

Fractionation of the organic matter contained in leachate resulting from two modes of landfilling: An indicator of waste degradation

C. Berthe^a, E. Redon^b, G. Feuillade^{a,*}

^a GRESE, Group of Water, Soil and Environment Research, ENSIL, Parc Ester Technopôle, 16 rue Atlantis, 87068 Limoges, France

^b CRPE, Research Center of Veolia Environment, Zone Portuaire de Limay, 291 avenue Dreyfous Ducas, 78520 Limay, France

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Abstract

Three experimental pilots were set up at the semi-industrial scale to assess the impact of leachate recirculation and Mechanical Biological Pre-treatment (MBP) before landfilling on the biological degradation of landfilled wastes. The organic matter contained in leachates resulting from these pilots has been used as an indicator of waste degradation. Fractionations were carried out (i) using XAD resins in order to divide the organic matter into several fractions according to the hydrophobic character of the molecules and (ii) using an ultrafiltration protocol to divide the organic matter into several fractions according to the apparent molecular weight of molecules. Three phases of degradation are determined according to the distribution of the organic matter and according to the humification rate. The humification process seems to be more rapid for MBP leachates than for Bioreactor leachate. These results were confirmed by the ultrafiltration results indicating that, to date, MBP leachates contain more molecules with a high molecular weight than Bioreactor leachate. However, this could be explained by an interruption of waste degradation due to an accumulation of volatile fatty acids.

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1. Introduction

Landfilling remains nowadays the most widely used MSW treatment in many European countries. At the same time the 1999 EU Landfill Directive sets targets to substantially reduce the amount of biodegradable MSW going to landfill. This Directive results from the former landfills (no controlled landfills) which do not guarantee sufficient technical and environmental performances. In France, the targets set in the EU Landfill Directive must be reached at a national level. Contrary to Germany and Austria, the French regulation (adopted on 9th Septem-

ber, 1997 and strengthened in 2006) does not set standards for landfilled wastes (for example, on biological activity, ...). It imposes, in particular, the recovery and the treatment of the leachate and the biogas produced during site exploitation and for the period of post-30-year exploitation. However, the end of the post-exploitation period does not inevitably mean that any risk of pollution has been isolated.

That is why the conventional landfill is lead to evolve in order to improve the stabilization of landfilled wastes and thus to limit the environmental impacts. Technological solutions are developing in order to accelerate the biological degradation of wastes outside and/or within landfills. It should be the Mechanical Biological Pre-treatment (MBP) prior to landfilling or the Bioreactor concept.

MBP is coming from Germany and Austria; it aims at reducing the biodegradable organic matter contained in waste going to landfill to limit biogas and leachate production and to reduce the landfill aftercare [1,2]. At the moment, only four full scale plants are operating or under construction in France.

The bioreactor consists in collecting generated leachate to reintroduce it into the landfilled waste. Reinhart et al. [3] specify that leachate recirculation reduces of 2–3 years the time

Abbreviations: AT₄, respiratory activity at the end of 4 days; BMP, biochemical methanogene potential; BOD₅, biological oxygen demand at the end of 5 days; DOC, dissolved organic carbon; DS, dry substances; HS*, humic-like substances; FA*, fulvic-like acids; HA*, humic-like acids; HPI*, hydrophilic-like substances; HPO*, hydrophobic-like substances; MBP, Mechanical Biological Pre-treatment; MSW, municipal solid waste; OM, organic matter; SUVA, specific ultraviolet absorbance; TOC, total organic carbon; TPH*, transphilic-like substances; VFA, volatile fatty acids.

* Corresponding author. Tel.: +33 5 55 42 36 95; fax: +33 5 55 42 36 80.

E-mail addresses: berthe@ensil.unilim.fr (C. Berthe),

Estelle.redon@veolia.com (E. Redon), feuillade@ensil.unilim.fr (G. Feuillade).

necessary to reach the stabilization of a landfill, as it supplies additional moisture which is crucial for organic matter degradation [3,4]. The leachate recirculation was used a long time by experimental way in France but since January 19, 2006, this technique is registered in the French regulation.

