients (fatty acids and steroids).

Table 7 : branched to linear fatty acids, stanols to sterols and styrene to toluene ratios

	D1	D2	D3	D4
Branched/linear	2.2	1.9	1.9	2.6
Stanols / Sterols	11.3	5.1	5.9	6.3
Styrene / Toluene	1.0	1.9	0.7	0.0
CPI (fatty acids)	2.8	3.2	3.5	2.8

CPI :odd fatty acids / Σ even fatty acids

4. Conclusions

The impact of 3 different drying processes on the physico-chemical characteristics of wastewater sludge has been studied. Thermally dried, digested and irradiated sludge were compared with the initial floated sludge. The OM has been characterised at the global and molecular scales using elemental analysis, infra-red spectroscopy and thermochemolysis.

The e-beam irradiation induced an acidification and the digested sludge showed a loss in OM content but globally after the drying step, the 3 studied WWS presented similar characteristics. However the OM chemical fractionation puts in evidence the strong influence of thermal drying processes on OM. Indeed, the pelletisation step at 120°C of the thermal drying process induced a weakening of OM which is traduced by an increase in lipids concomitant with a decrease in “humin”. At low doses, the e-beam irradiation resulted in a decrease in the lipidic fraction and distribution in the various humic fractions in line with a complexification. At the contrary, a higher dose induced a weakening of the organic matter. Thermal analysis corroborated these results while infrared spectroscopy demonstrated an oxydation and an aromatisation of OM with increasing irradiation dose.

At the molecular level, thermal drying resulted in a decrease in branched to linear fatty acids ratio and an increase in stanols to sterols ratio while e-beam irradiation resulted in a decrease in all the identified compounds. During the 5 weeks of digestion, the amount of fatty acids decreased while that of steroids did not change.

Finally our results suggested that drying which reduces the volume of WWS thus lowering its cost of management, but change in OM characteristics can have an impact on the choice of WWS disposal. Indeed, the weakened OM of thermally dried sludge aim to be used as fertilizer while the complex OM of sludge irradiated with a low dose should be used as amendment

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