Aim and Scope

The objective of the *Journal of Residuals Science & Technology* (JRS&T) 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 are also welcome.

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Research

Optimization of Thermal Desorption Conditions for Volatile Organic Compounds Emitted in Municipal Solid Waste Storage Under SBSE-TD-GC-MS

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ABSTRACT: Stir bar sorptive extraction and thermal desorption procedure coupled to capillary gas chromatography–mass spectrometry (SBSE-TD-GC-MS) was evaluated and optimized for analyzing volatile organic compounds emitted by municipal solid waste storage. Desorption analytical conditions have been optimized using a Box-Behnken experimental design. The main compounds identified in the samples were terpenes, saturated fatty acid meat cooking, antioxidant compounds such as butylated hydroxytoluene (BHT), and organophosphate flame retardants from plastics. For the desorption step, the optimum analytical conditions were: desorption temperature 300ºC, cryofocusing temperature –20ºC, flow of helium 50 ml min^{-1}, and desorption time 3 min.

INTRODUCTION

COLLECTION and handling of Municipal Solid Wastes (MSW) have caused odor problems for many years and many countries have regulations for the minimum distance between a treatment plant and dwelling areas as a result. Odor causing substances usually arise as a result of biological activity in storage, handling, or at the treatment plant. Ammonia and sulfide compounds are principal inorganic gases [1]. Mercaptans, terpenes, indoles, and various other nitrogen-bearing organics are important organic substances [2].

Dynamic dilution olfactometry is the most common method of measuring volatile organic compounds (VOCs) odor concentrations [3]. However, olfactometry is costly, labor intensive, time consuming, subject to error, no identified individual compounds, and incurs delays between sampling and measurement [4–6]. To avoid these problems, gas chromatography (GC) in connection with various detectors especially mass spectrometry (MS) has been applied for characterization of chemical composition of odorous gas samples [7]. In this sense, sorbent-based and canister-based sampling methods have been successfully used for collection of VOCs [8,9]. In sorbent-based methods, air is pulled through metal or glass tubes filled with appropriate sorbents such as activated charcoal, Tenax TA, XAD-2, Carbotrap, Carbopack, Carbosieve, and Carboxen 569. These sorbents have variable selectivity towards different types of VOCs [7,10]. Thus, a good combination of different sorbents may allow for determination of a wide range of VOCs in air. Regarding canister-based sampling methods, a whole air sample is pumped into a cleaned stainless steel canister. VOCs are then preconcentrated using either solid adsorbents such as Tenax followed by thermal desorption into the GC-MS or solid-phase microextraction (SPME) with desorption in the GC injector itself.

However, sorption passive sampling also has drawbacks. Analyte sorption is a dynamic equilibrium process, thus it is quite likely compounds trapped by the sorbent, when the analyte concentration in the surrounding medium is high, could be released back into the environment when their concentration in surroundings decreases. Martos and Pawliszyn [11] established that practically complete retention of solutes in polydimethylsiloxane (PDMS) may be obtained for analytes with coating/air partition coefficients greater than 1,000. Therefore, air sampling with SPME present many advantages over conventional sampling methods

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[12,13] due to its simplicity, reusability, excellent sample recovery, and hydrophobic property of SPME coatings. However, the enrichment that can be achieved with SPME is low because of the unfavorable partition between microlitre volumes of sorbent on the fibre and large sample volumes. To increase sensitivity of analyses, Baltussen *et al.* [14] developed stir-bar sorptive extraction (SBSE) in which analytes are enriched in a sorptive sleeve of rubber on a magnetic follower or stir-bar. This technique can be applied to both liquid and gas samples. Due to the larger volume of sorptive stationary phase used in this technique, sensitivity of this method is higher than that of SPME.

The following describes optimization of a thermal desorption procedure from stir bar sorptive extraction coupled to capillary gas chromatography–mass spectrometry for determination of volatile organic compounds odor in municipal solid waste storage emission. Parameters that effect thermal desorption are investigated using a chemometric approach based on use of an optimal set of experiments (experimental design) which allows for simultaneous variation of all experimental factors studied and distinguishing interactions among them that are not detectable with classical experimental methods. Desorption temperature, desorption time, helium flow, and cryofocusing temperature in the programmed-temperature vaporisation (PTV) injector were evaluated parameters (factors) on the obtained chromatographic area for the main compounds found in the gas. Effects have been estimated using a Box-Behnken design.

MATERIALS AND METHODS

Materials

MSW was collected from Villarrasa's (Huelva-Spain) urban waste treatment plant. Non-selective collected urban waste is processed in this plant. Centralized treatment prior to composting consists of screening (8 cm) through a bag-opener trommel, electromagnetic separation of ferrous metals, and manual separation of nonferrous materials. This MSW is used as raw material to obtain compost. Some relevant characteristics of the studied MSW (48% moisture) are seen in Table 1. Obtained MSW was placed on 200 L capacity acrylic barrel composting reactors (30 kg dry basis for each reactor). To minimize conductive heat loss along the reactor wall they were insulated with polyurethane foam. Each sample was taken individually to assure spatial variability.

Table 1. Properties of MSW Composted Wastes (dry basis and free of impurities).

		MSW Compost
Organic Matter	g kg^{-1}	385.4 ± 6.5
N	g kg^{-1}	27.2 ± 0.6
C/N		7.9 ± 1.3
pH (1:5 extract)		8.2 ± 0.2
EC (1:5 extract)	dS m^{-1}	15.7 ± 0.8

The pH and *electrical conductivity* (EC) were determined in a 1:5 ratio (in weight) MSW: water extracts using a pH and EC electrodes, respectively. Total organic matter was determined by the weight loss after dry combustion at 540°C. Organic carbon was estimated by multiplying organic matter by 0.58 [15]. Nitrogen was determined by steam distillation after Kjeldahl digestion. Organic matter and nitrogen determinations were done at the < 5 mm size fraction. Analyses were carried out in triplicate.

Air Sampling and Analysis Procedure

VOCs were collected from the MSW headspace from the air flow stream exit from the reactor. Sampling was carried out with a 10 mm × 0.5 mm (length × film thickness) PDMS commercial stir bar supplied by Gerstel (Mülheim and Ruhr, Germany). PDMS stir bars were hung on the reactor headspace during the 30 min. After the sampling, the stir bar was gently dried with a paper tissue and introduced into a 2 mL vial. The PDMS were stored in darkness at 6–20°C and were analyzed within 48 h of collection. The same procedure has been followed for one month taking two samples (triplicate) during this period.

Prior to use, SBSE was conditioned for 15 min at 300°C in a helium flow of 50 mL min^{-1} and was kept in new 2 ml vials.

SBSE were thermally desorbed using a commercial Thermal Desorption System (TDS) (Gerstel) equipped with a MPS-2 auto-sampler connected to a Programmable Temperature Vaporization (PTV) injector CIS-4 (Gerstel) by a heated transfer line. The PTV was installed on an Agilent 6890 gas chromatograph with a 5973 mass selective detector (Agilent Technologies, Palo Alto, CA, USA). Each SBSE were thermally desorbed by programming the thermal desorption unit to the final desorption temperature during a time under helium flow. Desorbed compounds were cryofocused on quartz wool packed liner with the PTV system with liquid carbon dioxide. Finally, the PTV system was ramped to the final temperature for analysis by GC–

MS. The inlet was operated in the solvent vent mode. Analyses were carried out using a HP-5 MS column (30 m × 0.25 mm I.D., 0.25 µm film thickness, and 5% phenyl–95% polydimethylsiloxane). The column was kept at 40ºC for 5 min, ramped at 5ºC min^{-1} to 270ºC, and held for 20 min. Helium was used as a carrier gas at a flow rate of 1 mL min^{-1}. The transfer line, ion source, and quadrupole analyzer temperatures were maintained at 280, 230, and 150ºC, respectively, and a solvent delay of 3 min was selected. In the full-scan mode, electron ionization mass spectra in the range 35–550 Da were recorded at 70 eV electron energy with an ionization current of 34.6 mA. Mass spectra volatile compounds were compared with the Wiley 275 L and NIST 02 library reference spectral bank (Agilent Technologies). Data recording and instrument control were performed by the MSD ChemStation software (Agilent Technologies). The MS was tuned to *m/z* 69, 219 and 502 for EI corresponding to perfluorobutylamine (PFBA).

Experimental Design and Statistical Analysis

In order to obtain optimized conditions for *the* desorption step, a Box–Behnken experimental design (CSS Statistica, StatSoft Inc., Tulsa, UK) was used to evaluate the significance of the variables as well as interactions among them. The number of experiments (N) is defined by the equation $N = k^2 + k + cp$, where k represents number of factors (variables) involved in the study and cp is number of replicates of the central point. Box–Behnken could be seen as a cube consisting of a central point and the middle points of the edges. Desorption temperature (T_{des}), desorption time (t), desorption flow (F), and cryo-focusing temperature (T_{cis}) were studied. All of these were evaluated at three levels: low (denoted as –1), center point or medium (denoted as 0), and high level (denoted as +1). Therefore, this design involved 27 experiments which were performed in random order. Levels for the experimental design are summarized in Table 2.

The data were analyzed by multiple regression analysis. The following polynomial equation [See Equation (1)] was derived to represent VOCs peak area signal as a function of the independent variables tested where y is the predicted VOCs peak area signal. Only the estimates of coefficients with significant levels higher than 95% ($p < 0.05$) were included in the final models.

$$y = \beta + \sum_{i=1 \text{ to } 4} \beta_i x_i + \sum_{i<j} \sum_{i=1 \text{ to } 4} \beta_{ij} x_i x_j + \sum_{i=1 \text{ to } 4} \beta_i x_i^2 \tag{1}$$

Where:

β, β_i, and β_{ij}, denotes regression coefficients and x_i and x_j are normalized values between pairs of independent variables (desorption temperature, desorption time, desorption flow, and cryo-focusing temperature).

RESULTS AND DISCUSSION

Volatile Organic Compounds Emitted in MSW

A great number of VOCs were detected and were identified on the *basis* of their mass spectra and the NIST Mass Spectral Database (NIST 02). Table 3 summarizes the most abundant VOC compounds found in the municipal soil waste storage emission by using

Table 2. Experimental Domain and Box-Behnken Design Matrix Used in the Study[a].

	T_{des} (ºC)	t (min)	T_{cis} (ºC)	F (mL min^{-1})
Low level (–1)	**200**	**3**	**–20**	**50**
High level (+1)	**300**	**1.0**	**20**	**100**
Centre (0)	**250**	**6.5**	**0**	**75**
Experiment				
1	–1	–1	0	0
2	1	–1	0	0
3	–1	1	0	0
4	1	1	0	0
5	0	0	–1	–1
6	0	0	1	–1
7	0	0	–1	1
8	0	0	1	1
9	0	0	0	0
10	–1	0	0	–1
11	1	0	0	–1
12	–1	0	0	1
13	1	0	0	1
14	0	–1	–1	0
15	0	1	–1	0
16	0	–1	1	0
17	0	1	1	0
18	0	0	0	0
19	–1	0	–1	0
20	1	0	–1	0
21	–1	0	1	0
22	1	0	1	0
23	0	–1	0	–1
24	0	1	0	–1
25	0	–1	0	1
26	0	1	0	1
27	0	0	0	0

[a]Desorption temperature (T_{des}), desorption time (t), crio-focusing temperature (T_{cis}), and desorption flow (F).

Table 3. VOCs Emissions Found, Retention Time, CAS Number, Formula, Mass, and Octanol-Air Partition Coefficients for the Wastes.

Compounds	t_r (min)	CAS Number	Formula	Mass	Log K_{oa}[1]
3-Carene	12.62	005989-27-5	$C_{10}H_{16}$	68, 93, 136	4.26
D-Limonene	13.80	005989-27-5	$C_{10}H_{16}$	68, 93, 136	4.26
Butanedioic Acid, Diethyl Ester	18.75	000123-25-1	$C_8H_{14}O_4$	129, 101	5.87
Octanoic Acid (caprylic acid)	19.06	000124-07-2	$C_8H_{16}O_2$	115, 101, 73, 60	7.59
N-Decanoic Acid (capric acid)	24.16	000334-48-5	$C_{10}H_{20}O_2$	129, 60, 71	8.35
Naphthalene	27.00	004630-07-3	$C_{15}H_{24}$	204, 106	4.85
Butylated Hydroxytoluene	27.45	000128-37-0	$C_{15}H_{24}O$	220, 205	8.87
Tetradecanoic Acid (Myristic acid)	33.17	000544-63-8	$C_{14}H_{28}O_2$	228, 185, 129	10.88
2-Propanol, 1-Chloro-, Phosphate (3:1)	33.95	013674-84-5	$C_9H_{18}Cl_3O_4P$	277, 157, 125	8.20
Bis(1-Chloro-2-Propyl)(3-Chloro-1-Propyl)Phosphate	34.27	137909-40-1	$C_9H_{18}Cl_3O_4P$	277, 157, 139	–
Pentadecanoic Acid	35.19	001002-84-2	$C_{15}H_{30}O_2$	242, 199, 129	9.52
1,2-Benzenedicarboxylic Acid, Bis(2-Methylpropyl) Ester (Diisobutyl phthalate)	35.27	000084-69-5	$C_{16}H_{22}O_4$	149, 223	8.41
Hexadecanoic Acid (Palmitic acid)	37.15	000057-10-3	$C_{16}H_{32}O_2$	256, 213, 129	10.26
Oleic Acid	40.39	000112-80-1	$C_{18}H_{34}O_2$	264, 97, 83	10.38
Octadecanoic Acid (Stearic acid)	40.86	000057-11-4	$C_{18}H_{36}O_2$	284, 241, 185	12.94

[1] log K_{oa} = Log (Octanol-Air Partition Coefficients)—(25ºC, KOAWIN v1.10).

SBSE-TD-GC-MS. In addition, retention time and octanol/air partition coefficients are shown for each compound.

Figure 1 shows a typical chromatogram for this study. Terpenes, esters, saturated fatty acids, and others such as organophosphate flame retardants and butylated hydroxytoluene (BHT) have been found in indoor air during municipal solid waste treatment emission [16]. Saturated fatty acids comprise most of the total emitted compounds. Thiébaut *et al.* [17] have identified carboxylic acids, fatty acid ester, and BHT in magnetic tape using DVB/CAR/PDMS coating SPME fibre. Saturated fatty acid such as oleic, palmitic, and stearic acids in emissions of fine particulate matter by meat cooking operations have been detected by other authors [16,18–23]. In this sense, BHT has been used

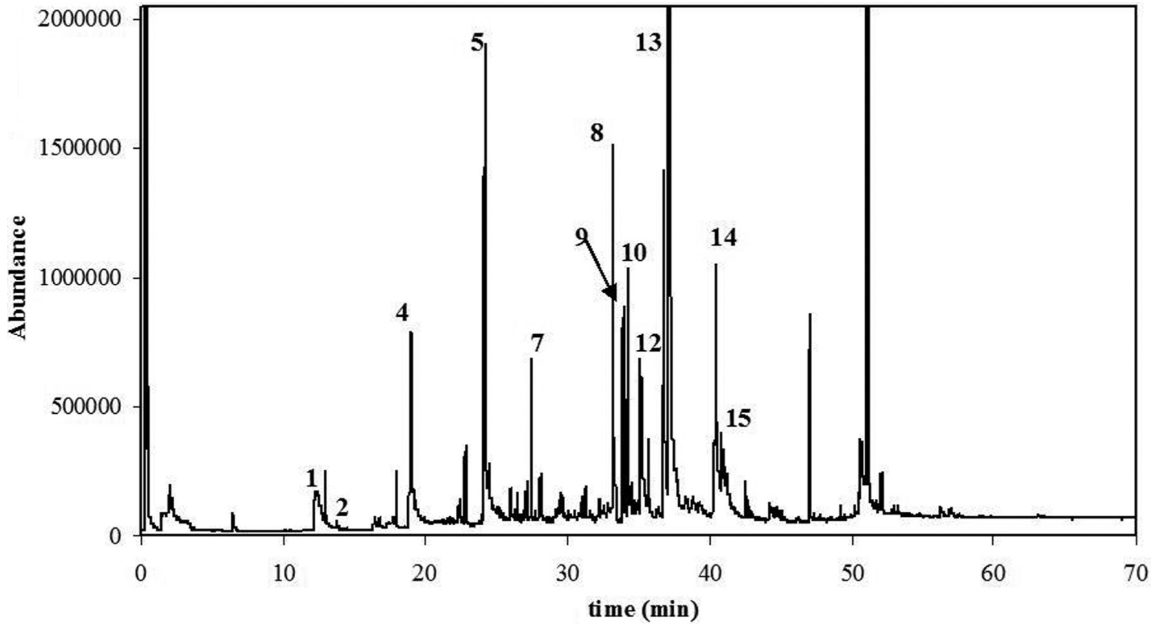

Figure 1. *Total ion chromatogram of MSW headspace during thermophilic phase by SBSE-TD-GC-MS using the optimised conditions. 1: 3-Carene; 2: D-Limonene; 3: Butanedioic Acid, Diethyl Ester; 4: Caprylic Acid; 5: Capric Acid; 6: Naphthalene; 7: Butylated Hydroxytoluene; 8: Myristic Acid; 9: 2-Propanol, 1-Chloro-, Phosphate (3:1); 10: Bis(1-Chloro-2-Propyl)(3-Chloro-1-Propyl)Phosphate; 11: Pentadecanoic Acid; 12: Diisobutyl Phthalate; 13: Palmitic Acid; 14: Oleic Acid; 15: Stearic Acid*

as an antioxidant since the 1950s [24] to preserve and stabilise the freshness, nutritive value, flavour, and colour of food and animal feed products [25]. BHT can also improve stability of pharmaceuticals, fat-soluble vitamins, and cosmetics [26]. Additionally, durability of rubber, elastomers, and plastics is increased by use of BHT [27]. Moreover, presence of terpenes as limonene were characterized in fruits, vegetables, and pine species [28]. Furthermore, organophosphate flame retardants in indoor air have been previously detected [29–31]. These compounds are extensively employed as plasticizers and flame retardant additives in textiles, wallpapers, varnishes, and polymeric materials [32,33].

On the other hand, organic sulfur compounds such as dimethyl sulphide (DMS) or dimethyl disulfide (DMDS) which have been previously detected in MSW [34–36], were not detected by SBSE-TD-GC-MS. These compounds have an octanol/air partition coefficient around 1,000 so no retention of the analytes in PDMS was obtained [11].

Optimizing SBSE-TD-GC-MS Analytical Conditions for VOCs Emitted by MSW

Several parameters thought to effect desorption efficiency of VOCs by SBSE-TD-GC-MS were chosen: desorption temperature, time and flow (helium flow), and cryofocusing temperature in the PTV injector. Optimization of the desorption step was performed using a Box-Behnken design. The number of experiments required to investigate the previously noted four parameters at three levels would be 64 (4^3). However, this was reduced to 27 using a Box-Behnken experimental design. Results from this limited number of experiments provided a statistical model used to identify high yield trends for the desorption step. The peak area of three extracted ions (m/z) for each compound was selected as the experimental response.

Estimations of model coefficients and statistics parameters (R^2, p and F) are calculated using polynomial regression (Table 4) between the analytical response and the variables. These equations may be used to estimate variation of dependent variables with changes in independent variables over ranges considered on the constancy of the other two variables. According to the proposed methodology, only the terms with statistically significant coefficients are shown. The different results have to be evaluated in order to assess the validity of the model. Concerning the response equation, for most cases an acceptable (> 0.8) R^2 and (> 20) F value has been found. In these cases, a rather important difference between values obtained by simulation and ones given by the statistical model can be observed. One possible explanation is that the corresponding peak area was found near to those compounds that have been considered as background.

Table 4 shows that for each compound regardless of extracting ions m/z the independent variables that confirm its influence on response are similar. These data could be used to verify accuracy of the model used for optimization. After this first evaluation, the optimization of desorption step is performed only with high R^2 and F values (gray color in Table 4). A positive value for the estimated effect shows an increase in the response if the variable increases to its highest level. A negative value indicates that a better response is obtained at lower levels for the variable. Regarding interactions, a positive value indicates the response will increase if both variables change to the same level, low or high. A negative value shows an increase in the response if the variables change in opposite directions (one variable increases to a high level and the other decreases to a low level).