Indicators of degradation and stabilization are necessary to determine the impact of these techniques on waste degradation. Many authors have tried to characterize a waste considered as “stabilized” without an only and common definition has been given. So, researchers must use one or more global parameters to define a stabilized state. The study described in this paper thus concentrates on the fractionation of the organic matter contained in leachates which appears such as a relevant indicator of waste degradation and stabilization.

The organic matter and more especially humic-like substances represent the major part of organic compounds contained in leachate. Organic matter can be classified into three fractions (Fig. 1):

- Simple compounds like carbohydrates, organic acids (mainly volatile fatty acids), amino acids and alcohols which are identifiable by specific analysis. They are easily biodegradable and present low molecular weights.
- Humic-like substances which include humins and humic-like acids which are characteristic of the humification stage and composed of high aromatic and high molecular weight cellulosic compounds, and fulvic-like acids with medium to high molecular weights. They are relatively rich in carboxylic and hydroxylic groups.
- Non humic-like substances which represent the dissolved organic carbon that belongs neither to the humic nor to the fulvic-like acids. This fraction is usually called hydrophilic acids and is expected to constitute a substantial fraction of the dissolved organic carbon content [5].

According to its complexity and heterogeneity, a common approach for the Humic-like Substances (HS^{*}) is to isolate functionally different fractions because there is no single analytical method which allows to define them directly. The relation between the high percentage of humified compounds (humic-

Table 1

Composition of input fresh Municipal Solid Wastes

Composition	%
Organic waste	55
Plastic	14
Textile	7
Metal	2.6
Hazardous waste	0.4
Glass	11
Other	10

like and fulvic-like acids, noted down HA^{*} and FA^{*}), the apparent molecular weight of molecules and the state of the stabilization of a landfill has been established: the highest degree of humification corresponding at the most stable state. Several authors have compared the percentage of humic and fulvic-like acids in leachates resulting from landfills of different ages [6–8].

A CRPE long-term research program named ELIA (Environmental Landfill Impact Assessment) aims at comparing on the environmental, technical and economical levels leachate recirculation and MBP before landfilling. The impact of the duration of the MBP has been also studied by using wastes which were more or less pre-treated (12 and 25 weeks according to the composting stage). A CRPE long-term research program named ELIA aims at comparing on the environmental, technical and economical levels leachate recirculation and MBP before landfilling. The impact of the duration of the MBP has been also studied by using wastes which were more or less pre-treated (12 and 25 weeks). For that, experimental pilots were set up at the semi-industrial scale by the CRPE which has studied the economical and technical impacts of these two methods and the biogas quality and quantity.

2. Material and methods

2.1. Experimental cells

Four experimental cells were set up in October 2003: a test cell with conventional landfilling, a bioreactor cell with leachate recirculation and two MBP cells with pre-treated wastes. Results of test cell are not discussed in this paper because they don't give relevant and supplementary information for this study. Each cell of 23 m³ contains around 11 tonnes of wastes. Fresh MSW were collected from a sorting and composting plant in France; Table 1 gives the mass composition of MSW.

Cell 1 (Bioreactor cell) was filled with fresh MSW which were coarsely ground with an industrial high-speed hammer shredder for the homogenisation of waste and to open the plastic bags. This cell is exploited according to the bioreactor concept. Four phases of recirculation have been applied (Table 2). Until approximately the 16th month, 1347 L/t_{DS} of leachate was recirculated. However leachate analysis have been realized and showed an accumulation of volatile fatty acids (Fig. 2) which blocked the waste degradation. Yuen [9], showed that the degradation of the easily biodegradable organic matter could involve a significant salting out of volatile fatty acids and consequently

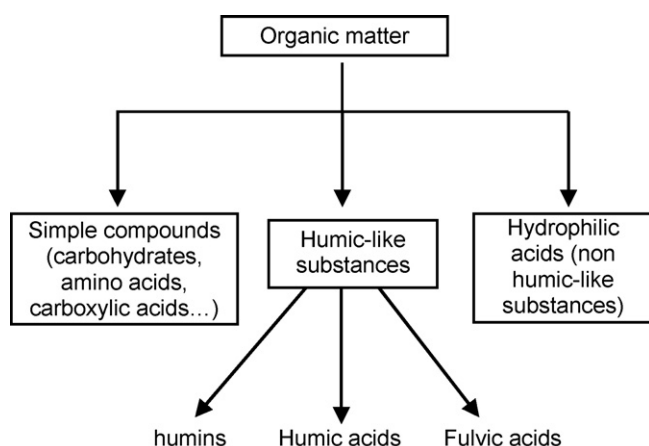


Fig. 1. Composition of the organic matter.

Table 2
Phases of bioreactor leachate recirculation

Phase	Start (month)	End (month)	Recirculated leachate (L/t _{DS})
Phase 1			
Recirculation	0	15.8	1347
Draining	15.8	17.5	/
Phase 2			
Recirculation	17.5	18.5	97
Draining	18.6	21.1	/
Phase 3			
Recirculation	21.1	22.5	129
Draining	22.5	26.7	/
Phase 4			
Recirculation	26.7	28.8	193
Draining	28.8	30.8	/

block the later phases of the biological breakdown of waste. That is why a new strategy of recirculation has been adopted in alternating recirculation phase with rest phase in order to increase the lateral dispersion and to avoid saturation and accumulation phenomenon. The following phases were shorter and the quantity of recirculated leachate was respectively around 97 L/t_{DS}, 129 L/t_{DS}, and 193 L/t_{DS}.

Cells 2 and 3 (MBP1 and MBP2 cells) have received MBP wastes. MSW have been pre-treated mechanically by passing through a hammer shredder to open bags and reduce particle size in order to enhance the biological degradation. 48% of the shredded waste had a particle size superior to 50 mm. 37.5 kg of MSW were set in a windrow 21 m long, 6 m wide and 2 m high. The experimental biological treatment device used positive forced aeration. A ventilator, working depending on the oxygen content within the windrow, has been used to improve the biological degradation. Cells 2 and 3 were, respectively, filled after 12 and 25 weeks of biological treatment that is described entirely in Lornage et al. [10]. The quantity of injected water for MBP1 and MBP2 cells was respectively around 393 L/t_{DS} and 405 L/t_{DS} to simulate precipitation.

Table 3 gives characteristics of wastes in each cell before the landfilling. The volatile solids content, assimilated to the ignition loss at 550 °C (European standard NF EN 13037), estimates the total organic content of a sample. It takes into account the

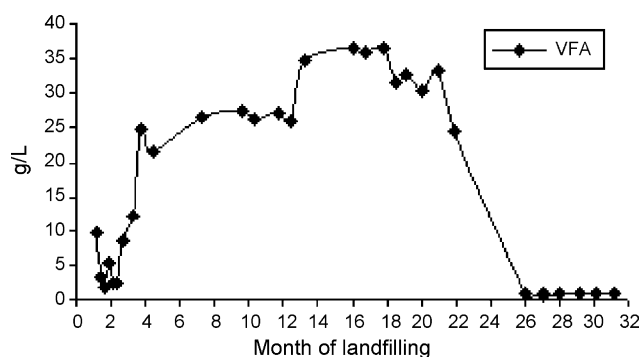


Fig. 2. Evolution of volatile fatty acids in Bioreactor leachate.

Table 3
Characteristics of landfilled wastes in each cell

Parameters	Bioreactor cell	MBP1 cell	MBP2 cell
Wet mass (tonnes)	11.72	11.3	10.66
Initial moisture (%)	28 ± 1	40 ± 1	37 ± 1
Volatile solids (% DS)	62 ± 2	48 ± 2	39 ± 2
AT ₄ (mg O ₂ g/DS)	83	29	16

biodegradable organic matter but also the plastics, the lignin and the humic-like substances. The AT₄ index is a respiration measurement that describe the amount of organic matter easy available for biodegradation under aerobic conditions. The AT₄ is the amount of oxygen consumed in 4 days by the microorganisms. Raw MSW can reach values on the order of 100 mg O₂/g_{DS} [11]. The AT₄ measurements were carried out according to the Austrian standard method [12].