In the selected equations, identifying the independent variables with the strongest and weakest influence on the dependent variables is not so easy since the former contains quadratic terms and the others involve interactions between two independent variables. In this form, a Pareto chart, also called a Pareto distribution diagram, are used for analyzing what independent variables ($p > 0.05$) have the greatest cumulative effect. Figure 2 displays a plot of each dependent variable (compound) and its Pareto chart of standardized effects (as percentages) based on independent variables. Each bar graph (independent variable) displays variances by the number of their statistical effect on the selected compound area.

According to Figure 2, the cause which makes time the most influential variable on the maximum obtained area may be deduced. In this way, the T_{cis} shows high influence on 4 of 6 equations selected. The second variable that shows high statistical weight is T_{des}. The desorption temperature influence was stronger in the higher octanol-air partition coefficient such as octadecanoic acid. Nevertheless, a significant influence of this operational variable has been found in 3-carene and d-limonene that shows the lowers values in octanol-air partition coefficient.

In that form, each compound has a distinct response to the selected variables; 3-carene is more highly influenced by flow than by desorption temperature and

Table 4. Equations Yielded for Each Compound and Mass as a Function of the Independent Variables (normalized values)[a].

Compound	*Mass*	*Equation*	*R^2*	*p*	*F*
3-Carene	67	$\mathrm{Area} = 614523 - 543084t - 1520387F + 614523T_{des}^2 - 788777tF$	0.893	0.00002	22.384
	93	$\mathrm{Area} = 2728034 - 431985t - 1193165F + 516474T_{des}^2 - 683065tF$	0.688	0.00002	12.115
	136	$\mathrm{Area} = 940761 - 143007t - 402126F + 174264T_{des}^2$	0.652	0.00002	14.386
Limonene	67	$\mathrm{Area} = 162619 + 32884T_d - 139057T_{cis} - 45431T_{des}\,t - 64328T_{des}T_{cis} + 53311tT_{cis}$	0.878	0.0000	29.332
	93	$\mathrm{Area} = 120971 + 24040T_d - 107706T_{cis} - 31385T_{des}\,t - 57564T_{des}T_{cis}$	0.856	0.0000	32.772
	136	$\mathrm{Area} = 47680.1 + 10748.7T_{des} - 38428T_{cis} - 11671.2T_{des}t - 17051.0T_{des}T_{cis}$	0.892	0.0000	45.338
Butanedioic Acid, Diethyl Ester	129	$\mathrm{Area} = 520012 - 390009T_{cis}^2 - 39009F^2$	0.332	0.0094	5.699
	101	$\mathrm{Area} = 726455 - 544841T_{cis}^2 - 544841F^2$	0.328	0.0085	5.845
Octanoic Acid	115	$\mathrm{Area} = 193361 - 367257T_{cis} + 420051F^2$	0.256	0.0288	4.128
	101	$\mathrm{Area} = 622161 - 816154T_{cis} + 820507F^2$	0.196	0.0730	2.924
	73	$\mathrm{Area} = 1384042 - 2175388T_{cis} + 2356741F^2$	0.224	0.0479	3.458
	60	$\mathrm{Area} = 1695919 - 2766132T_{cis} + 3078674F^2$	0.231	0.0426	3.608
N-Decanoic Acid	129	$\mathrm{Area} = 1716974 + 7909827F^2 + 6878604\mathrm{F}T_{cis}$	0.315	0.0107	5.521
	60	$\mathrm{Area} = 2280129 + 11311853F^2 + 8766242\mathrm{F}T_{cis}$	0.314	0.0109	5.487
	71	$\mathrm{Area} = 1071024 + 11311853F^2 + 8766242\mathrm{F}T_{cis}$	0.328	0.0084	5.871
Naphthalene	204	$\mathrm{Area} = 54290 - 162140T_{cis} - 35403t - 30121F + 32593T_d^2 + 130946T_{cis}^2$	0.895	0.0000	32.413
	161	$\mathrm{Area} = 148993 - 302117T_{cis} - 59123t - 45163\ \mathrm{F} + 233651T_{cis}^2 + 77743T_{des}T_{cis}$	0.875	0.0000	29.372
Butylated Hydroxytoluene	220	$\mathrm{Area} = 1127436 - 1366009T_{cis} + 665441T_{cis}^2 - 599881F^2$	0.824	0.0000	20.090
	205	$\mathrm{Area} = 4381773 - 5321823T_{cis} + 2606120T_{cis}^2 - 2339614F^2$	0.721	0.0000	19.791
Tetradecanoic Acid	228	$\mathrm{Area} = 170641 + 252939t^2 - 448773T_{des}t$	0.295	0.0150	5.032
	185	$\mathrm{Area} = 244795 + 435704t^2 - 692541T_{des}t$	0.312	0.0113	5.429
	129	$\mathrm{Area} = 363484 + 620145t^2 - 991069T_{des}t$	0.308	0.0122	5.329
2-Propanol, 1-Chloro-, Phosphate (3:1)	277	$\mathrm{Area} = 3204714 + 591058T_{des} + 537851t - 1133145T_{des}t + 1063218T_{des}T_{cis}$	0.235	0.1874	1.693
Bis(1-Chloro-2-Propyl) (3-Chloro-1-Propyl) Phosphate	157	$\mathrm{Area} = 1228061 + 235487T_{des} - 463907T_{des}\mathrm{t} + 444300T_{des}T_{cis}$	0.195	0.164	1.860
Pentadecanoic Acid	242	$\mathrm{Area} = 55407 + 82601t + 117154t^2 - 243567T_{des}$	0.834	0.0051	25.189
	199	$\mathrm{Area} = 54840 + 70777t + 100311t^2 - 207176T_{des}t$	0.766	0.0134	14.428
	129	$\mathrm{Area} = 80861 + 152188t + 191495t^2 - 443574T_{des}t$	0.792	0.0062	24.947
1,2-Benzenedicarbo-xylic Acid, Bis(2-Methylpropyl) Ester	223	$\mathrm{Area} = 514005 - 82355T_{cis} - 148132T_d^2 + 143348t^2 + 239396T_{des}t + 395549T_{cis}\mathrm{t}$	0.506	0.0075	4.302
N-Hexadecanoic Acid	256	$\mathrm{Area} = 1587861 + 1662395t^2 - 3158174T_{des}t$	0.302	0.0135	5.182
	213	$\mathrm{Area} = 1114672 + 1248842t^2 - 2262508T_{des}t$	0.310	0.01162	5.394
	129	$\mathrm{Area} = 1846596 + 1861616t^2 - 3552234T_{des}t$	0.299	0.142	5.110
	73	$\mathrm{Area} = 3407060 + 3739663t^2 - 6680533T_{des}t$	0.298	0.0144	5.086
Oleic Acid	264	$\mathrm{Area} = 91232 + 60300t + 67050t^2 - 143144T_{des}t$	0.358	0.0155	4.269
	97	$\mathrm{Area} = 271104 + 178116t + 166365t^2 - 429465T_dt$	0.374	0.0117	4.580
	67	$\mathrm{Area} = 295485 + 188178t + 152147t^2 - 369775T_{des}\mathrm{t}$	0.346	0.0189	4.055
Octadecanoic Acid	284	$\mathrm{Area} = 457595 + 245765T_{des} + 139125T_{cis} - 241038F^2$	0.806	0.0067	25.249
	241	$\mathrm{Area} = 228945 + 123171T_{des} + 78733T_{cis} - 111840F^2$	0.713	0.0059	12.391
	181	$\mathrm{Area} = 217644 + 107422T_{des} + 69353T_{cis} - 106624F^2$	0.560	0.0150	4.307

[1] Desorption time (*t*), Desorption Temperature (T_{des}), Cis Temperature (T_{cis}) and Flow (*F*)

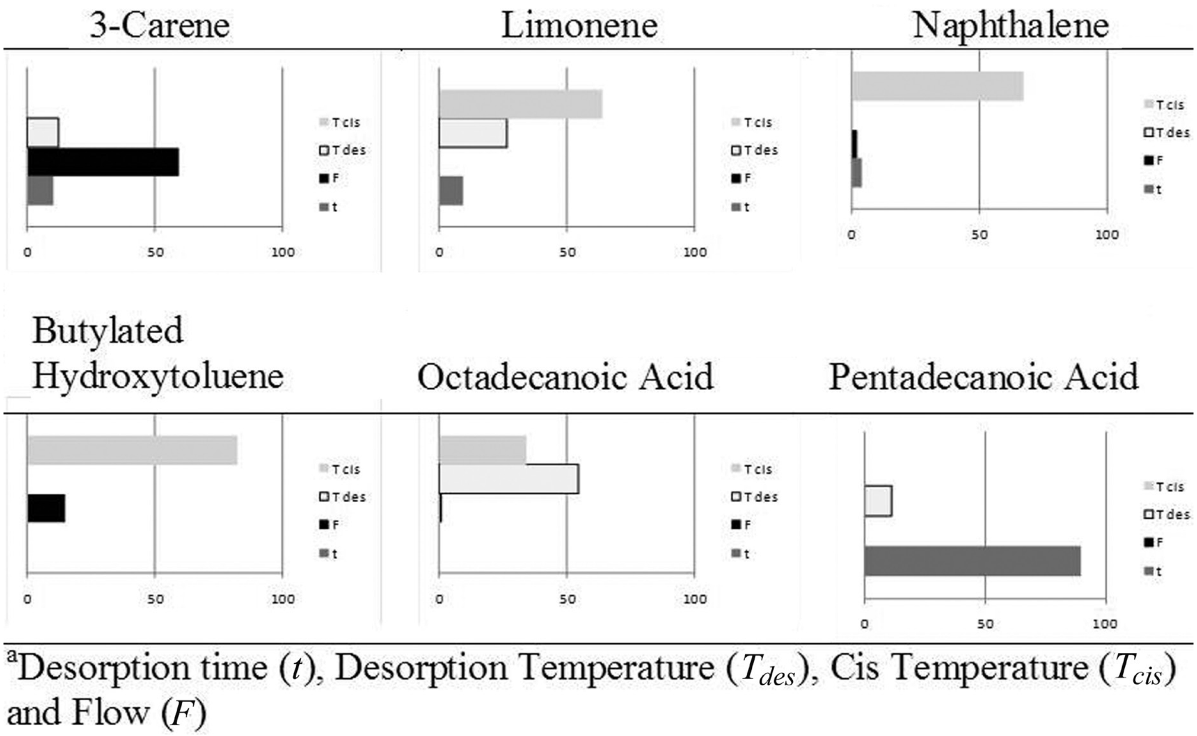

Figure 2. *Pareto charts yielded for each selected compound as a function of each independent variable.*

time and no influence by the T_{cis} has been found; limonene, naphthalene, and butylated hydroxytoluene are mainly influenced by T_{cis} than by the others variables. However, octadecanoic acid shows an influence by the desorption temperature and T_{cis} and pentadecanoic acid is highly influenced by time.

Different models were analyzed in order to determine the range of the operational variables giving optimum values for dependent variables. Moreover, the response surface for all dependent variables was plotted (Figures 3–8) at three levels for the three levels of the most influential variable to get a suitable visual observation of produced changes to determine range of operational variables giving optimum values for those dependent variables. A high negative influence (lower response) of flow and time are found in the 3-carene (Figure 3) area. A decreasing signal was obtained by increasing both flow and time in the Twister©. Therefore, smaller amounts of this compound have been desorbed under high flow rates and high time. Lower variations with respect to T_{des} have been found. In this sense, a low response has been obtained under medium T_{des} values. Then, the highest area is obtained at low values of flow (50 mL min^{-1}), longer time (10 min), and high (300°C) or low (200°C) T_{des} value.

Seen in Figure 4 TCIS is the variable most strongly influencing the area for d-limonene. However, a negative influence of this parameter has been found and a higher d-limonene area under low T_{cis} values has been observed. Also, the area was less influenced by time than by T_{des} and a high negative influence has been found in this parameter. This influence is more evident under lower T_{cis}. Relative influence of time was similar at different T_{cis} while it was slightly more marked un-

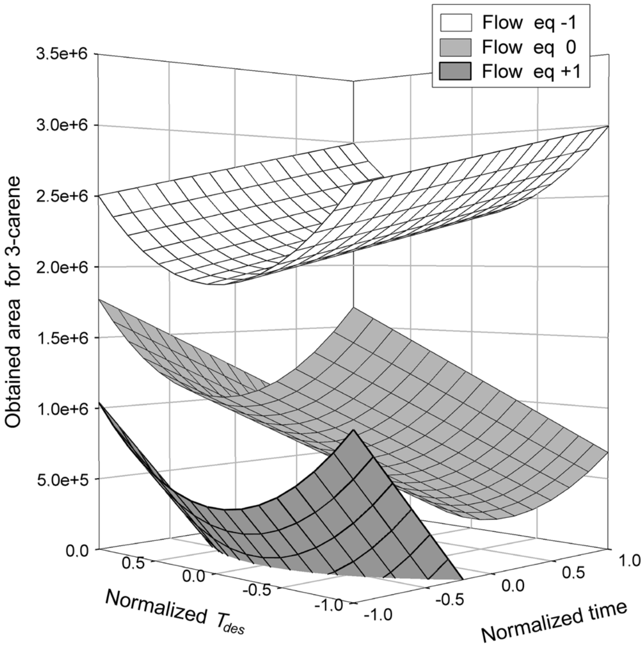

Figure 3. *Obtained area for 3-carene variation as a function of time and T_{des} at three flow levels.*

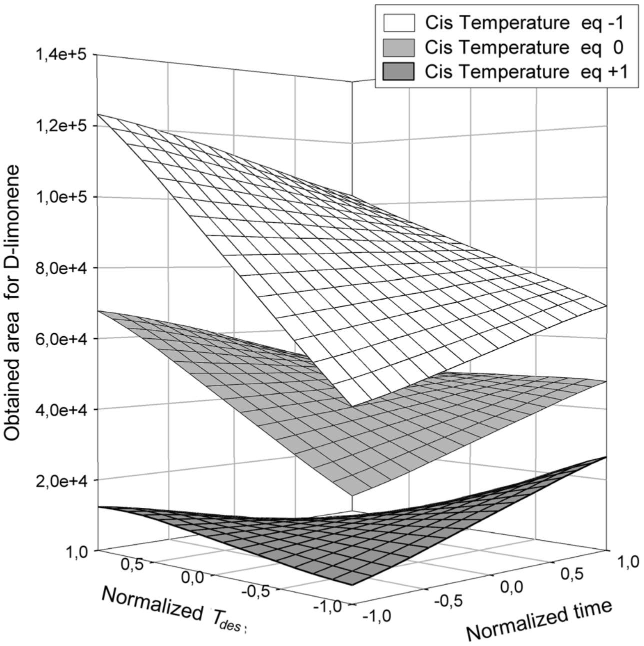

Figure 4. *Obtained area for D-limonene variation as a function of time and T_{des} at three T_{cis} levels.*

der low T_{des}. The highest area is obtained at low values of T_{cis} at –20°C, at time of 3 min, and at high T_{des} values of 300°C.

As seen in Figure 5, the obtained area for naphthalene was much more sensitive to changes in T_{cis} than for the others independent variables. In this case, a low T_{cis} value produces a much higher value in the obtained area than those obtained by the use of medium or high T_{cis} values. Moreover, a negative influence (high area) of almost all independent variables has been found. To obtain maximum area it is advisable to use a low T_{cis} (–20°C), low time (3 min), and low flow (50 mL min^{-1}).

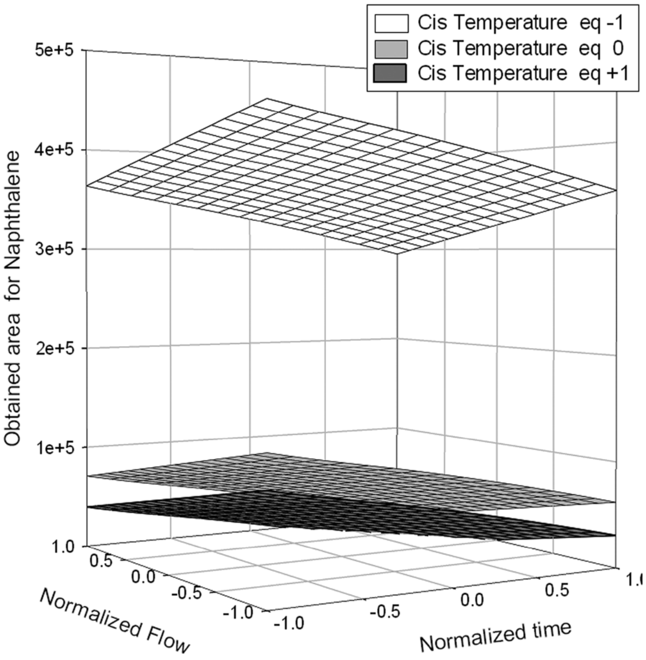

Figure 5. *Obtained area for Naphthalene variation as a function of time and flow at three T_{cis} levels.*

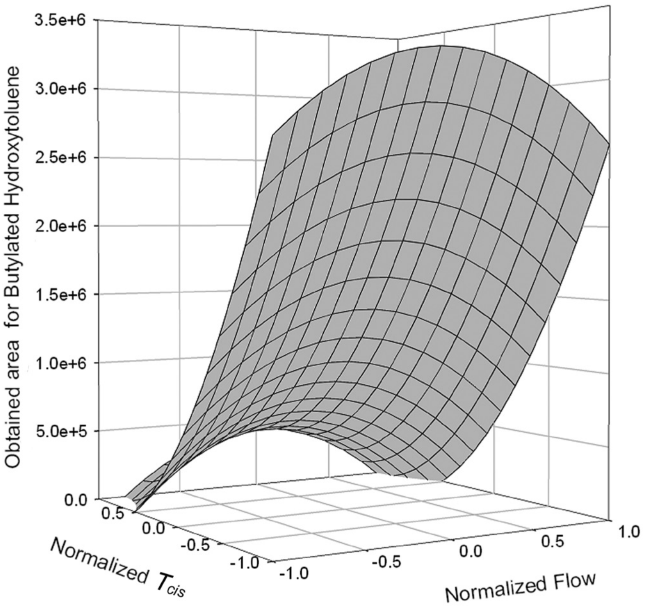

Figure 6. *Obtained area for Butylated Hydroxytoluene variation as a function of T_{cis} and flow.*

As seen in Figure 6, at lower values of T_{cis} higher area values may be obtained. The main parameter on butylated hydroxytoluene obtained area variation is T_{cis}. Moreover, higher areas may be found under high

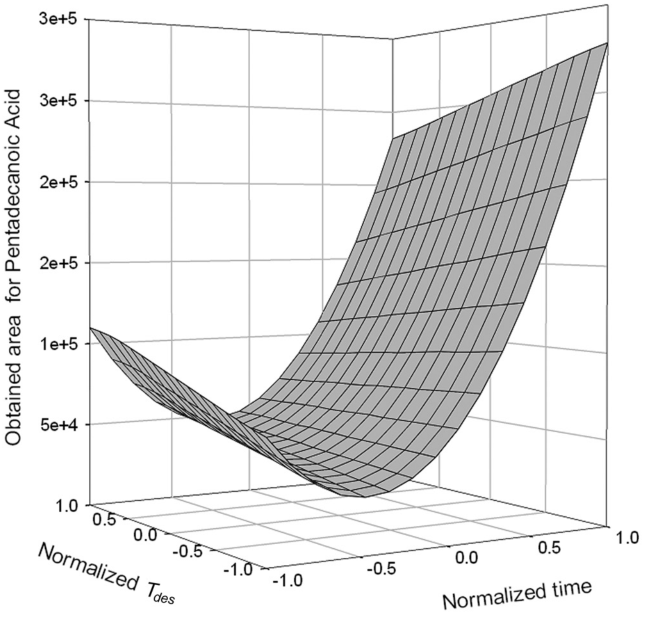

Figure 7. *Obtained area for Pentadecanoic Acid variation as a function of T_{des} and time.*

values of T_{cis}. That is to say, by using lower T_{cis} (–20°C) and medium flow (100 mL min^{-1}) values the maximum area may be obtained.

The area for pentadecanoic Acid (Figure 7) shows the very important influence of time and lower influence of T_{des}. Furthermore, time has a positive influence on pentadecanoic acid area values. Subsequently, obtaining a relatively high area is favored by a long time (10 min) and low T_{des} values (200°C) in the Twister©.

Seen in Figure 8 the obtained area for octadecanoic acid was sensitive to changes in both T_{cis} and T_{des} and had a negligible statistical influence on other independent variables. Additionally, a positive influence of both parameters is observed. Subsequently, a higher area for octadecanoic acid could be obtained operating under high values of T_{cis} at 20°C and T_{des} at 300°C.