For the three cells, cowpat was added to help the start of the biodegradation. Compost has been laid out around the cells to isolate them thermically. The objective is to maintain an optimal temperature, inside the waste mass, for the waste degradation that is to say around 55 °C [4]. A sprinkler device to simulate rain, and a biogas collecting system were installed. Biogas and leachate quantity and quality have been studied during the ELIA research program but only results about leachate quality are given in this paper. Leachate analysed within the framework of this study result from the three experimental cells.

2.2. Leachate analysis

Leachate samples have been stored in a refrigerator at 4 °C to limit biological activity. Analyses were carried out as soon as possible from the receipt of samples. Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC) measurements have been carried out by a TEKMAR DOHRMANN (model Apollo 9000) carbon analyzer. Measurements of Chemical Oxygen Demand (COD) were carried out according to standards methods (NFT 90-101). Biological Oxygen Demand (BOD₅) was measured using OxiTop[®] made by WTW Company. UV_{254nm} was measured using a SAFAS mC2 spectrophotometer with 1 cm-long quartz cells to determine the Specific UV Absorbance (SUVA) which is defined as the ratio of the absorbance at 254 nm to the dissolved organic carbon concentration of a given solution. SUVA index is characteristic of the hydrophobic and aromatic characters of molecules contained of a given sample.

2.3. Fractionation of the organic matter

2.3.1. Fractionation of the organic matter according to the hydrophobic character of molecules

Leachate samples were filtered through a 0.45 μm membrane to eliminate humins which are insoluble at any pH. The extracted humic-like substances have been separated into humic and fulvic-like acids fractions after acidification with HCl (37%) solution at pH 2 and precipitation of the humic-like acid fraction.

After removal of the humic-like acids by filtration through a 0.45 μm membrane, leachate at pH 2 was fractionated accord-

ing to the hydrophobic character of molecules. For that, the method proposed by Aiken et al. [13] and Croué et al. [14] depending on the solubility of the organic compounds was applied. The protocol allows the separation of the organic matter in three different fractions; each fraction grouping together molecules which presents the same physicochemical properties.

The fractionation of the dissolved organic matter is carried out using non-ionic resins in series (DAX-8 and XAD-4). The DAX-8 resin has an acrylic nature and is slightly polar whereas the XAD-4 resin has a similar structure to the styrene-divinylbenzene type and is regarded as non-polar. The sample is successively passed through the DAX-8 resin and then through the XAD-4 resins (Fig. 3). This protocol allows the determination of hydrophobic-like substances (HPO*) adsorbed on DAX-8 resin. HPO* are essentially represented by the humic-like substances that is to say by the fulvic-like acids. The transphilic-like substances (TPH*) are adsorbed on XAD-4 resin. The hydrophilic-like substances (HPI*) which include the dissolved organic carbon are not adsorbed on these resins. The higher the percentage of hydrophobic-like substances, the more the leachate has an advanced state of humification. These different fractions of organic matter represent families of molecules which the structure are not well defined. The volumes of resin and sample used were, respectively, 5 and 156 mL and the percolation flow was fixed at 50 mL/h. The relative concentration of each fraction is quantified by the measurement of DOC.