To establish a single condition useful for extraction of samples for determination of all analytes, working values of T_{des}, t, T_{cis}, and F must be fixed as 300°C, 3 min, –20°C, and 50 ml min^{-1}, 8C, 90W and 9.0 min, respectively. It is important to note that under these conditions a high response for the desorption process in the obtained compounds area may be achieved with the exception of pentadecanoic and octadecanoic acid. In relation to pentadecanoic acid, the response area is increased by 66% by operating under low T_{des} and long time. However, the response of Octandecanoic acid increased to 54 % for high levels of T_{cis} and F or high levels of T_{cis}, F and t.

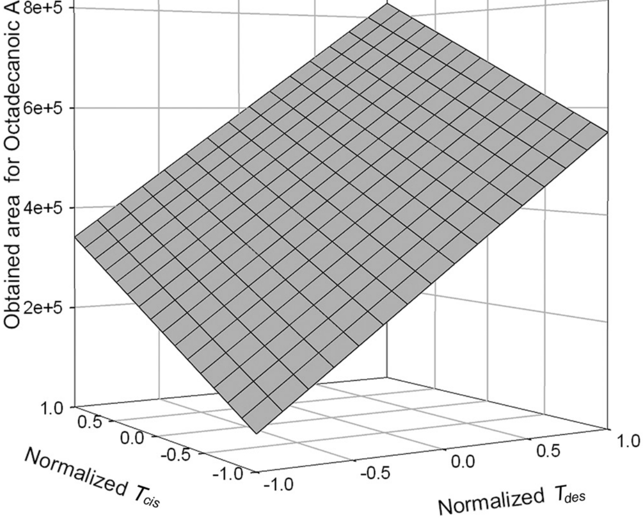

Figure 8. Obtained area for Octadecanoic Acid variation as a function of T_{cis} and T_{des}.

CONCLUSIONS

Parameters affecting thermal desorption of analytes have been optimized by means of a Box-Behnken experimental design. Among the volatile compounds emitted by Municipal Solid Waste, 15 components were identified using SBSE-TD-GC-MS. The main compounds identified in samples were terpenes, saturated fatty acid meat cooking related compounds, antioxidant compounds such as butylated hydroxytoluene, and organophosphate flame retardants from plastics. Optimum analytical conditions for obtaining a maxima response area for the desorption step were desorption temperature at 300°C, cryofocusing temperature at –20°C, flow of helium at 50 ml min^{-1}, and desorption at time 3 min.

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Characterisation of Residence Time Distribution in a Continuous Paddle Dryer

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ABSTRACT: A method to determine residence time distribution (RTD) of municipal sewage sludge in a continuous contact dryer with agitation has been developed. Experiments were conducted using a pulse injection of chloride sodium and by sampling and analysing the electrical conductivity of sludge leachate offline. Experiments were performed with the same operating conditions in triplicate but with a sampling interval at the wastewater treatment plant of several weeks. Accuracy and reproducibility of the method was quantified with an averaged mean residence time of 160 ± 7 min. The RTD curves shows sludge flow behavior is intermediate between a plug flow and a perfectly mixed flow. This is due to presence of paddles which induces axial dispersion on the flow.

INTRODUCTION

A drying operation is an essential and unavoidable stage to valorize sludge in incineration, pyrolysis or gasification. For instance, dry solids content from 60% to 90% are expected for co-incineration with municipal solid wastes while more than 85% are needed for pyrolysis and gasification [1]. Considering the limited separation yields of the conventional mechanical dewatering devices, those targeted dry solid contents can only be reached by partial or full drying.

Besides a uniform treatment, the flexibility of the process to adapt the final solid content of the dried sludge to the demand will be a major requirement of any sludge drying system in the near future. Presently, this flexibility does not exist. A third of the driers in operation are designed to reach a dry solid content of 65%. Whereas in the other two thirds, the dry solid content of the sludge exceeds 90%. Most often, the sludge is over dried and energy consumption of the drying system is much higher than needed. Modeling the drying process is essential to improve sustainability of sludge drying operations. Several approaches exist. The classical approach based on integral heat and mass balance equations written for input and output parameters of the process does not take into account local conditions of heat and mass transfer that may vary significantly over the apparatus. Much closer to the real process, the local approach which employs differential momentum heat and mass conservation equations requires special skills in mathematics making them inconvenient for engineers. Chemical engineers use a simpler approach which couples a hydrodynamic characterization of the reactor using the concept of Residence Time Distribution (RTD) with a kinetic model to predict average outlet concentration in a real reactor. The principle of RTD measurements [2] is to inject an inert tracer into the reactor at some initial time and to measure the tracer concentration in the outlet stream as a function of time. The RTD function which describes in a quantitative manner how much time different fluid elements have spent in the reactor is computed from the concentration-time curve. A recent literature review lists different methods and techniques which can be used for RTD determination in processes involving solids such as dryers, grinders, extruders, or mixing devices [3]. The chosen tracer should be a non-reactive species, easily detectable, and must have physical properties similar to those of the bulk product. Colored [4,5,6], chemical, and electrolyte materials [4,7] are the most common types of tracers. Drastic constraints related to safety [8] limit uses of radioactive tracers [9,10].

The present study concerns evaluation of flow pattern in a lab-scale paddle dryer (first stage of modeling methodology mentioned above) through RTD experiments. Paddle dryers are frequently used for sludge treatment but excessive drying is often noted. These dryers consist of a horizontal heated trough containing at least two rotating heated shafts with wedge-shaped

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paddles welded on each shaft. The only function of these paddles is to ensure a good mixing in the radial direction to homogenize product temperature and to avoid clogging. Since these paddles do not contribute to product transport, a plug flow is expected to occur. To date we only identified one study characterizing the RTD in a sludge paddle dryer [11]. Nickel chloride ($NiCl_2$) and manganese chloride ($MnCl_2$) were used as tracers. Dried sludge samples were pretreated using dry ash and wet digestion methods before amounts of nickel and manganese are determined by flame atomic absorption spectrometry. Results emphasize that the flow pattern in a large-scale paddle dryer equipped with four rotating shafts is not a simple plug flow. Back mixing of the sludge occurs, especially near the middle of the dryer where the sludge consistency is sticky. However, the RTD analysis was subjected to large inaccuracies as the concentration-time curve was incomplete. Indeed, even if the RTD experiment lasted six hours, no experimental data were collected to describe the tail of the concentration-time curve. Consequently, the area under the concentration-time curve and residence time were under-estimated. In addition, reproducibility and accuracy of the method are not discussed. The proposed analytical protocol is time-consuming. Therefore, a simpler method based on a pulse injection of sodium chloride into the dryer and detection by conductimetry is proposed in the present paper. The analytical protocol and lab-scale dryer used for the experiments are described in section 2. Special attention is paid to the calibration curve in particular. Reproducibility and accuracy of the method are discussed in section 3.

Table 1. Initial Dry Solid Contents.

Experiment 1	Experiment 2	Experiment 3
19.1 ± 0.1%	19.3 ± 0.1%	21.6 ± 0.1%

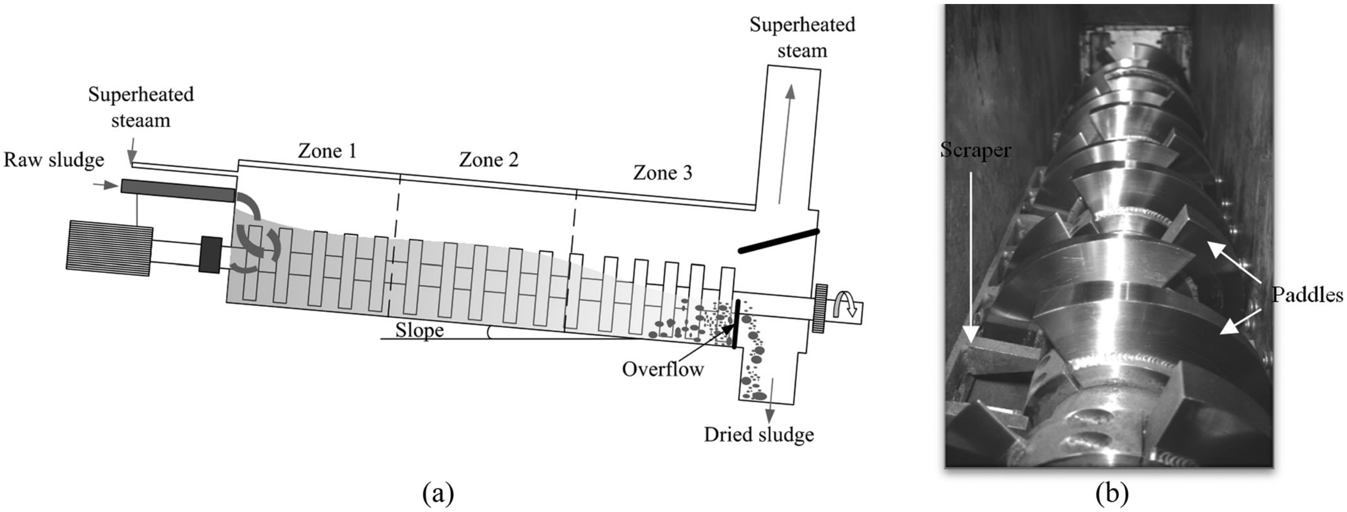
MATERIAL AND METHODS

Feed Material

Sewage sludge was sampled in the urban wastewater treatment plant (WWTP) of Albi city (France). The WWTP, designed for a capacity of 91,000 population equivalent (PE) but operating at 60,000 PE, implements a conventional extended aeration process, a nitrification/denitrification process, a biological phosphorus removal, and an anaerobic digestion process. Three drying experiments were performed requiring sampling of three different sludge batches. Sludge was sampled after centrifugation and stored at 4°C in a tight container. Experiments were performed within 1 week after sampling.

Continuous Contact Dryer

Currently, drying and RTD experiments are performed on a lab-scale (15 kg/h) continuous agitated contact dryer designed and built by the authors [See Figure 1(a)]. This dryer consists of a U-shaped jacketed trough with a rotating shaft. The trough is 1m long, 0.32 m high, and has an inner diameter of 0.16 m. Three U-shaped electrical resistances (Chromalox, Soissons, France) 0.33 m long each are inserted in the double wall. Each can supply up to 6.10^4 W/m^2. Three



(a) (b)

Figure 1. *(a) Schematic of the laboratory indirect dryer and (b) photo of the mixing device.*

temperature sensors, one for each electrical resistance, are used for thermal regulation of the dryer wall. These sensors set at 0.001 m from the wall front side in contact with the sludge are positioned at 0.16, 0.50, and 0.83 m from the dryer inlet, respectively. To limit thermal losses towards the outside, the trough is insulated with a 5 cm thick Superwool® HT Fibers (Eurotech, Cessales, France).

This trough is closed by a removable and tight hood with three trap doors. For each zone of 0.33 m length, four heating cartridges (Chromalox, Soissons, France) are inserted in the 6 cm diameter hollow shaft. Each can supply up to 10^5 W/m^2. Three temperature sensors, one for each zone, are used for thermal regulation of the rotor. These sensors set at 0.015 m from the outward are positioned at 0.12, 0.46, and 0.79 m from the dryer inlet. Eighteen full wedge-shaped paddles are screwed onto the rotor and heated by conduction. In the current configuration, paddles are regularly distributed along the shaft. Scrapers formed to interact with paddles are positioned on the trough [See Figure 1(b)]. A 4 kW asynchronous motor with a variable frequency drive (Leroy Somer, Colomiers, France) permits a precise adjustment of the rotor's speed between 10 and 60 rpm. A contactless DR2112 torque meter (LR Mesures, Libourne, France) for measurements up to 500 Nm max equips the stirrer. The drier rests on a support which can be tilted ± 5°. A Moineau 2.6 IVA pump (PCM, Levallois Perret, France) conveys mechanically dewatered sludge from the feed hopper of a capacity of 40 l to the dryer. Pump speed is controlled with a frequency inverter. Sludge is fed into one end of the trough and flows due to gravity into the dryer slope and mechanical agitation at the opposite end where dry material is discharged. Solids hold-up in the dryer is controlled through an adjustable overflow. Superheated steam (1 atm, 160°C) produced by a 4 kW steam generator and a 0.3 kW superheater (TATT, Eybens, France) is used as sweeping gas. The sweeping gas and vapors exhausted during processing are carried out through a central exhaust port.

Operating conditions were selected and set for drying experiments. They are summarized and may be seen in Table 2.

Table 2. Operating Conditions.

Wet basis mass flow rate		4.7 kg/h
Dryer slope		2°
Dryer wall temperature		160°C
Stirrer speed		7 rpm
Superheated steam	Temperature	160°C
	Mass flow rate	1.1 kg/h
	Pressure	1 atm

Tracer

Choice and Test Validation

Choice of tracer was made considering tracers currently used in wastewater treatment studies, measurement techniques available in the lab, repeatability and accuracy of the measurement techniques in regard to the required degree of precision, and "thermal stability" with the drying conditions [12]. In the field, three tracers are mainly used: lithium chloride LiCl [13,14,15], sodium chloride NaCl [16], and rhodamine [17,18,19,20]. Sodium chloride is a popular choice for tracer test studies given its low cost and ease of monitoring. Electrical conductivity was retained as the detection method and NaCl was selected as the tracer.

Influence of the tracer powder dispersion method on sludge structure and viscosity, drying kinetics, and sticky phase were investigated. Even if mixing in a planetary mixer changes rheological properties of raw sludge and increases its stickiness, it does not have any influence on the drying kinetic and sticky phase [21].

Concentration Determination with Calibration Curve

To implement the detection method, sludge samples must be dried at 105°C for 24 h and leached during 24 h with demineralised water ($m_{\text{water}}/m_{\text{DM}} = 10$, where m_{water} and m_{DM} are water and dried matter masses, respectively).

A series of standards in demineralised water and sludge samples across a range of concentration close to

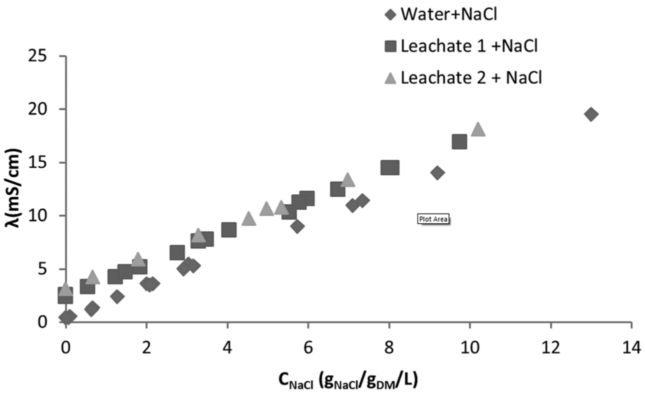


Figure 2. Calibration curves.

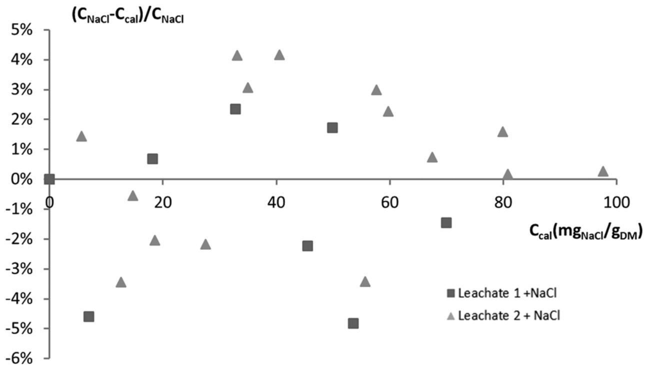


Figure 3. *Accuracy of the calibration curve.*

the expected concentration of NaCl in the leachate has been prepared. Concentration of NaCl was measured with a DCM210 conductivity meter (MeterLab, Copenhagen, Denmark). Calibration curves for NaCl in water and NaCl in sludge leachates are plotted in Figure 2. To investigate influence of sludge composition, two batches were sampled at an interval of one month at the WWTP (leachate 1 and leachate 2).

As expected, electrical conductivity (λ) for standards prepared in demineralised water and sludge leachates varies linearly with NaCl concentrations. Data were fitted according to Equation (1). The slope parameter, *a*, and the conductivity of the background (demineralised water and sludge), λ_{ini}, are displayed in Table 3.

$$\lambda = \lambda_{ini} + a * \mathrm{C}_{\mathrm{NaCl}} \tag{1}$$

Translation of the curves induced by conductivity of the background has to be considered for each sludge batch. Indeed, a change of initial sludge conductivity will induce an over- or under- estimation of tracer concentration.

Table 3. Coefficients of Equation (1).

	Water + NaCl	**Leachate 1 + NaCl**	**Leachate 2 + NaCl**
λ_{ini} (mS.cm^{-1})	0.44	3.18	2.46
a (mS.gDM.L.cm^{-1}.gNaCl^{-1})	1.48	1.47	1.49
r^2	0.991	0.98	0.990

The calibration equation that should be used to calculate NaCl concentration for unknown samples Ccal is given by Equation (2).

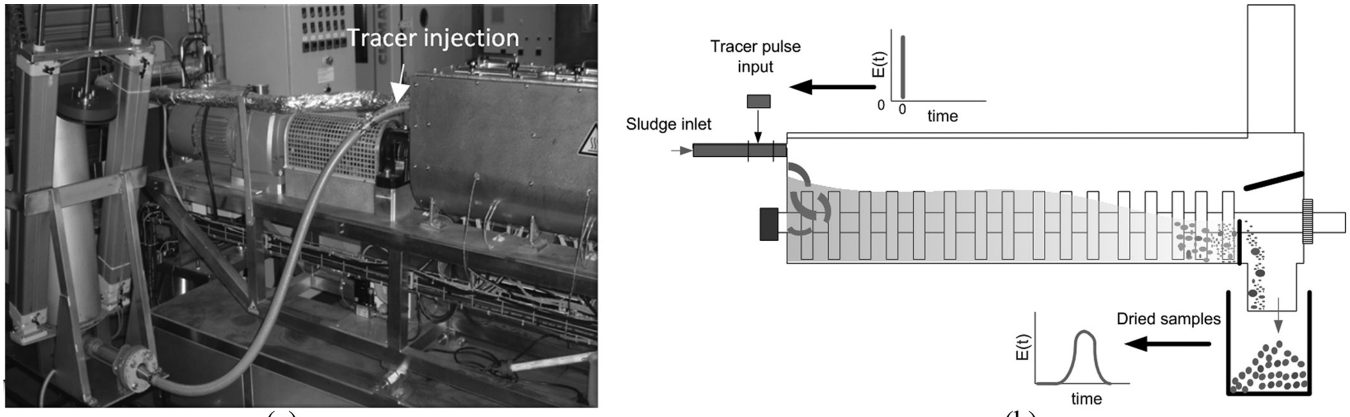
$$C_{cal} = \frac{\lambda - \lambda_{ini}}{1.48} \tag{2}$$

Figure 3 shows the relative error in the calculation of the concentration by using the calibration equation. Residual errors are randomly distributed for two leachates and maximal residual error on the prediction is at 5%.

Tracer Injection and Sludge Sampling

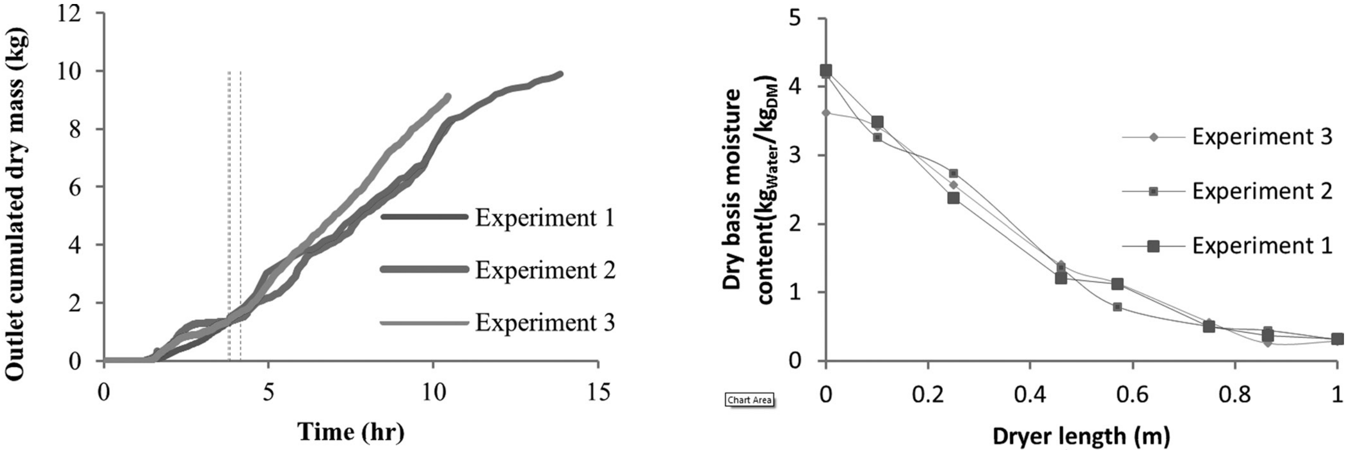
An amount of 90 g of NaCl powder, determined in order to have a minimum pic of conductivity three times higher than the background conductivity, was mixed with raw pasty sludge. Preparation was then injected at the inlet of the dryer [See Figure 4(a)] in a short time to obtain a Dirac function.

The whole sludge outflow mass was sampled and analysed [See Figure 4(b)]. After introduction of the tracer, samples were taken every 5 or 10 min during a minimum of 6 hrs, then dried, and then leached as described before.



(a) (b)

Figure 4. *(a) Tracer injection and (b) sampling method.*



(a) (b)

Figure 5. *(a) Outlet cumulated dry mass and (b) dry basis moisture content distribution along the dryer (kg_{Water}/kg_{DM}).*

Data Analysis

Knowing the NaCl concentration, the exit age distribution function $E(t)$ was calculated according to Equation (3):

$$E(t) = \frac{C_{NaCl}(t)}{\int_0^\infty C_{NaCl}(t)dt} \quad (3)$$

The mean residence time, t_s, the variance of the residence time, σ^2, and the dimensionless variance, σ_D^2, are given in Equations (4)–(6):

$$t_s = \int_0^\infty t.E(t)dt \quad (4)$$

$$\sigma^2 = \int_0^\infty (t - t_s)^2 E(t)dt \quad (5)$$

$$\sigma_D^2 = \left(\frac{\sigma}{t_s}\right)^2 \quad (6)$$

The averaged dryer velocity, v_{mean}, is then given by Equation (7):

$$v_{mean} = \frac{L}{t_s} \quad (7)$$

where L is the length of the dryer.

RESULTS AND DISCUSSION

Drying Experiments

Three drying experiments were performed with operating conditions displayed in Table 2. In particular, the wet basis mass flowrate at the inlet is kept constant for the three experiments. Cumulated mass of dry solids recovered at the dryer outlet during each experiment is plotted in Figure 5(a). As dry solid content of the raw sludge is higher for experiment 3, the slope of the corresponding curve on Figure 5(a) is slightly larger.

As seen in Figure 5(b), the dry basis moisture content distribution along the dryer is reproducible for the three experiments. Drying drastically reduces dry moisture content from 4 kg_{Water}/kg_{DM} at the entry of the dryer to 0.39 kg_{Water}/kg_{DM} at the outlet.

Drying rate of indirect dryers usually ranges between 5 and 20 $kg/m^2/h$ [1,22]. Average drying rate for the three experiments is lower than 5. Drying rate has been calculated here taking the whole heated wall surface into account (1 m^2) like for industrial paddles dryers. However, the filling rate of the dryer is low and the heating surface (wall and stirrer) is partially covered by the sludge (See Figure 6). As a result the effective drying rate is under estimated.

The sludge looks like a viscous fluid from the dryer entry to 0.33 m in the first zone [See Figure 6(a)]. Averaged drying rate for the three experiments is 5.22 $kg/m^2/h$ and a decrease of dry basis moisture content from 4 to 2 kg_{water}/kg_{DM} is observed. In the

Table 4. Characteristics of the RTD.

	Experiment 1	Experiment 2	Experiment 3
t_s (min)	156	169	157
σ_D^2	0.36	0.17	0.17
v_{mean} ($m.h^{-1}$)	0.29	0.27	0.27
t_{app}/t_s	0.28	0.27	0.30

(a) (b) (c)

Figure 6. *Photo of the sludge in zone 1 (a), zone 2 (b), and zone 3 (c).*

second zone [See Figure 6(b)], from 0.33 m to 0.66 m, a change of the sludge consistency from pasty at 2 kg_{water}/kg_{DM} to sticky at 0.75 kg_{water}/kg_{DM} may be observed. This change induces a decrease in the drying rate to 3.61 $kg/m^2/h$. Volume of the sludge considerably decreases and the heated surface is less covered than in zone 1 [See Figure 6(b)]. In the third zone of the dryer, from 0.66 m to 1 m, the material is granular and average drying rate strongly decreases to 0.97 $kg/m^2/h$ as the dry basis moisture content is reduced from 0.75 to 0.39 kg_{water}/kg_{DM}. Withdrawal resulting from water evaporation further reduces contact surface.

RTD Experiments

Figure 7 shows conductivity and percentage of recovered tracer versus sampling time after the tracer injection. As background conductivity was higher for experiment 1, the corresponding curve is shifted upwards. Nevertheless, the shapes of the three curves are similar.

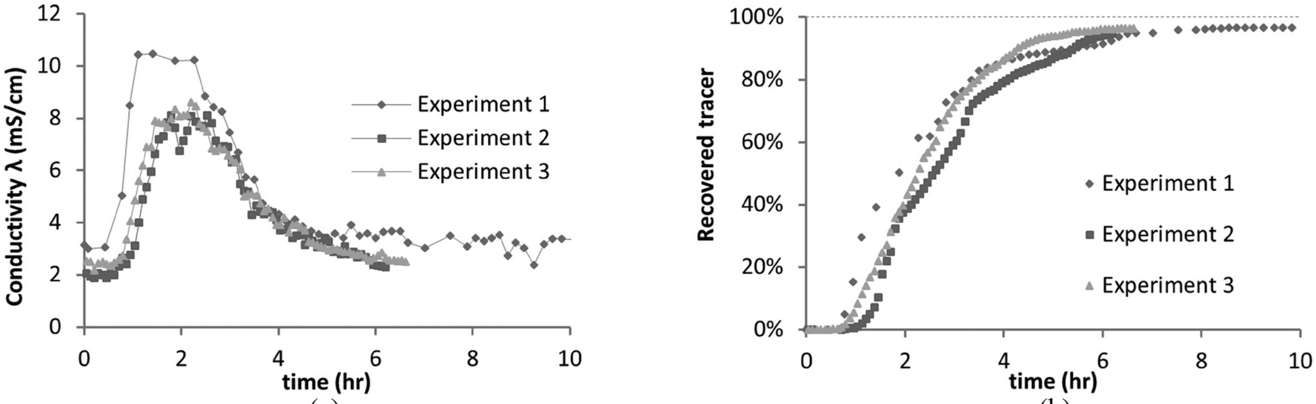
Approximately 6 hr after tracer injection, electrical conductivity of the leachates tends towards its initial value. Percentage of tracer recovered reaches at least 95%. Values for mean residence time and averaged velocity in the dryer are listed in Table 4 for each of the drying experiments. For an averaged mean residence time of 160 min, the standard deviation obtained is 7 min which represents 4.5% change and thus establishing acceptable reproducibility of results.

Figure 8 shows the normalized, $E(\theta)$, and cumulative, $F(\theta)$, exit age distribution plotted against normalized time θ defined as the ratio t/t_s.

Cumulative exit age distributions of a perfect plug flow (PFR) and perfectly mixed flow (CSTR) reactor are also added on Figure 8(b). RTD distribution of the sludge in the paddle dryer lies between these two ideal cases.

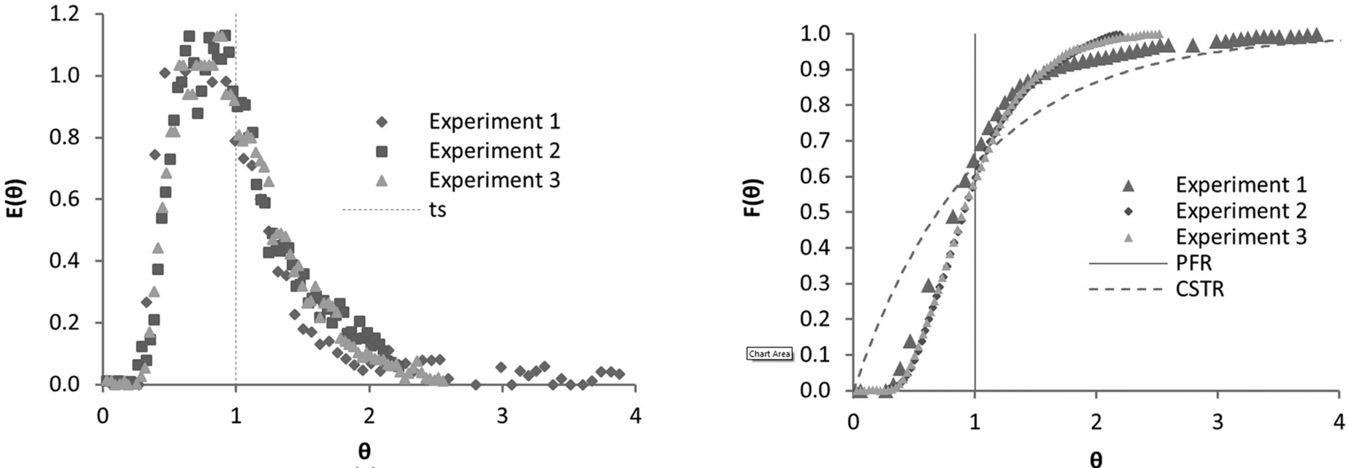
Onset time, t_{app}, is introduced corresponding to time at which the beginning of the peak is detected. The ratio t_{app}/t_s can provide information about flow. It is equal to 1 for a plug flow and to 0 for a perfectly mixed reactor. This ratio reaches 0.28 here. Flow behavior is closer to a perfectly mixed flow than a plug flow as a result.

Figure 9 shows cumulative RTD curves for different solids unit operations together with the one achieved for experiment 2. In rotary drums and milling processes, the product flow is theoretically only due to gravity. The flow in a rotary drum process is known to tend toward a plug flow (curve a). The axial dispersion is low



(a) (b)

Figure 7. *(a) Conductivity measurements and (b) percentage of recovered tracer versus sampling time.*



(a) (b)

Figure 8. (a) Normalized exit age distribution and (b) normalized cumulative exit age distribution.

and all particles have practically the same residence time [23]. On the contrary, flow in the majority of the milling processes is considered as fully mixed flow (curve b) with high dispersion induced by milling balls and particles having different residence times [24].

In an extruder made up of a screw conveyer and a continuous screw blender the product flow is due to the rotation of the screw. The screw is designed only to displace the solid and a flow close to plug flow is chosen for solids conveying [See Figure 9(c)] [25]. On the contrary, high mixing is searched in a continuous blender and the screw is designed to obtain a flow close to a perfectly mixed flow [curve (d)] [5]. Different flows in extrusion may be obtained [curves (e) and (f)]. For example, Zuilichem *et al.* (1999) demonstrated the impact of different screw geometries on RTD distribution of food materials [26]. Axial mixing is improved by using paddles but there is a lack of conveying. Lead element provides reasonable conveying but axial mixing is very poor. Paddles induce dispersion of the RTD which tends toward a perfectly mixed flow. A combination of paddles and lead elements seems to be the solution to achieve strong and homogeneous treatment in the system.

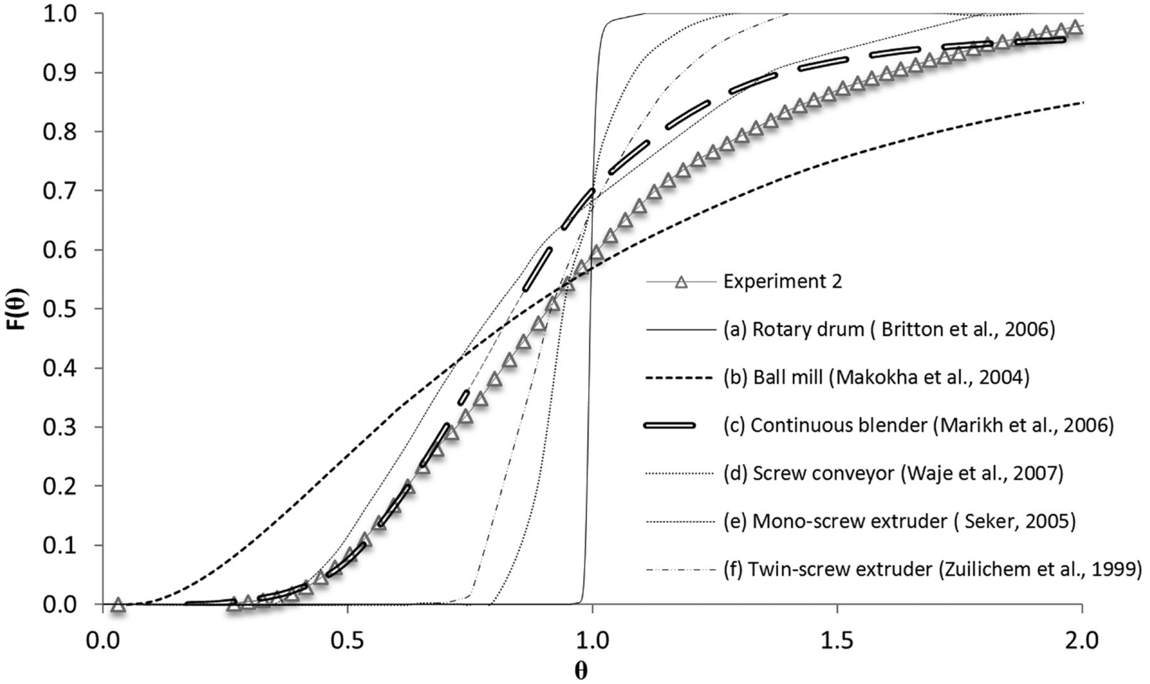


Figure 9. Normalized cumulative curves F(θ) for experiment 2 and for different solid technologies found in the literature: (a) rotary drum, (b) ball mill, (c) screw conveyor, (d) continuous blender, (e) single-screw extruder, and (f) twin-screw extruder.

CONCLUSION

A method used to characterize residence time distribution (RTD) of sewage sludge in a contact dryer with agitation has been developed. Injection and detection of a NaCl tracer in the leachate is a simple and accurate method for determination of RTD curves. A calibration curve is required to implement this method and conductivity of the raw sludge must be characterized for each experiment.

Reproducibility of drying and RTD experiments has been characterized for three sludge batches. The dry basis moisture content distribution along the dryer was reproducible and normalized exit age distributions are superimposed for the three experiments. A standard deviation of 4.5% for an average mean residence time distribution of 160 min was noted.

It appears that sludge flow behavior is intermediate between a plug flow and a perfectly mixed flow. Although part of the flow is due to gravity, presence of paddles induces axial dispersion.

Response surface methodology will be used to study influence of the main processing parameters such as stirring speed, angle of inclination, and mass flow rate in future works. Use of a model based on the theory of Markov is actually under development. Flows of sludge and vapor in the dryer are represented by two parallel chains which can exchange heat and/or mass. Each chain contains a finite number *n* of perfectly mixed cells. The transport of the medium along a chain is described by the matrix of transition probabilities. Transition probabilities between cells of the product chains are governed by a single parameter known as parameter of internal recirculation, *R*. The study should show if the evolution of this parameter in the model can be linked to drying kinetics and viscosity evolution in the dryer.

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Effect of Environmental Conditions on Phenol Biodegradation by Newly Isolated Bacterium (*Alcaligenes sp. ATHE8*) from Coke Processing Wastewater

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ABSTRACT: Phenol biodegradation potential of isolated bacteria from polluted wastewater was evaluated. One strain was found to be highly effective in removing phenol as a sole carbon and energy source. Effects of temperature (20 to 45°C), pH (4 to 9), aeration (0 to 200 rpm), and glucose concentration (0 to 4 g/L) on phenol degradation rate were studied in presence of 1,000 mg/L phenol. Phylogenetic analysis showed a 98% DNA sequence identity to *Alcaligenes faecalis sp.* The present study determined optimum conditions for phenol biodegradation with a temperature of 35°C, pH of 7, shaking rate of 150 rpm, and glucose concentration of 0.5 g/L. Phenol biodegradation efficiency was 100% at 72 h. Therefore, it was concluded that efficiency of phenol biodegradation increases by utilization of native bacterial strains from wastewater in optimum conditions.

INTRODUCTION

PHENOL is a moderately soluble (roughly 8 g/100ml water) and highly mobile compound. It may eventually reach the downstream water sources where it can be toxic to aquatic organisms and may cause taste and odor problems in drinking water [1,2,3]. Phenol can also be toxic in concentrations of 0.2 mg/ml and above, and it can kill the cells within an hour. However, the skin cells appear to be less sensitive to the effects of phenol than fibroblast cells [4].

Biodegradation of phenolic wastes by bacteria has been extensively studied and a large number of phenol-degrading bacteria have been isolated and characterized at the physiological and genetic level [5,6,7]. Currently, phenol is removed by methods such as precipitation/coagulation, osmosis, ion-exchange, ultra filtration, electro dialysis, electrochemical degradation and floatation which are costly and highly time- and energy-consuming. These treatment methods often produce other toxic end products requiring further processing steps [8,9,10]. Biodegradation on the other hand has been studied as an alternative approach due to low costs (does not need any expensive instruments) as well as the possibility of complete mineralization of the xenobiotic [11,12]. Studies have shown that phenol can be aerobically degraded by a wide variety of fungi and bacteria such as *Candida tropicalis, Alcaligenes eutrophus* [13], and *Pseudomonas putida* [14]. Removal of phenol from industrial effluents by bacteria can be a complicated practice. The rate of pollutants biodegradation in natural environments is affected by a variety of factors, including adaptation of the microbial community to a particular chemical, aeration, acidity, carbon source and temperature of media. Adaptation may be operationally defined as an increase in the ability of a microbial community to degrade a chemical after a prolonged exposure to the degradative material. In other words, it may be the result of several alterations in both structure and function of microbial communities [15].

Rate of phenol degradation for different environmental conditions was investigated using indigenous bacteria isolated from phenolic wastewater from the Esfahan Steel Company in 2012.

MATERIALS AND METHODS

Sampling

Samples were collected from coal tar processing phenolic wastewater from the Isfahan Steel Company, Isfahan, Iran. The bacterial consortium was isolated

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from a mixture of wastewater samples in mineral salt media supplemented with phenol as a sole carbon source. Some properties of the wastewater such as pH, electrical conductivity (EC), and phenol concentration were also determined.

Mineral Salts Medium (MSM)

Bacterium was grown in the liquid salt medium with 1,000 mg/L phenol. MSM contained deionized water of 1,000 ml, Na_2HPO_4 of 5.3 g, NH_4Cl of 2.6 g, $CaCl_2.H_2O$ of 2.6 mg, $MgSO_4$ of 0.6 mg, $FeSO_4.H_2O$ of 24 mg, and $MnSO_4.H_2O$ of 9 mg. Phenol was added from sterile stock solution to the autoclaved medium prior to inoculation [16].

Phenol Degradation Experiment

The experiment was started by inoculating 15 ml mineral cultures with 1,000 mg/L phenol using 1 ml of wastewater. The mixture was incubated at 25°C on a rotary shaker at 120 rpm for 1 week. Enrichment culture of 5 ml was transferred to a fresh medium and incubated under the same conditions after observing the growth for one week. Subsequently, the culture was transferred into a phenol containing medium three times to enrich the bacterium.

Isolation and Biochemical Analysis of the Best Phenol-Degrading Bacterium

The above enriched cultures were serially diluted and spread on MSM agar plates supplemented with 1,000 mg L^{-1} phenol and incubated at 28°C for 3 to 5 days. Isolation of bacteria was based on the colony morphology such as size, shape, color, margin, and texture. Different colonies were picked and streaked on LB plates for identification and selection of the best isolate. Pre-selected isolates were repeatedly streaked on agar plates in order to obtain a pure culture of bacteria. Gram staining of each bacterium was conducted before identification. Finally, only one isolate with the highest growth rate with presence of phenol after 24 h was selected for assay by polymerase chain reaction and optimization of experimental conditions. Catalase activity, Nitrate reduction, indole production, acid or gas production from d-glucose, monitol, Voges–Proskauer reactions, citrate utilization, and hydrogen sulfide production were also tested as described in Bergey's Manual of Systematic Bacteriology [17].