2.3.2. Fractionation of the organic matter by ultrafiltration

The molecular size distribution of dissolved organic matter contained in leachates was determined by the ultrafiltration method. It allows studying the evolution of the organic matter according to the degradation of waste. The greater the advancement of the humification process, the more the leachate is characterized by molecules with high molecular weight [13,15,16]. The tests were carried out with a diafiltration method: the volume of sample is kept constant in the cell by adding a sodium nitrate solution having the same ionic force as the

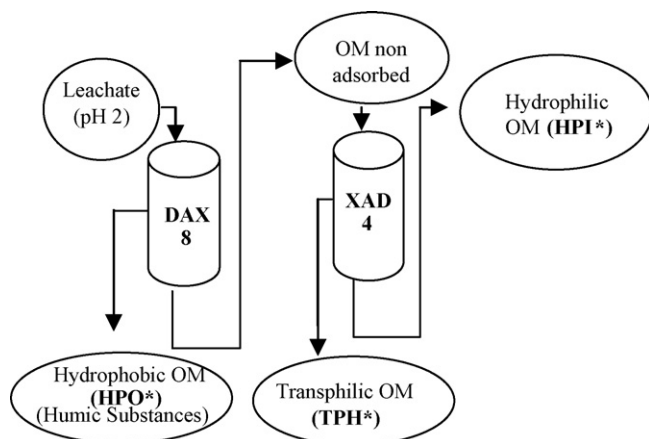


Fig. 3. Protocol of OM fractionation according to the hydrophobic character of molecules.

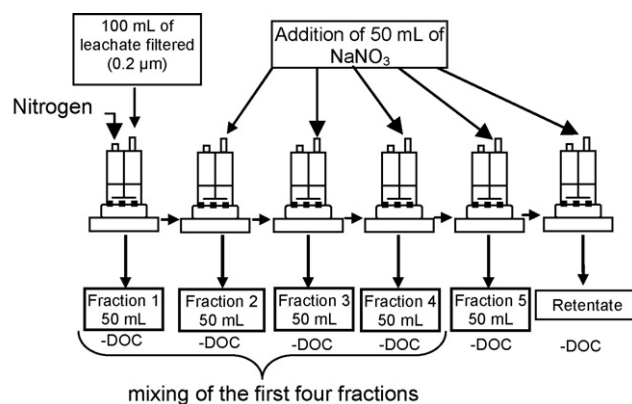


Fig. 4. Protocol of ultrafiltration.

leachate. It allows reducing the phenomena of polarization of concentration at the surface of the membrane [17]. Frontal ultrafiltration cells of 400 mL (Millipore) with magnetic stirring are used. YM (Millipore) membranes with a diameter of 76 mm and molecular cutoffs of 30, 3 and 1 kDa were used. The applied pressure was 3 bars. The protocol is described in Fig. 4.

100 mL of leachate filtered through a 0.2 µm cellulose nitrate membrane were introduced into the cell. When 50 mL was recovered, 50 mL of sodium nitrate with the same ionic force as the filtered leachate were added to the cell. Five fractions of 50 mL were recovered after filtration through the 30 kDa membrane and the dissolved organic carbon content of each fraction was measured. Then the first four fractions were mixed and 100 mL of this mixture were sampled for the filtration on a lower cutoff membrane; the aim is to obtain a distribution of the dissolved organic matter in leachates according to the apparent molecular weight.

3. Results and discussion

Wastes were not landfilled at the same date because of the different pre-treatments applied, so we will reason in number of months of landfilling for each cell. The month 0 correspond to the date of landfilling.

3.1. Measurements of chemical oxygen demand and dissolved organic carbon

3.1.1. Evolution of COD and DOC concentrations in Bioreactor leachate

The organic load gradually increases in Bioreactor leachate until reaching values near 100 g/L for the COD and 30 g/L for the DOC (Fig. 5). These strong concentrations can be explained by an accumulation of species, especially volatile fatty acids, during the first phase of recirculation. Following the new strategy of recirculation alternating phases with injection of leachate and phases of rest, an important decrease of VFA concentrations was noted. Consequently, the organic load decreases considerably from the 20th month and seems to stabilize near 5 g/L for the COD and 1.5 g/L for the DOC. These values