Optimal Conditions Assay

The best bacterium with the highest growth rate at presence of phenol after 24 h was selected for optimization of biodegradation experiments. Effects of adding a carbon source (0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 g/L glucose), pH (4, 5, 6, 7, 8, and 9), rate of shaking (50, 100,150, and 200 rpm), and temperature (20, 25, 30, 35, 40, and 45°C) on phenol degradation were investigated. All samples were periodically taken for biomass and phenol concentration determination. All of the experiments were carried out in duplicate [18].

Biomass and Phenol Determinations

Cell density and phenol concentration were spectrophotometrically monitored by measuring absorbances at wavelengths of 560 and 630 nm, respectively [19]. Suspended culture of 3 ml was centrifuged at 6,000 rpm for 10 min. Free supernatants were used to determine concentration of phenol using Gibbs reagent and the spectrophotometric method [20].

DNA Extraction and Polymerase Chain Reaction (PCR) Application

Genomic DNA extraction of the bacterium was done using a DNA extraction kit (Sinaclon Co). The extraction procedure was carried out according to manufacturer's instruction. In brief, 100 µl of overnight bacterial culture was pelleted on protease buffer and followed by addition of 5 µl protease to the cells, mixed, and then exposed to 55°C for 30 min. 100 µl of the sample was mixed with lysis solution and a short vortexing at the lowest vibration setting was followed to lyse bacterium cells. Precipitation solution of 400 µl was added to precipitate DNA. The DNA was washed with a 1 ml wash buffer, dried, and dissolved by a solvent buffer. Extracted DNA was analyzed using 1% agarose gel electrophoresis. Accordingly, extracted and purified DNA was stored in –20°C before use.

Standard PCR amplification was performed in a 25 micro liter reaction volume using smart Taq polymerase. The reaction mixture contained 2.5 U smart Taq polymerase, 2 mM dNTP mix, 100 micro liter 10× PCR reaction buffer, 2 mM $MgCl_2$, and 2 micro liters of 100 picomole each of the primers F27 (5-AGCGGTCCAGAGTTTTCCTGG-3) and R1492 (5-CTCTCTGCAGCCCTTGTTACG-3). The reaction mixture was subjected to an initial 5 m of incubation at 95°C to denature DNA. This was followed by 33 cycles of amplification which included a 20 s denaturation at 94°C, a 25 s annealing at 60°C, and a 30 s extension at 72°C. A 1 m extension at 72 °C was performed at the end of the final cycle. Amplified products were stored at 4°C prior to analysis by agarose gel 1% electrophoresis [21].

RESULTS AND DISCUSSION

Initial phenol concentration of the studied wastewater was found to be 1,207 mg/L (acceptable phenol concentration in wastewater is 0.5 mg/L according to the United States Environmental Protection Agency (USEPA)) [16]. Moreover, the pH and EC of the wastewater were 7.56 and 2.9 dS/m, respectively.

Six bacterial strains were found to be growing in a mineral salt medium containing 1,000 mg/L of phenol during the early screening. Figure 1 shows growth rate of the isolated bacteria after 24 h. The isolate with the highest growth ability in presence of 1,000 mg/L phenol was selected as the best isolate (isolate 1) (See Figure 1).

Although phenol has the ability to cause cell lysis, some bacteria can tolerate and even utilize it in absence of another carbon or energy source. Many studies have reported presence of such bacteria [11,22–28].

According to the biochemical analysis, the selected bacterium (isolate 1) was gram negative, oxidase and catalase positive, manitol and glucose negative, and VP negative. 16S rDNA sequence analysis of isolate 1 also showed a 98% DNA sequence identity to *Alcaligenes faecalis.* This strain is referred as *Alcaligenes faecalis strain ATHE8* with the accession number of KC145574.1. Eduardo *et al.* (2000) also isolated such a bacterium from Amazonian soil samples able to remove high concentration of phenol [29].

Phenol biodegradation was carried out with pure cells of *Alcaligenes faecalis strain ATHE8* under different conditions using the same phenol concentration.

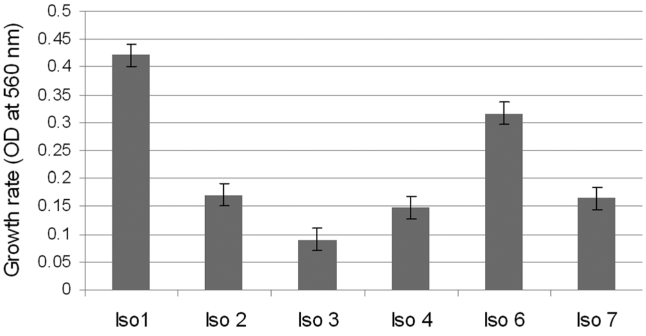

***Figure 1.** Growth rate of 6 isolates in 1,000 mg/L phenol after 24 h.*

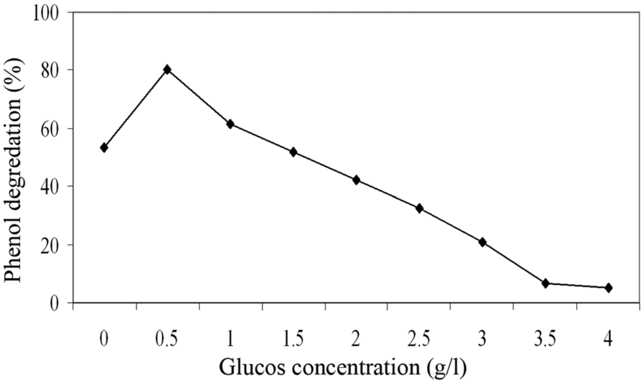

***Figure 2.** Effects of glucose concentration on phenol degradation by Alcaligenes faecalis strain ATHE8.*

Effect of glucose addition has been shown in Figure 2. Phenol removal efficiency was determined at different glucose concentrations (0–4 g/L), pH = 7, and 25°C at time intervals. Maximum phenol removal efficiency was 80% which occurred at 0.5 g/L of glucose concentration (See Figure 2).

Glucose, due to its simple structure in comparison with phenol, can act as a growth substrate in wastewater. Regarding low concentrations of glucose (0–0.5 g/L), the phenol biodegradation rate increased without any inhibitory effect. However, during higher concentrations of glucose (> 0.5 g/L), the phenol biodegradation decreased due to utilization of glucose by the bacterium to synthesize new cells. Kar *et al.* (1996) showed the effect of glucose on phenol degradation. Their results indicated that when a mixed substrate (phenol and glucose) was used the phenol adopted bacteria showed an initial preference for phenol to glucose concentration [30]. Chakraborty (2010) also showed that a glucose concentration of 0.5% repressed induction of phenol oxidation though glucose did not fully repress utilization of phenol [31]. Such results were reported by Santos *et al.* (2003) and Khaled (2006) in their studies [32,33].

Effect of temperature (20 to 45°C) on the phenol biodegradation is illustrated in Figure 3. Observed at 35°C, the maximum phenol biodegradation occurred within 96 h while at 20°C and 45°C it was observed within 165 h and 192 h, respectively (See Figure 3). Degradation was inhibited both at low as well as high temperatures. Previous studies by Polymenakou and Stephanou [34] and Rosa *et al.*, [35], on phenol degradation by soil Pseudomonad support these results. Maximum degradation rates for phenol were reported at 30°C in studies on *Pseudomonas pictorum* [36]. However, in these studies a temperature of 35°C showed a considerable amount of degradation.

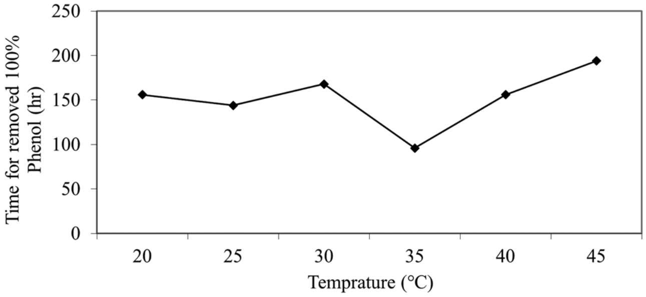

***Figure 3.** Effects of temperature on phenol degradation by Alcaligenes faecalis strain ATHE8.*

The effect of aeration (shaking at 0–200 rpm) on phenol-degradation ability of ATHE8 is displayed in Figure 4. Optimum speed of aeration was 150 rpm in which phenol degradation of 100% occurred within 96 h as compared to 160 h under static conditions at 200 rpm.

Kotresha *et al.* (2008) also studied effect of shaking rate on phenol-degrading ability of P. aeruginosa. They found the speed of 100–125 rpm was optimum requiring 66 h for 100% degradation as compared to 84 h under static conditions. However, at 200 rpm the time required for 100% degradation was 108 h [11].

The effect of pH (4 to 9) on complete degradation of phenol is displayed in Figure 5. In 96 h, 100% phenol was removed at pH 7 while at pH's of 6 and 8 100% of phenol was removed in 120 h. At a pH of 9 192 h was required for phenol degradation.

At low (4) or high (9) pH values, acids or bases can penetrate into cells more easily because they tend to exist in unseparated form under these conditions and electrostatic forces fail to prevent them from entering cells [11].

Studies by Karigar [37] on *Arthrobacter citreus* and also by Chakraborty [31] on native microorganisms isolated from coke processing wastewater support these results. This may be due to effects of pH on ionization and hence binding and interaction of various molecular processes which consecutively affect metabolic pathway.

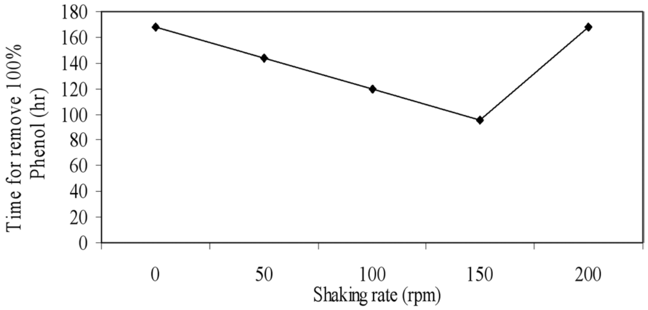

***Figure 4.** Effects of shaking rate on phenol degradation by Alcaligenes faecalis strain ATHE8.*

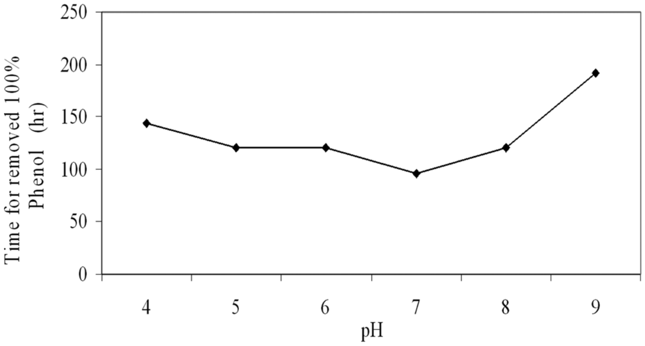

***Figure 5.** Effects of pH on phenol degradation by Alcaligenes faecalis strain ATHE8.*

Phenol Biodegradation in Optimal Conditions

Phenol biodegradation in optimal conditions (pH = 7, 0.5 g/L glucose, 150 rpm shaking, and 35°C) was also investigated (See Figure 6). Time required for 100% degradation was 72 h for the previously mentioned optimal conditions.

CONCLUSION

Environmental pollution from toxic chemicals is one of the most important problems facing industrialized, high-consumption, and/or high waste-producing nations. Some native bacterial strains isolated from coke processing wastewater can be good phenol degraders at an optimum pH of 7, a shaking rate of 150 rpm, a temperature of 35°C, and with 0.5 g/L glucose. The phenol biodegradation efficiency was found to be 100% within 72 h for above conditions. This study revealed the important role of the newly isolated strain *Alcaligenes faecalis strain ATHE8* in phenol biodegradation. Therefore, this strain may be a good choice for cost effective application in bioremediation and waste-

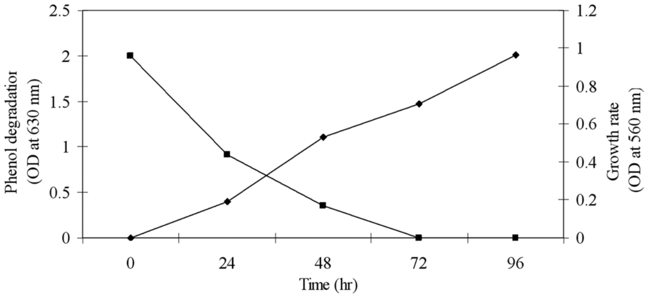

***Figure 6.** Effect of optimal conditions on phenol degradation by Alcaligenes faecalis strain ATHE8.*

water treatment at a large scale especially for detoxification of phenolic effluents.

ACKNOWLEDGEMENTS

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Current Situation and Future Perspectives in Municipal Wastewater Treatment and Sludge Management in Turkey

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ABSTRACT: Appropriate management of wastewater and sludge requires several systems. One of these systems is the collection of data about generation rates and characteristics of sludge. This paper aims to summarize the work done as a part of a three-year project requested by the Turkish Ministry of Environment and Urbanization. Efforts involved preparation and evaluation of a detailed questionnaire for currently operated wastewater treatment plants (WWTPs) in Turkey, collection and confirmation of information from visits to large scale plants, calculation of theoretical sludge generation rates from data provided, and its comparison to reported sludge amounts.

INTRODUCTION

According to the World Resources Institute (WRI), in developing countries annual urban population growth rate is 3.5% while it is less than 1% in developed countries. Especially in developing countries, the number of wastewater treatment plants and level of wastewater treatment have been increasing due to increases in population densities. In Turkey, the percentage of population having secondary or tertiary wastewater treatment services has increased from 63% in 1994 to 91% the present [1]. As the number of wastewater treatment systems and level of treatment increase, quantity of sludge also increases [2, 3]. Wastewater treatment processes effect quantity and the quality of sludge due to type of wastewater treatment processes applied and received wastewater quality. Due to such increases, volumes of generated wastewater and wastewater sludge have been increasing concerns related to wastewater and sludge management. Especially for sewage sludge, more mindful management and treatment, disposal and reuse cost options, practicability, possible environmental impacts, and public perception are required [4]. However, at present, sludge management systems are often inefficient and unsustainable mainly because no single process or treatment is able to solely address all mentioned factors. Development of sustainable sludge management procedures requires two important factors:

- assessment of management routes capable of maximizing the recycle/recovery benefits through low energy impact systems
- and development of innovative procedures and of operational systems appropriate to local circumstances, including economy, geography, climate, and more [5].

To implement this, an appropriate management of wastewater and sludge requires several systems including a dynamic system enabling collection of data about generation rates and characteristics of wastewater and sludge, a methodological approach to decide about proper treatment and disposal methods, and comprehensive legislation systems addressing all related issues.

There are some studies related to WWTP inventories. In one of the studies, 24 Spanish WWTPs were compared in terms of their environmental and economic performance such as size of flows, level of treatment, removal efficiencies, sludge disposal and operational costs. As assessing tools, life cycle assessment

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(LCA) and Global Warming Potential (GWP) were used [6]. In another study, 13 WWTPs in Galicia were inventoried and the results were discussed with respect to eutrophication, electricity usage, and comparison of technologies, removal efficiency and sludge dewatering units. Life cycle assessment (LCA) was used to determine the environmental impact of different technologies used by wastewater treatment plants [7].

In Turkey, European Legislation for wastewater control in general and for sludge treatment and disposal in particular has been transposed to the Turkish Environmental Law. The increased number of WWTPs has showed that the quantity of the treatment sludge will increase. Further, better management of sludge will be more significant in future and systematic on sludge management should be developed regarding the Turkey's local conditions [8]. Due to this fact, in order to manage urban/municipal wastewater sludges in Turkey, a three-year project, requested by Ministry of Environment and Urbanization in Turkey, was initiated in 2010. The aim of the project is to develop local sludge management strategies, examination of current legislations related to sludge management and proposing new regulations and preparing a road-map to be used by the Ministry for sludge management. In the project, there are 15 work packages which include data collection associated with wastewater treatment and sludge management from currently operated wastewater treatment plants, laboratory based characterization of sludge from selected wastewater treatment plants to determine local similarities/dissimilarities at 7 geographical region in Turkey , evaluation of proper minimization, stabilization, beneficial usage and final disposal alternatives, examination of current legislations related to sludge management and proposing new regulations, and preparing a road-map to be used by the Ministry for sludge management.

In this study, the results of the work of the first few work packages is discussed within the scope of the data derived from detailed questionnaires for the currently operated wastewater treatment plants. The data is discussed in terms of the wastewater treatment processes, sludge treatment processes, amounts of sludge produced and ultimate disposal routes for sludges in the wastewater treatment plants in order to perceive the current situation and forecast the future perspectives in Turkey.

MATERIALS AND METHODS

In the first work package of the project, a detailed survey was prepared for currently operated wastewater treatment plants in Turkey. The survey includes the essential questions to get information about the flow of wastewater received by wastewater treatment plants; whether this flow includes industrial discharge or not; wastewater treatment processes; sludge treatment processes and ultimate sludge disposal alternatives. In addition, the characteristics of incoming wastewater, treated effluent and produced sludge are also included in the questionnaire.

The surveys were sent to the water and sewerage departments of municipalities by electronic or regular mail. They were filled out by the wastewater treatment plant managers and operators and sent back. The information obtained this way from surveys were then evaluated in order to analyze the current situation in Turkey and to get background information to be used in other upcoming work packages.

Additionally, visits were made to larger scale wastewater treatment plants with flows greater than 10,000 m^3/day in order to gather further information and complete the missing data if there were any. Predicted theoretical amounts of sludge were calculated by ATV-DVWK-A 131 E standard. This standard uses BOD5 and COD of wastewater for the process calculation. Then, the results were compared with the reported amounts of sludge of the plants. Furthermore, wastewater treatment plants that are in the planning stage were also considered and evaluations were also made on.

RESULTS AND DISCUSSIONS

According to the data provided by the Municipality of Environment and Urbanization, there are 234 urban/municipal wastewater treatment plants (WWTP) in Turkey with a total daily wastewater flow of 8,621,713 m^3. Out of 234 wastewater treatment plants, 28% of them report that they receive wastewater from industries which are either untreated or partially treated (and we considered them as urban WWTP) and 71% of them do not receive any wastewater from industrial contributions (categorized as municipal WWTP). One percent of wastewater treatment plants provided no information on this issue (NA) (Figure 1).

In order to analyze the level of wastewater treatment and biological processes in Turkey, the number of wastewater treatment plants and the total wastewater treated are used. According to the results of the number of treatment plants, 86% of the plants have secondary treatment and 14% of them have physical treatment.