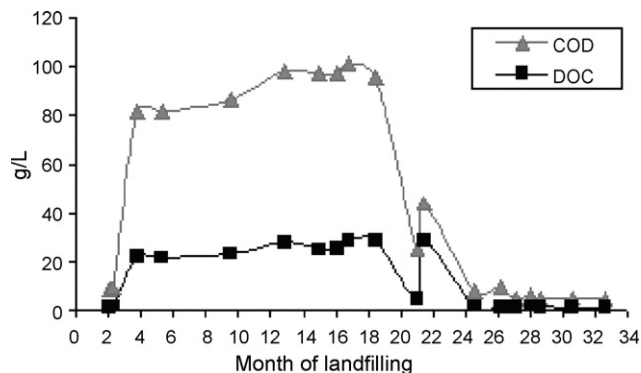


Fig. 5. Evolution of COD and DOC concentrations in Bioreactor leachate.

correspond to values found in the literature for methanogenic leachates.

3.1.2. Evolution of COD and DOC concentrations in MBP1 leachate

During the first months after landfilling, the organic load of MBP1 leachate is weaker than that observed in the case of the Bioreactor leachate (Fig. 6). The COD of MBP1 leachate is near 20 g O₂/L after 1 month of landfilling. This concentration indicates that wastes are always in the acidogenic phase. According to the results of Qasim and Chiang [18] obtained for leachates of different ages, MBP1 leachates would correspond to a leachate resulting from a landfill in exploitation since 1 year, with a range of values varying between 10.000 and 40.000 mg O₂/L. However the COD and DOC concentrations are quickly reduced to be around 5 g O₂/L for the COD and near 1.5 g C/L for the DOC from the 4th month. These results are identical to those found in the Bioreactor at the end of the 24th month of landfilling.

3.1.3. Evolution of COD and DOC concentrations in MBP2 leachate

The same evolutions were observed for MBP2 leachate (Fig. 7). Nevertheless the COD after 1 month of landfilling is twice less important than in MBP1 leachate. This value of COD would correspond, according to Qasim and Chiang [18], with a leachate resulting from a landfill in exploitation since 5 years. These results show the total absence of the first phases of degradation in the case of MBP2 wastes. However this difference between the two MBP leachates disappeared quickly. The val-

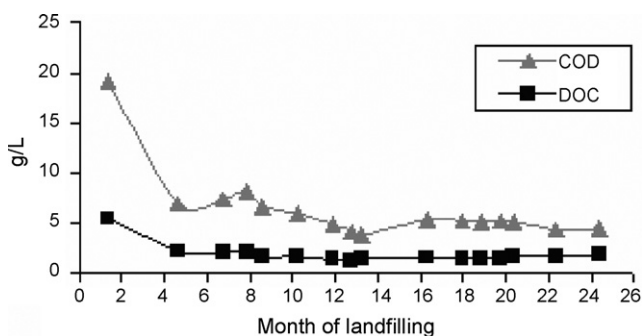


Fig. 6. Evolution of COD and DOC concentrations in MBP1 leachate.

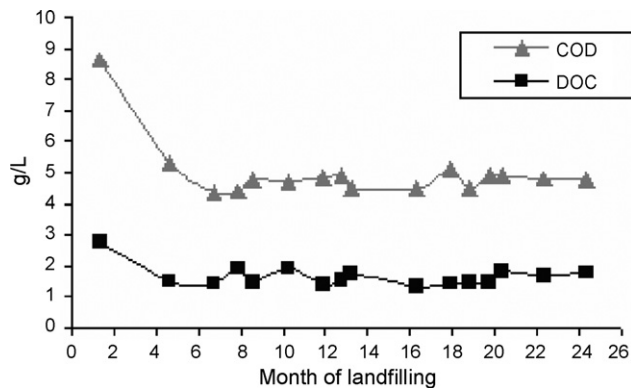


Fig. 7. Evolution of COD and DOC concentrations in MBP2 leachate.

ues of COD and DOC seem respectively stabilize near 5 g O₂/L and of 2 g C/L. Indeed it seems that the wastes deposited in the two cells tend very quickly (as from the 4th month) towards the same state of degradation.