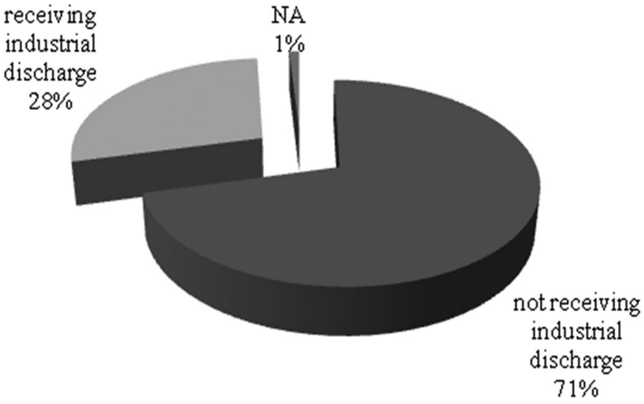


Figure 1. *Percentage of wastewater treatment plants in terms of receiving industrial discharges in Turkey.*

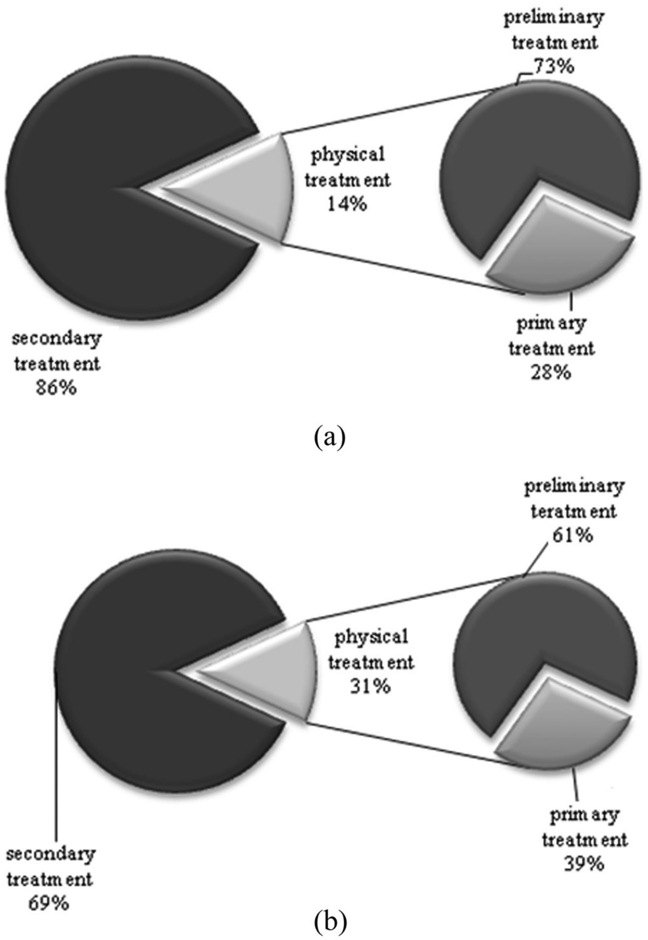


Figure 2. *Percentage of (a) wastewater treatment plants operating primary and secondary treatment in Turkey with respect to number of treatment processes and (b) total flow of wastewater treated.*

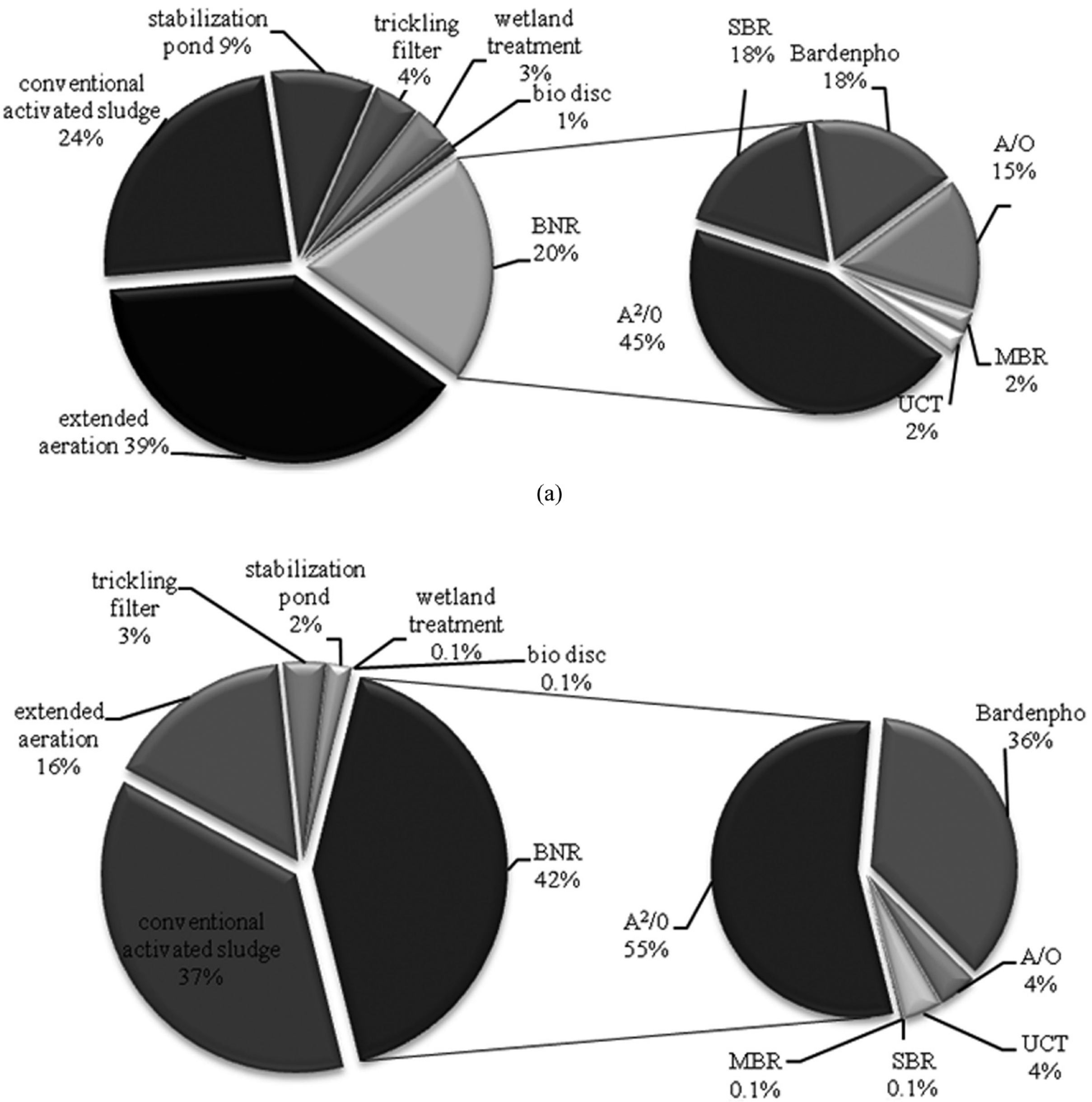
Seventy-three percent of plants having physical treatment have preliminary treatment (i.e., screens and grit chambers). Additionally, 28% of them have primary treatment (i.e., preliminary treatment and primary sedimentation) [Figure 2(a)].

If results are analyzed with respect to total treated wastewater flow, the majority of the plants (69% of total wastewater treated) have secondary. Whereas, the others have physical treatment (31% of total wastewater treated). Sixty-one percent of the plants having physical treatment use preliminary treatment and 39% of them use primary treatment. Plants which have preliminary treatment (61%) are mainly located by seashore and discharge the partially treated wastewater into the deep sea [Figure 2(b)]. Since the flows of these plants are higher, the difference between percentages of physical treatment in two figures [Figure 2(a) and Figure 2(b)] is observed.

Wastewater treatment processes with respect to number of plants may be seen in Figure 3(a) and the wastewater treatment processes with respect to volumetric flow of treated wastewater may be seen in Figure 3(b). According to results with respect to number of plants, the most common type of process is extended aeration activated sludge (39%). Conventional activated sludge (24%) and biological nutrient removal systems (BNR) (20%) and small portions of stabilization ponds, trickling filter, wetland treatment and bio disc are also used in Turkey. Out of BNR process, A^2/O (45%) is the most commonly used process.

The most commonly used biological wastewater treatment system with respect to total wastewater treated is the biological nutrient removal systems (BNR) (42% of total wastewater treated). As given above, the A^2/O process is the most commonly used BNR system (55% of total wastewater treated with BNR systems) which is followed by Bardenpho process (36%). Membrane Bioreactor (MBR), Sequential Batch Reactor (SBR), University Capetown (UCT), and A/O are other processes with small percentages used among BNR processes in Turkey. Apart from BNR processes, conventional activated sludge (37% of total wastewater treated), extended aeration activated sludge (16%), and in small percentages of tricking filters, wetland treatment systems, bio disc treatment systems, and stabilization ponds are other biological wastewater treatment systems used in Turkey [Figure 3(b)].

For plants which have higher flow of wastewater, BNR and conventional activated sludge systems are used. Although, extended aeration systems seem to be preferred by a much higher number of plants, the flows are lower when compared to plants which use BNR and conventional activated sludge systems. Stabilization ponds, wetland treatment, and bio disc processes are among other systems preferred by smaller flow wastewater treatment plants.



(a)

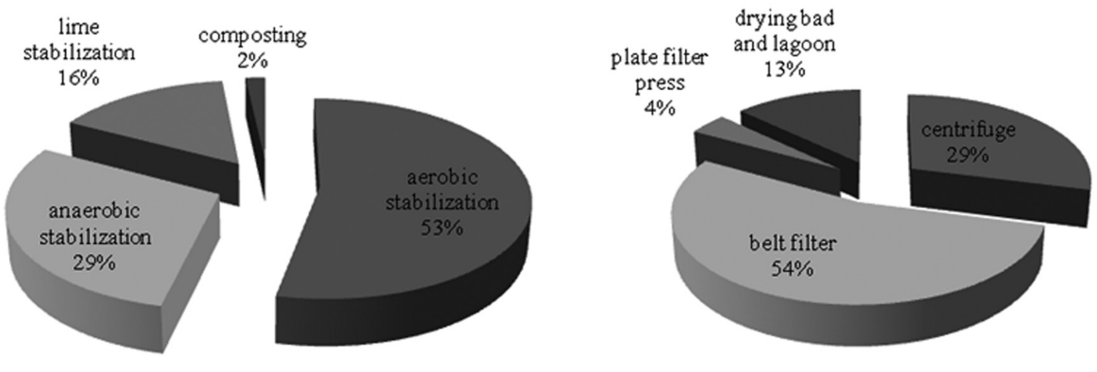
(b)

***Figure 3.** Types of biological wastewater treatment processes applied in Turkey with respect to (a) number of treatment processes and (b) total wastewater treated.*

During sludge treatment, stabilization is used in a rather smaller number of treatment plants and dewatering processes are utilized by a larger number of wastewater treatment plants in Turkey. Approximately 25% of sludge generated is stabilized and aerobic digestion (53%) constitutes the most common type of stabilization process. Anaerobic digestion (29%), lime stabilization (16%), and composting (2%) are applied as other stabilization processes in Turkey [Figure 4(a)].

According to results here for sludge dewatering, 165 of the plants operate one type of sludge dewatering unit. Sludge is typically dewatered in belt filters (54%), centrifuges (29%), drying beds and lagoons (13%), and plate filter press (4%) [Figure 4(b)].

Although the dried solids contents of the produced sludges vary from plant to plant, it is observed throughout the study that daily total sludge production on dry basis in Turkey is 910 tons according to surveys filled out by wastewater treatment plant operators. Within the scope of the project, the sludge production was also calculated using the ATV-DVWK-A 131 E standard. Daily predicted theoretical amount of sludge was observed as 1,087 tons on dry basis. These two results are considered to be well- matching with each other [9].



(a) (b)

Figure 4. Percentages of (a) sludge stabilization and (b) sludge dewatering processes applied in wastewater treatment plants in Turkey.

Mainly landfilling in municipal landfill areas (46%) are used in Turkey as an ultimate disposal route for sludge. Landfilling in special storage areas (30%), land application (10%), usage of sludge as a supplementary fuel in cement factories (6%), and other disposal methods (sewage truck and catch basin) (7%) are other ultimate disposal routes for sludge. In addition, incineration composes only 1% of ultimate disposal routes (Figure 5).

CONCLUSION

Wastewater treatment plants in Turkey were analyzed in terms of whether receiving industrial discharge or not. They were also analysed in terms of wastewater treatment processes, sludge treatment processes (stabilization and dewatering), amount of sludge production on dry basis, and ultimate disposal routes for sludge based on surveys.

According to these results, a big portion of plants do not receive industrial discharges in Turkey. As biological wastewater treatment systems, BNR processes are the most commonly used systems based on volume of wastewater treated. Additionally, conventional activated sludge and extended aeration systems also have considerable application among Turkish wastewater treatment plants.

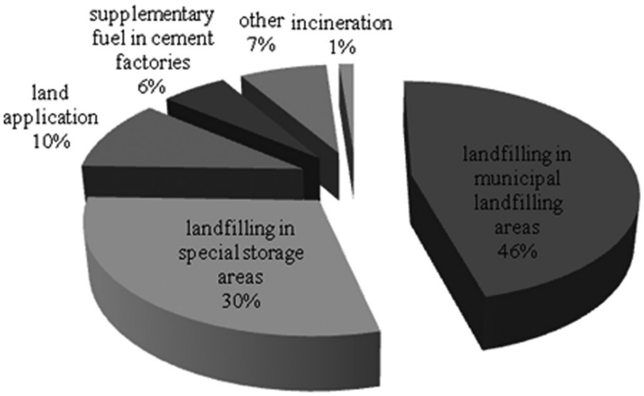


Figure 5. Percentages of ultimate disposal routes for sludge in Turkey.

In sludge treatment, the aerobic digestion process is the most commonly used stabilization process. This process is followed by anaerobic digestion, lime stabilization, and composting. Regarding the dewatering process, belt filter is the most commonly preferred unit. Centrifuges, drying beds and lagoons, and plate filter press are other processes that are less common. Amount of sludge produced in Turkey was analyzed with different methods (i.e., survey data versus ATV-DVWK-A 131 E standard) and results matched well. For ultimate sludge disposal routes, landfilling (municipal and special storage) is the most commonly used application. Other methods such as land application and usage as a supplementary fuel are currently applied in much lesser amounts in Turkey.

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European Union (EU) End of Waste Regulation: Requirements for Input Materials and Compost Quality for Sludge and other Biodegradable Wastes

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ABSTRACT: *Directive 2008/98/EC, Dec 2, 2008,* requires *the assessment of the of bio-waste management. MS are encouraged to set up measures to promote separate collection and recycling of biowaste, oriented to Composting and Anaerobic Digestion.* Sewage sludge although falling into the definition of *"biodegradable waste"* provided by the Directive is not considered *"bio-waste"*, composed only of *"biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants"*. The revised Directive introduces the possibility that certain waste streams that have undergone a recovery operation can cease to be waste, if certain criteria are fulfilled—so-called End-of-waste (EoW) criteria, that may act as reference point for any future recycling targets on biodegradable waste. *2nd Working Document EoW Criteria for Compost and Digestate* was released in Oct 11th, 2011. Annex 9 contains a preliminary standard list of input materials suitable for EoW Compost, excluding sewage sludge from the List. Sewage sludge and Compost from Sludge (no matter what its quality could be), even complying with EoW quality, will be then classified between second and third class products, worsening the public perception and the conditions for its recycling.

INTRODUCTION

THE Waste Framework Directive *(Directive 2008/98/EC, Dec 2, 2008)* [1], had a two year period for being adopted by MS. Waste legislation and policy of the EU Member States shall apply as a priority order the following waste management hierarchy shown in Figure 1.

The Directive requires the assessment of the of biowaste management. Member States are encouraged to set up measures to promote separate collection and recycling of biowaste, oriented to Composting and Anaerobic Digestion.

It sets when waste ceases to be waste and becomes a secondary raw material (so called End-of-Waste criteria), and how to distinguish between waste and by-products, introducing the possibility that certain waste streams that have undergone a recovery operation can cease to be waste, if certain criteria—so called End-of-waste (EoW) criteria—are fulfilled.

End-of-waste criteria for Compost and Digestate may act as reference point for any future recycling targets on biodegradable waste (e.g., targets set by article 11.4. of Directive). The inclusion of Digestate at the same level than Compost for qualifying as EoW product appear to be more as a result of some lobbying near the IPTS-JRC in charge of the reporting, than really complying with environmental an market EoW requirements previously sat up by the Commission.

In parallel, the Commission is conducting studies on possible extension of regulation on mineral fertilizers into organic fertilizers. Once adopted, regulation on End-of-Waste criteria may constitute a reference point for organic fertilizers/soil improvers/growing media produced from biodegradable waste.

The development of *"EoW Regulation for Compost and Digestate"* is on the way, with the "Second Working Document" released on October 2011, and further "Stakeholder Consultation" closed in January 2012. The preliminar FATE-COMES Study on different biowaste samples collected across the EU has been finished now, and final report and conclusions should be published by Autumn 2012 A final proposal for "EoW for Compost and Digestate" should be released before the end of 2012.

The pieces of legislation should be released in the next few years, namely revision of *Directive 86/278/*

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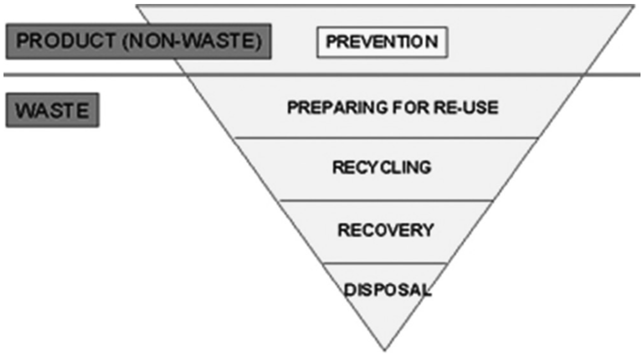

Figure 1. *WFD management hierarchy.*

CE on Sewage Sludge [2] and regulation on Compost (Stabilised Biowaste) not complying with EoW requirements, to complete the related legislative frame.

Although impressive quality improvements and pollutants reduction have been made in many EU countries during the last decades, sewage sludge will be probably excluded from positive list of input materials suitable for EoW Compost production. The future conditions for sewage sludge treatment and use on land will depend on EU and MS next to come specific regulations that are awaited for long time, especially in the MS that are lacking updated national regulation, and being still relying in the old *86/278/EC Directive*.

DEFINITIONS

Is important to know the definition of bio-waste, biodegradable waste, and other terms. As indicated in COM(2010)235 Annex [3] Future steps on Biodegradable Waste:

"Bio-waste" is defined in the Waste Framework Directive (WFD) as *"biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants"*. It does not include forestry or agricultural residues, manure, sewage sludge, or other biodegradable waste (natural textiles, paper or processed wood).

"Biodegradable waste" is a broader concept defined in the Landfill Directive as *"any waste that is capable of undergoing anaerobic or aerobic decomposition, such as food and garden waste, and paper and paperboard"*. All biodegradable waste can have negative impacts on the environment when improperly managed, notably in landfills. Better environmental options include composting (mainly of food and garden waste), recycling or use as renewable energy (e.g. paper, paperboard, treated wood).

"Compost" is the solid particulate material that is the result of composting and which has been sanitised and stabilised. Composting is a process of controlled decomposition of biodegradable materials under managed conditions, which are predominantly aerobic and which allow the development of temperatures suitable for thermophilic bacteria as a result of biologically produced heat.

"Digestate" is the semi-solid or liquid product of anaerobic digestion of biodegradable materials. It can be presented as whole digestate or separated in a liquor phase and a fibrous semisolid phase. Anaerobic digestion is a process of controlled decomposition of biodegradable materials under managed conditions, predominantly anaerobic and at temperatures suitable for mesophilic or thermophilic bacteria.

In comparison, the *Directive 86/278/EEC* [2] defines the *"Sewage Sludge"* as residual sludge from sewage plants treating domestic or urban waters and from other sewage plants treating waste waters of a composition similar to domestic and urban waste waters.

LEGISLATION

Main Biowaste Related Legislation

The biodegradable waste related EU legal framework comprehends the following elements:

Directive 86/278/EEC of 12 June 1986

The purpose of this Directive is to regulate the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animals and man, thereby encouraging the correct use of such sewage sludge. In Annexes I A, I B and I C values are given respectively for concentration of heavy metals in soil to which sludge is applied, concentration of heavy metals in sludge and the maximum annual of such heavy metals which may be introduced into soil intended for agriculture. nSludge shall be treated before being used in agriculture.

Directive 1999/33/EC on Landfill

Targets of Biodegradable waste diverting from Landfill (Landfill Directive) with reference to the generation data of 1995 are the following:

- 75% July 2006
- 50% July 2010
- 35% July 2016

However, the Landfill Directive does not prescribe specific treatment options for the diverted waste. In practice, Member States are often inclined to choose the seemingly easiest and cheapest option disregarding actual environmental benefits and costs. This has triggered a long standing discussion on the possible need for supplementary regulation. In December 2010 the EC published a *Stakeholder Consultation* proposing a 36.5% target for recycling biowaste, corresponding to the average biowaste recycling rate in the EU. The UK has opposed setting such targets for biowaste.

Directive 2008/98 EC Waste Framework [1]

It was published on December 2nd, 2008, and substitutes and derogates the Directive 2006/12 (the called Waste Framework Directive), Directive 91/689 on Hazardous Waste and Directive 75/439.

Member States had two years to adopt the Directive by its national legislations. It sets the basic concepts and definitions related to waste management, such as definitions of waste, recycling, recovery. It explains when waste ceases to be waste and becomes a secondary raw material (so called end-of-waste criteria), and how to distinguish between waste and by-products.

The Directive lays down some basic waste management principles: it requires that waste be managed without endangering human health and harming the environment, and in particular without risk to water, air, soil, plants or animals, without causing a nuisance through noise or odours, and without adversely affecting the countryside or places of special interest.

Includes two new recycling and recovery targets to be achieved by 2020: 50% preparing for re-use and recycling of certain waste materials from households and other origins similar to households at least paper, metal, plastic and glass. This can work in favour of bio-waste recycling since bio-waste is the largest single fraction of household waste and Member States can include appropriate parts of it in the calculation of the 50% target. The target is subject to review by 2014.

Regarding biowaste, it is requested by Article 22 of the Waste Framework Directive, assessing the management of bio-waste. Member States are encouraged to set up measures to promote:

- separate collection and recycling of biowaste, oriented to Composting and Anaerobic Digestion, and allows to include it when calculating the binding recycling target for municipal waste.
- biowaste treatment in order to assure a high level of environmental protection.
- the use of safe materials produced from biowaste.

Furthermore, the Directive enables the setting of EU minimum requirements for bio-waste management and criteria for the quality of compost from bio-waste, including requirements on the origin of the waste and treatment processes. Such criteria have been called for to enhance user confidence and strengthen the market in support of a material efficient economy. (End of Waste)

The Directive required the Commission to carry out an assessment on the management of bio-waste with a view to submitting a proposal if appropriate. The analysis prepared by the Commission forms the basis for the COM(2010)235.

Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (Integrated Pollution Prevention and Control)

Sets up the classification of industrial activities by groups regarding its contaminant potential, establishing the obligation of the application of the BATs, and the procedures of permitting, reporting, following the previously mentioned classification. Sets up operational and process conditions for disposal of non-hazardous waste in treatment plants with a capacity exceeding 50 t/day by biological treatment and other waste treatment plants (IPPC). Sets up regulation for emissions coming from Composting (and other waste treatment plants with a capacity of more than 75 t/day, as well as anaerobic digestion plants with a capacity of at least 100 t/day).

Regulation (EU) Nº 142/2011 of 25 February 2011, Implementing Regulation (EC) Nº 1069/2009 of the European Parliament and of the Council on ABPs [5]

In Annex V, chapter I, section 2, establishes the requirements for composting plants; and in the chapter II the same annex, the hygienic conditions applicable to such plants. Moreover, in chapter III, section 2, shows the standard transformation parameters.

Latest EU Pre-legislative Developments

Green Paper on the Management of Bio-waste in the European Union COM(2008) 811 final, December 2008

Green Paper aims to explore options for the further development of the management of bio-waste. It summarizes important background information about current policies on bio-waste management and new research findings in the field. It aims to prepare a debate on the possible need for future policy action, seeking views on how to improve bio-waste management in line with the waste hierarchy, possible economic, social and environmental gains, as well as the most efficient policy instruments to reach this objective.

Communication on Future Steps in Bio-waste Management in the European Union (COM(2010)235), May 18, 2010.

This Communication sets out the measures the Commission considers necessary in this stage to optimize the management of bio-waste. In particular, its aim is:

- Draw conclusions from the analysis of the Commission;
- Make recommendations to fully exploit the benefits of proper management of bio-waste;
- Describe the main lines of action to be taken at national level and the EU and the best way to implement it.

The most important benefit of improving the management of bio-waste would avoid emissions of greenhouse gases, which would result in considerable benefits for society in relation to possible additional costs. Simultaneously, the compost and biogas production quality would help to strengthen the quality of soil and the efficiency of resource use and improve energy self-sufficiency.

In conclusion, the analysis by the Commission confirms that the improvement of bio -waste management in the EU has a potential for significant environmental and economic benefits is untapped. This Communication proposes measures to exploit this potential making the best use of existing legislation and leaving the MS a wide discretion to choose the best options according to their respective circumstances.

Working Document on Sludge and Biowaste, September 21, 2010. [4]

In the "Working Document Sludge and Biowaste" the Commission intends to set a three tier system, proposing the separation of sludges and composts/digestates which are to be used in agriculture into three "classes" (Table 5).

The three proposed categories are characterised as follows:

- First class is composed of "product class" compost/digestate under the EoW, which are freely tradable in the EU, under fertiliser legislation.
- Second class is a "waste class" for sludges and treated biowaste suitable for application in agriculture.
- A third "waste class" below the minimum quality limits, which is excluded from any agricultural use.

From *Working Doc on Sludge and Biowaste,* further restrictions are generally list of actions to limit the risk of transmission of pathogens and diseases by sludge, having also an effect on soil safety leading to quicker decomposition of some contaminants of organic character:

Table 1. Legislative Regime for Different Qualities of Sludge and Bio-waste.

	"Product" Quality Compost/Digestate (End of Waste)	Minimum Quality for Sludge and Bio-waste	Below Minimum Quality Limits
Input material	Source segregated waste	All biodegradable waste (including mixed MSW and sewage sludge)*	All biodegradable waste*
Use	Not restricted	Allowed to be used in agriculture, but not on soils subject to high risk of contamination	Not to be use in agriculture, possible use on non-agri soils, for land reclamation or for construction purposes
Monitoring	Only in production phase	During production and use on soils, also periodic monitoring of soils	Not regulated on EU level (left for national regulation)
Regulated by	End of waste criteria for bio-waste	Revised sewage sludge directive	Left for national regulation

*It should be ensured, though, that sludge and bio-waste from mixed municipal waste are exempt as much as possible of non-organic material (e.g. metal, plastic, glass). In any case the new system shall not affect other relevant legislation—especially Animal By-Product Regulation (ABPR) or Nitrates Directive—all such legislation shall apply accordingly.

- ban the use of untreated sludge
- the sludge should be sufficiently stabilised so as not to cause unreasonable odour nuisance to the nearest dwellings, - possible indicators: lack of oxygen demand; volatile solid (VS) reduction of 38% or specific oxygen uptake rate of less than 1.5 mg/h/g total solids
- sludge should be sanitised—possible indicators could be: absence of *Salmonella* in 25–50 g or reduction of *E. coli* to less than 5×10^5 colony forming units per gram (wet weight).
- ban the use of sludge on water-saturated, flooded, frozen or snow-covered ground,
- time period between use of sludge on grasslands and allowing its use by grazing animals
- time period between use of sludge and cultivation of fruit and vegetable crops which are normally in direct contact with the ground and normally eaten raw.

Policy Development at EU and MS Level

Differences are made evident of biowaste (clean or separatadly collected organic fractions of msw and garden waste of municipal concern) vs biodegradable waste (forestry or agricultural residues, manure, sewage sludge, or other biodegradable waste (natural textiles, paper or processed wood) of industrial origin and management not corresponding to municipal authorities, but included for setting compost/digestate standards.

A good balance between what is needed at EU level and what could be done at national or local levels is indispensable to improve bio-waste management in a cost effective way, taking into account the local constraints and conditions.

Mandates from WFD and EP

- Landfill directive targets on recycling (ban on landfilling biowaste . . . ?)
- Guidance on biowaste Prevention EU targets, tools?
- Assessment on biowaste management

Activities Developed at EU level

- Ruling on ABP restrictions and special management
- Development of operational and process conditions for Waste Treatment Plants over 50 t/day (IPPC) and under 50 t/day (non IPPC)
- Development for regulation for emissions coming from Composting plants with a capacity of more than 75 t/day, as well as anaerobic digestion plants with a capacity of at least 100 t/day. (2010/75/EC Directive IPPC)
- Developing Positive List Biowaste and Biodegradable waste materials for EoW for Compost and Digestate
- Developing standards for Compost and Digestate and processes Composting, Digestion under the EoW regulation.
- Developing standards and conditions for soil application for other biodegradable waste derived products non EoW compliants (sewage sludge, industrial sludge, stabilised biowaste, etc)
- Setting common compost standards for the EU countries (biowaste, sludge and related)
- Developing quality assurance system for Compost (Digestate?/Biochar?)
- Setting minimum quantitative targets for biological treatment? (“Biowaste coalition”)

Activities to be Developed at MS level

- Ban on landfilling biowaste . . . ? landfill taxation?
- Development of biowaste and biodegradable waste prevention programmes
- Setting up separate collection systems
- Planning of infrastructure for the treatment of the collected biowaste.
- Setting up of national benchmarks, targets and indicators on different related fields (prevention landfills, separate collection, recycling rates, etc)

END OF WASTE FOR COMPOST (AND DIGESTATE), SLUDGE SITUATION

The four basic conditions for End of Waste as they have been defined in the Waste Framework Directive (Directive 2008/98/EC 19 November on Waste) are the following:

> *“Certain specified waste shall cease to be waste within the meaning of point (1) of Article 3 when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions:*
>
> *(a) the substance or object is commonly used for specific purposes;*
> *(b) a market or demand exists for such a substance or object;*
> *(c) the substance or object fulfils the technical*

requirements for the specific purposes and meets the existing legislation and standards applicable to products;

(d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

The criteria shall include limit values for pollutants where necessary and shall take into account any possible adverse environmental effects of the substance or object".

The IPTS of the Joint Research Center belonging to the DG Environment is in charge of a Working Group of parties and experts, for elaborating the proposal of EoW for Compost and Digestate. Sampling and characterisation campaign (the called FATE-COMES Program) of EU representative bio-waste, compost and digestate materials, has been performed in 2011 to assess the significant presence and prevalence of pollutants, and set the "Positive List of input materials".

Data for the typical bio-waste and biodegradable waste plants have been gathered:

1. Green waste compost from green waste originating from gardens and parks through separate collection
2. Sewage sludge compost, made up of sewage sludge and green waste from separate collection as input materials
3. Compost derived from separately collected bio-waste from households (biobin) as well as garden and park waste from separate collection
4. Liquid digestate from thermophilic digestion of biowaste derived from separate

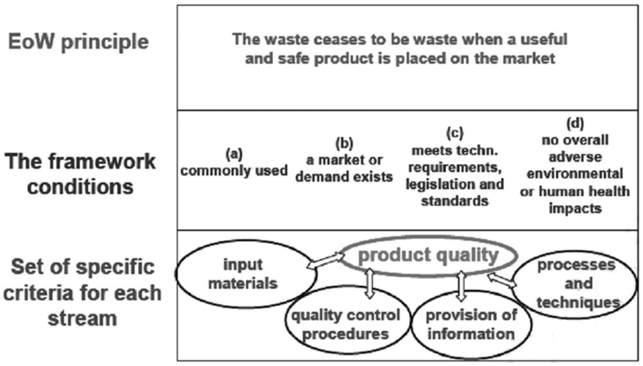

Figure 2. *Conceptual illustration of the elements of EoW criteria.*

The following parameters have been analyzed: Heavy metals, Organic pollutants (Polychlorinated biphenyls (PCB) and dioxins, Polybrominated diphenyl ethers (PBDE), Polycyclic musks, Fluorosurfactants (PFC).

The data could be compared to the values in Table 2 that shows the quality standards for sludge and bio-waste, compost and derivates in different pieces and legislation drafts.

In general, it can be concluded from the preliminary data that:

- MBT compost samples contain very high concentrations of heavy metals and organic pollutants, compared to the other sampled materials. This was confirmed by the measurements of both the JRC sample and the sample provided by the plant.
- The concentration of heavy metals and organic pollutants in sewage sludge compost was often comparable with that of the other materials, except for Hg, certain polybrominated diphenyl ethers, polycyclic musks and certain fluorosurfactants, where the measured concentration was much higher than in the materials from separate collection of biowaste and

Table 2. Quality Standards for Sludge and Bio-waste, Compost, and Derivates.

Contaminants (mg/kg dm)	Organic Farming [6] (from household waste)	Eco-label [7]	Draft EoW***	Proposal Sludge	Proposal Stabilised Biowaste	Directive 86/278/EEC (current)*
Cd	0.7	1	1.5	10	3	20 to 40
Cr (total)	70 (total) / 0 (CrVI)	100	100	1,000	300	–
Cu	70	500	100	1,000	500	1000 to 1750
Hg	0.4	1	1	10	3	16 to 25
Ni	25	50	50	300	100	300 to 400
Pb	45	100	120	500	200	750 to 1200
Zn	200	300	400	2,500	800	2500 to 4000
PAH (or benzo-a pyrene)**		–	–	6 (2)**	6 (2)**	
Impurities ≥2 mm		0.5%	0.5		2%	

*Parameters given for illustrative purposes

**Exact value as well as other organic contaminants (e.g. PCBs) subject to verification by JRC study (FATE)

***Values resulting from JRC IPTS study—as the issue of End-of-Waste of bio-waste will be subject of separate debate the values are given for illustrative purpose only.

Table 3. Draft Positive List of Input Material for EoW Compost.

1	Waste for biological treatment from exclusively vegetable origin (no animal by-products)
1.1	Organic vegetable waste from garden & parks and other greens
1.2	Vegetable waste, from the preparation and consumption of food, luxury food & beverages
1.3	Organic residues from commercial, agricultural and industrial production, processing and marketing of agricultural and forestry products—purely of vegetable origin
1.4	Other Organic residues—purely of vegetable origin
2	Waste for biological treatment with parts of animal origin
2.1	Animal waste, especially waste from the preparation of foodstuffs
2.2	Organic residues from commercial, agricultural and industrial production, processing and marketing of agricultural and forestry products—with parts of animal origin
2.3	Digestion residues from anaerobic treatment of waste materials which may contain parts of animal origin
3	Further waste for biological treatment with [*these wastes might need additional approval of origin and involved processes*]
4	Additives for composting (added in minor quantities—up to 10-15% at maximum—in order to improve the composting process, humification and maturation

green waste. This suggests that sewage sludge forms a sink for mercury and many persistent organic pollutants.

Given the limited data that are available, no firm conclusions can be drawn up at this moment. However, based on the available preliminary data, and in respect of the precautionary principle, it is recommended that MBT compost and digestate as well as sewage sludge compost and digestate are to be excluded from eligibility for end of waste status. Following discussion during the first workshop in March 2011 and subsequent stakeholder consultation in April 2011, it emerged that the vast majority of stakeholders supports the application of a positive list of input materials suitable for EoW compost (Table 3).

The following decisions seem to receive agreement for compost:

- Micelles from antibiotics production: only allowed if no antibiotics are present
- Municipal waste: other fractions not otherwise specified: Excluded
- Silage leachate water: Included
- Off-speciation compost: included only if is derived from materials coming from the positive list, so that it does not imply the content of any undesired input material
- Liquor/leachate from a composting process: included if material is coming from same plant
- Liquor from anaerobic treatment of municipal waste: include only if anaerobic treatment is using materials coming from the positive list
- Municipal sewage sludge: Excluded
- Municipal solid waste- not source separated: Excluded

Moreover, there was large support to include manure (already in the list as item 2.2.07) and renewable primary products such as energy crops for compost and digestate, as long as the composting or digestion process is considered as a waste treatment operation. The rationale behind this decision is that good quality materials containing primary products would otherwise not be able to receive the product status and its continued waste status would hinder the competition with EoW products.

In general, stakeholders favor that it should be mentioned in large terms what the compost or digestate is made of (e.g. green waste or biobin waste) without the need to detail every input material present. For other types of compost or digestate that fall out of a certain general category, any specific material present in a quantity of more than 5% of the initial weight should be declared. Furthermore, it should be clearly indicated whether any animal by-products are present in the produced material. The stakeholders commonly agreed that additives should only serve to improve the composting or digestion process, or improve environmental performance of the process. Certain metal compounds for instance can improve the biogas formation in the digestion process. Additives that are used to increase the usefulness or economical value of the product, such as fertilizers, should be added after the product receives EoW status.

The additives list *(Item 4 in Annex 9 of 2nd Working Document on EoW for Compost and Digestate)* for compost, after some new materials are accepted is the following:

- Rock dust
- Limestone dust
- Bentonite

- Ash for combustion plant tissue (straw, wood)
- Excavated soil (not polluted)
- Washing soil from sugar beet and potato processing
- Commercial inoculants for composting
- Bio-dynamic compost preparations

After a second meeting in Sevilla (Spain), *2nd Working Document EoW Criteria for Compost and Digestate* was released in Oct 11th, 2011. Annex 9 is generally indicated as an acceptable standard list of input materials suitable for EoW Compost, excluding sewage sludge from the List based on the criteria of the majority of the stakeholders.

CONCLUSIONS

- Future *End of Waste for Compost and Digestate Regulation* together with the EU harmonized *Fertilizers regulation* both to be released in 2014 and 2015, will address the production, quality, labelling and marketing conditions of Compost (as well as Soil improvers, Growing media and Organic fertilizers) across the EU.
- Composts elaborated from MBT-MSW and Sewage sludge have been excluded from the End-of-Waste proposal. They will probably regulated by additional regulations to be released, namely revision of Directive 86/278/CE on Sewage Sludge and regulation on MBT Compost.
- Following the FATE-COMES Analytical Campaign, non separately collected MSW and Sewage sludge do not regularly attempt the pollutant limits set up in the *End-of-Waste for Compost and Digestate* proposal, so they were excluded from the *"Positive List"* that qualifies residues and by-products for the EoW category.
- The future for the recycling and marketing of these *"second and third class composts"* will be seriously compromised and efforts at MS and EU should be made to assure a proper and sustainable biowaste and sludge management in the EU in the next decades.

LIST OF ABBREVIATIONS

ABPs: Animal By-Products
BATs: Best Available Technologies
COM: Communication from the Commission to the Council and the European Parliament
DG Environment: Directorate-General for the Environment
EoW: End-of-waste
EC: European Commission
EP: European Parliament
EU: European Union
IPPC: Integrated, Prevention, Pollution and Control
IPTS: Institute for prospective and Technological Studies (of the JRC)
JRC: Joint Research Centre of the DG Environment
MBT: Mechanical Biological Treatment
MS: Member States
MSW: Municipal Solid Waste
PBDE: Polybrominated Diphenyl Ethers
PCB: Polychlorinated Biphenyls
PFC: Perfluorinated compounds
UK: United Kingdom
WFD: Waste Framework Directive

REFERENCES

1. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives
2. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture
3. Communication on future steps in bio-waste management in the European Union (COM(2010)235), 18 May 2010
4. Working Document on Sludge and Biowaste, 21 September 2010
5. Regulation (EC) No 1069/2009 of the European Parliament and of the Council of 21 October 2009 laying down health rules as regards animal by-products and derived products not intended for human consumption and repealing Regulation (EC) No 1774/2002 (Animal by-products Regulation)
6. Organic farming (the Organic Farming Regulation- Regulations 2092/91/EEC (until 31.12.2008) and 834/2007/EC (as from 1.1.2009) lays down conditions for the use of compost in organic farming).except of the quality requirements has also requirements concerning sources of compost, i.e.: product obtained from source separated household waste, which has been submitted to composting or to anaerobic fermentation for biogas production, need recognised by the inspection body or inspection authority. It also should be noted that for composts made out of vegetal matter there are no contamination limits—just requirement that compost is recognised by the inspection body or inspection authority.
7. Positive list of input materials is also set for eco-labelled composts (Soil improvers / growing media, Decision 2006/799/EC.).

Inverted Phase Fermentation and Ultrasound Pre-treatments of Sewage Sludge: Biochemical Methane Potentials

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ABSTRACT: Ultrasound disruption and Inverted Phase Fermentation -IPF- (enzymatic hydrolysis) were applied to sewage sludge. IPF is a novel technique for sludge thickening resulting in a clarified phase ("Liquid Phase" -LP-) beneath a thickened fraction ("Solid Phase" -SP-). An increased hydrolysis rate is obtained in both phases. Biochemical Methane Potentials after applying these pre-treatments were compared: 0.054 LCH_4/gVS_o for untreated sludge, 0.065 LCH_4/gVS_o for sludge pre-treated with ultrasound at 7,500 kJ/kgTS, 0.226 LCH_4/gVS_o for the SP, and 0.264 LCH_4/gVS_o for the LP. Sludge pre-treated with ultrasound at 15,000 kJ/kgTS did not achieve the level of methane production untreated sludge did.

INTRODUCTION

SLUDGE biomethanization may increase up to two orders of magnitude if a pre-treatment is implemented prior to anaerobic digestion [1]. Sewage sludge is a complex substrate with varying proportions of water, bacterial cells, extracellular polymeric substances (i.e. carbohydrates, proteins, humic compounds, lipids, uronic acids and deoxyribonucleic acids), and other microscopic debris [2]. Thus, while for many substrates methane production is limited by the methanogenesis step, hydrolysis constitutes the rate-limiting step for sewage sludge [3]. Scientific effort is focussing on overcoming this difference by means of a pre-treatment. Apart from enhancing the kinetics, pre-treatments frequently produce more methane [1]. Many strategies implying mechanical, thermal, chemical or biochemical processes have been employed as pre-treatments. The choice of the pre-treatment to use in each particular case is justified in terms of the economic balance and technical feasibility for each waste water treatment plant (WWTP) [4].

One advantage of ultrasound pre-treatment is the practicability of its implementation by means of an ultrasonicator, the specific energy to use being the key. Ultrasound irradiation may be technically expressed in different ways, although the Specific Energy (E_S) is the term generally employed [5]. The formula expressing the E_S is:

$$E_S = \frac{P \cdot t}{V \cdot TS_o} \tag{1}$$

where P = ultrasound power, t = time of exposure of the sample to ultrasound, V = volume of the sample pre-treated, and TS_o = initial concentration of total solids. In summary, by the effect of cavitation ultrasound pre-treatment produces cell disruption, hygienisation of the sludge and an increased solubility of the organic compounds, which often results in an increase in the biogas production [6].

Enzymatic pre-treatments have been broadly discussed in the literature [7]. In 2008, Le *et al.* presented "Inverted Phase Fermentation -IPF-" as an enzymatic pre-treatment in which hydrolysis is achieved by promoting endogenous enzymes in the sludge [8]. IPF was initially implemented as a method for controlling pathogenic microorganisms, resulting in a reduction in *Escherichia coli* of 99.9%. However, there is no destruction of enzymes or other microorganisms responsible for the decomposition of organic matter. IPF is a technique for sludge thickening which takes advantage of the nascent bubbles in anaerobic heated sludge. Up to a two-fold increase in solids concentration is achieved employing this form of hydrolysis. As a result, a clarified phase (Liquid Phase -LP-) remains beneath the top thickened fraction (Solid Phase -SP-). An increased hydrolysis rate is obtained in both phases [9].

The aim of the current research is to study the influence of the ultrasound disruption and IPF pre-treatments on the methane production of sewage sludge.

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The effects of these pre-treatments were assessed by means of Biochemical Methane Potential tests (BMP). The pre-treatments were chosen due to the possibility of implementation and relative low cost for real development at a Spanish WWTP.

MATERIALS AND METHODS

Sample Collection

Sludge samples were characterized on reception at the laboratory. The samples were collected prior to dewatering in the centrifuge at the WWTP (before the addition of reagents). The WWTP is characterized by a maximum flow rate of 3,210 m^3/h and a high load of wastewater of industrial origin. It only produces one type of sludge, which comes from biological treatment without previous primary settlement. The SRT is very short (around one day), while removal efficiencies are >75% SS and >65% BOD_5. $FeCl_3$ and a cationic polyelectrolyte are added prior to centrifugation; subsequently, the sludge is sent to landfill disposal. $FeCl_3$ is added not only for dewatering purposes, but also to enhance clarification in the secondary settling tank.

Pre-Treatments

Ultrasound Disruption

Ultrasound disruption was applied to the sludge samples using a Hielscher UP400S ultrasonicator (400 W, 24 kHz). Two specific energies were applied: 7,500 and 15,000 kJ/kgTS. This choice of E_S was made considering preliminary results obtained in the range 3,500–21,000 kJ/kgTS [9].

Inverted Phase Fermentation (IPF)

To carry out the IPF, 2 L plastic bottles were filled with fresh sludge. An outlet hose connected the bottles to a large flask containing water to achieve anaerobic conditions. The sludge was heated to 42°C for 48 hours, achieving effective separation of the phases by gas displacement (mainly due to the dragging caused by CO_2). The phases were subsequently separated and characterised.

Biochemical Methane Potential Tests

The anaerobic biodegradability tests were performed in 2 L glass bottles connected to 5 L Tedlar bags for biogas collection. The bottles were kept at 37°C (mesophilic regime) for 32 days. To ensure the contribution of anaerobic microorganisms, mesophilic digestate from our own continuous stirred-tank reactors co-digesting mixtures of sewage sludge, food waste and cattle manure was used as inoculum. The ratio between volatile solids provided by the sludge and those provided by the inoculum ($VS_{sludge}/VS_{inoculum}$) was approximately three.

After pre-treatment, sludge/inoculum mixtures were prepared and introduced (1.75 L) into the glass bottles. Prior to sealing the recipients with rubber stoppers and silicone, each bottle was purged with N_2 for a couple of minutes. All experiments were carried out in duplicate. Biogas volume and composition was measured on a daily basis. The tests were designed as follows:

- Blank (inoculum; not shown, only as a control)
- Untreated sludge (raw sludge, without pre-treatment)
- Sludge pre-treated by ultrasound at 7,500 kJ/kgTS
- Sludge pre-treated by ultrasound at 15,000 kJ/kgTS
- Sludge pre-treated by IPF: Solid Phase (SP)
- Sludge pre-treated by IPF: Liquid Phase (LP)
- Sludge pre-treated by IPF: mixture of Solid and Liquid Phases (Mixture)

As the volume of sludge produces different amounts of SP (around 40%) and LP (around 60%), it may be of interest to report the methane production for the joint phases (i.e. the sludge). Therefore the overall yield considering the initial amount of sludge pre-treated by means of IPF is also provided as “SP+LP”.

Analytical Methods

Total Solids (TS) and Volatile Solids (VS)

The TS concentration was determined by weighing the remaining solid after drying a known volume of sample to 105°C for 24 hours. The VS concentration was determined by means of the difference between TS and the fixed solids that remained after calcinating the sample at 550°C for 2 hours. This procedure was in accordance with Method 2540 of the Standard Methods for the Examination of Water and Wastewater [10].

Chemical Oxygen Demand (COD)

Both the total Chemical Oxygen Demand (tCOD) and the soluble (sCOD) were determined using the closed reflux colorimetric method, the organic matter being oxidized with a mixture of potassium dichromate in strongly acid medium in the presence of Ag_2SO_4 and $HgSO_4$ at 150°C. After digestion of the sample for 2 hours, the Cr^{3+} formed is determined colorimetrically using a Perkin Elmer Lambda 35 Visible-UV system ultraviolet-visible spectrophotometer, at a wavelength of 600 nm. This procedure corresponds to Method 5222 of the Standard Methods for the Examination of Water and Wastewater [10].

Samples were previously centrifuged (3500 rpm, 15 minutes) and filtrated (1.2 µm pore filter paper) to determine the sCOD [8].

Ammonium Nitrogen (NH_4^+-N)

Ammonium nitrogen was determined using an Orion 95-12 selective electrode for ammonium.

pH Value

pH measurements were performed at 20°C. A CRISON Model 507 pH-meter was used.

Total Alkalinity (TA) and Volatile Acidity (VA)

A known volume of the sample was centrifuged (4350 rpm, 15 minutes) and the pH of the supernatant was then measured. This was titrated with H_2SO_4 (0.1 N) from the initial pH to pH = 4. The H_2SO_4 volume consumed led to the TA, expressed in $gCaCO_3/L$. After acidification to pH = 3.5, the sample was heated to boiling for 3 minutes. After cooling, it was titrated with NaOH (0.1 N) to pH = 4 and, finally, to pH = 7. The NaOH volume consumed in both cases led to the VA, expressed in gCH_3COOH/L. This procedure corresponds to Method Number 805 [11].

Table 1. Composition of the Sludge Sample.

	Value	Units
TS	61.72 (6.17%)	g/kg
VS	50.25 (5.03%)	g/kg
VS/TS	81.42	%
sCOD	4.00	g/L
tCOD	91.16	g/L
sCOD/tCOD	4.39	%
N-NH_4^+	0.09	g/L
pH	5.3	–
TA	1.58	g $CaCO_3$/L
VA	2.16	g CH_3COOH/L
VA/TA	1.37	–

Table 2. Composition of the Solid and Liquid Phases after IPF.

	Solid Phase	Liquid Phase	Units
TS	125.93 (12.59%)	6.10 (0.61%)	g/kg
VS	101.45 (10.15%)	4.51 (0.45%)	g/kg
VS/TS	80.56	73.93	%
sCOD	13.82	5.54	g/L
tCOD	170.61	15.74	g/L
sCOD/tCOD	8.10	35.20	%
N-NH_4^+	0.88	0.22	g/L

Biogas Composition and Volume

Biogas composition was determined on an Agilent 7890A gas chromatograph using a Thermal Conductivity Detector and a Porapack N packed column plus a molecular sieve. The temperature ramp was: starting 35°C (1.5 min), increasing up to 55°C at a rate of 1.5°C/min. Biogas was collected in Tedlar bags and the volume was measured using a flow meter. All the gas volumes in this paper were converted to standard temperature and pressure (273.15 K and 101.3 kPa).

RESULTS AND DISCUSSION

Physicochemical Characteristics of Sludge

Composition of the sludge sample is shown in Table 1. Notice organic matter content of the sludge is very high (81.42% of solids are volatile). As expected, most of this organic matter is insoluble (sCOD/tCOD = 0.0439) [9].

Table 2 shows the composition of the two phases obtained after pre-treating the sludge by IPF. It can be observed that the solids are concentrated in the SP, increasing from 6.17% to 12.59%, while the LP only contains 0.61%. This fact may be seen in Figure 1.

Biochemical Methane Potential Tests: Methane Production

Duplicates from each experiment achieved a low scattering of the results of biogas production (standard deviations were less than 5%). Biodegradation of VS and tCOD were above 85% in most of the experiments. Methane content in the biogas ranged between 50–70%.

Figures 2, 3, and 4 show average methane production for the two trials. Figure 2 shows the cumulative methane production. Trials lasted 32 days, although methane production was practically negligible from day 15 on.

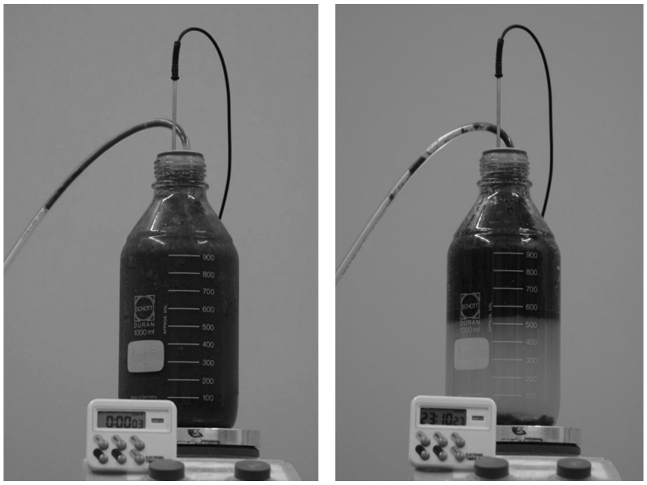

Figure 1. *Pictures of the sludge: (a) before IPF and (b) after IPF.*

For this reason, Figures 2, 3, and 4 show methane production up until day 15. Due to poor results obtained by the SP and LP mixture leading to lower methane production than untreated sludge (Figure 2), no further discussion of the mixture will be made. This situation may have been due to inhibition of methanogenesis by excess volatile fatty acids when mixing phases. Nonetheless, as the major interest of performing IPF lies in the effective separation of the phases and their corresponding separate processes, the authors consider that the mixture is of no value for the purpose in hand.

Figure 3 shows daily methane production. When the sludge was pre-treated by IPF, methane began to appear from the first day of the trial, whereas the untreated sludge or ultrasonicated sludge produced methane from the fourth day.

Specific methane production -SMP- (litres produced per gram of $VS_{substrate}$) is shown in Figure 4. In comparison with the untreated sludge, the lowest E_S (7,500 kJ/kgTS) produced a slight increase in the SMP. However, the contrary effect was achieved when applying the highest E_S (15,000 kJ/kgTS). Reduction in methane production with highly ultrasonicated sludge has been observed elsewhere [12]. The optimum E_S is not the highest. There may even be some decoupling between organic matter solubilisation and methane production [13].

A higher SMP can be clearly observed in the sludge pre-treated by IPF. The SP methane production is 3.68 times higher than the SMP of the initial sludge, obtaining 0.197 LCH_4/gVS_o or 9.90 $LCH_4/kg_{wet\ sludge}$. Also worthy of note is the marked SMP of the LP: 0.264 LCH_4/gVS_o.

These values represent methane potential recovered from anaerobic biodegradability tests (discontinuous assays). The anaerobic digestion process is normally carried out in continuous operation mode at an industrial scale, resulting in higher methane yields [14]. Nonetheless, this fact should in no way invalidate the comparison of the BMP results for the different pre-treatments carried out here.

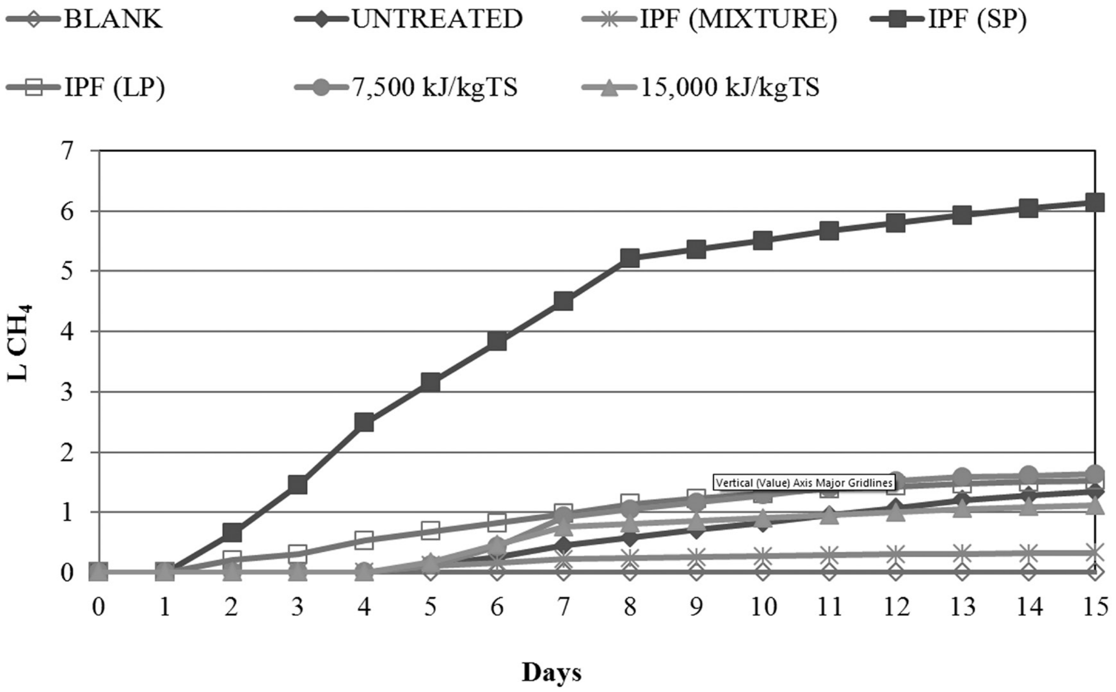

Figure 2. *Cumulative methane production at standard temperature and pressure.*

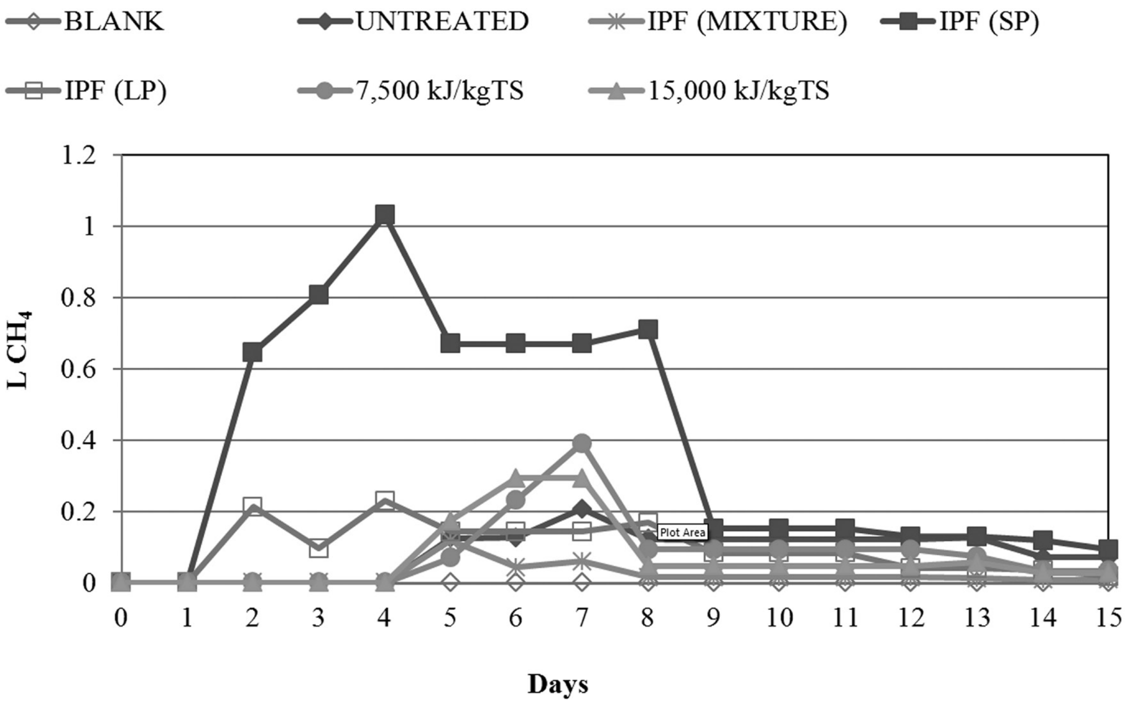

Figure 3. *Daily methane production at standard temperature and pressure.*

CONCLUSIONS

An increase of up to 21% was achieved in the SMP obtained by ultrasound pre-treatment at 7,500 kJ/kgTS with respect to the untreated sludge. However, no benefit was obtained when applying higher energy (15,000 kJ/kgTS).

The SMP increased up to 268% in the sludge pre-treated by IPF, thus pointing to the profitability potential of this low energy consuming pre-treatment.

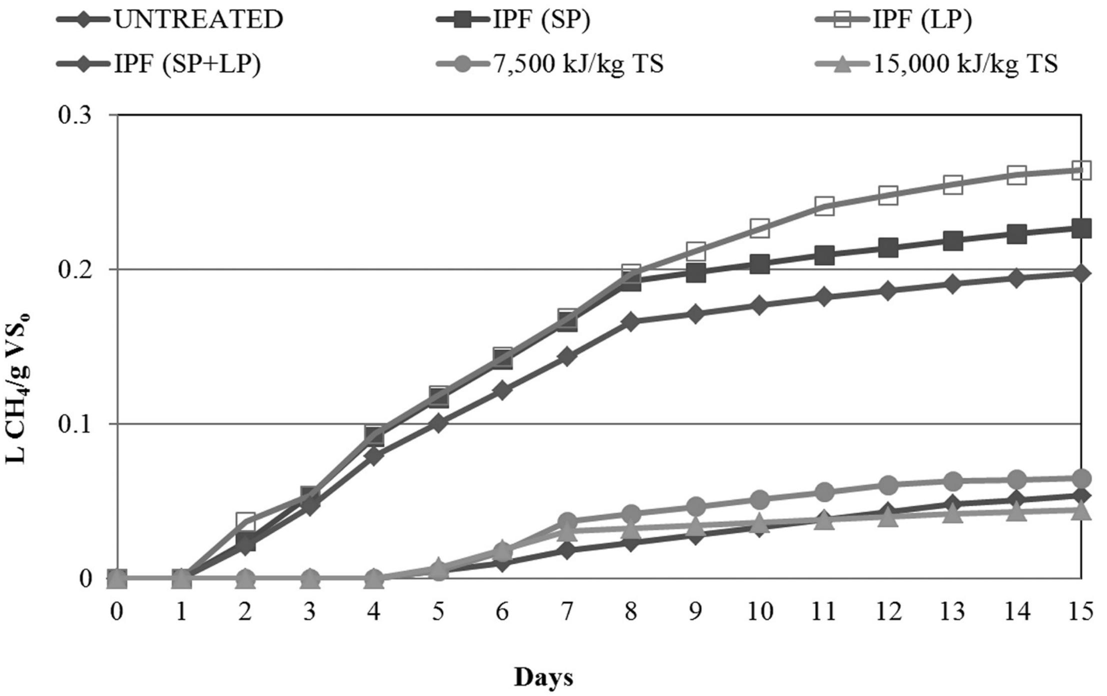

Figure 4. *Cumulative specific methane production at standard temperature and pressure.*

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