3.2. Measurements of BOD₅/COD ratio

In general, BOD₅/COD ratio represents the proportion of biodegradable organics in leachate. Landfill leachate from a young landfill usually had a higher BOD₅/COD ratio and a leachate from an older or stable one had a lower BOD₅/COD ratio.

3.2.1. Evolution of BOD₅/COD ratio in Bioreactor leachate

BOD₅/COD ratio of the Bioreactor leachate (Fig. 8) decreases passing from 0.6 in the second month, value corresponding to a very biodegradable leachate, with values lower than 0.1 during the last months what would classify bioreactor leachate among stabilized leachates with a very low biodegradability.

3.2.2. Evolution of BOD₅/COD ratio in MBP1 and MBP2 leachates

Concerning MBP leachates, BOD₅/COD ratio (Fig. 9) also decreased in the course of time for finally stabilizing around 0.07. This value corresponds to a very low biodegradable leachate. According to the low values observed from the 5th month of landfilling for MBP1 and MBP2 leachates, it would seem that the easily and fairly biodegradable organic fraction

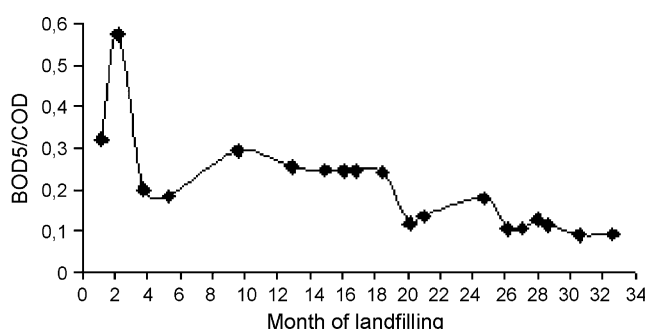


Fig. 8. Evolution of BOD₅/COD ratio in Bioreactor leachate.

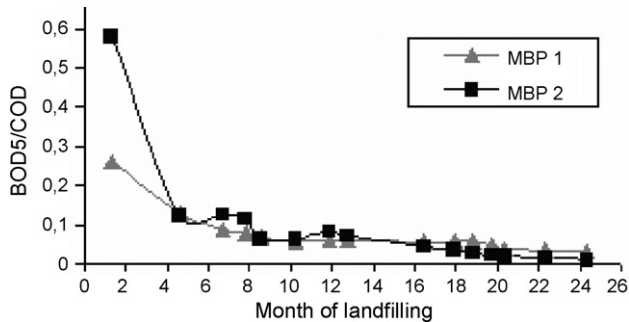


Fig. 9. Evolution of BOD₅/COD ratio in MBP1 and MBP2 leachates.

were already degraded during the phase of mechanical and biological pre-treatment and during the first months of landfilling. In term of comparison, Tränkler and Visvanathan [19] showed that BOD₅/COD ratio of a leachate resulting from fresh waste just landfilled was 0.9.

3.3. Measurements of specific UV absorbance

Measurements of UV absorbance at 254 nm and measurements of DOC allow calculating, for each leachate, specific UV absorbance which is characteristic of the aromaticity and the hydrophobicity of the molecules.

3.3.1. Evolution of SUVA index in Bioreactor leachate

In the case of Bioreactor leachate (Fig. 10), SUVA index is very weak until the 24th month, i.e., during all the acidogenic phase implying that the molecules present during this phase of degradation are not aromatic and hydrophobic molecules (mainly VFA). From the 25th month, SUVA index increases gradually passing from 11 to 22 L/cm/g C. Molecules thus become increasingly aromatic and their hydrophobic character is more and more important.

3.3.2. Evolution of SUVA index in MBP1 and MBP2 leachates

In the case of MBP leachates (Fig. 11), the evolution of the SUVA index is the same than in the case of Bioreactor leachate, with an increase in the course of time. SUVA index of Bioreactor leachate at the 33th month is twice weaker than

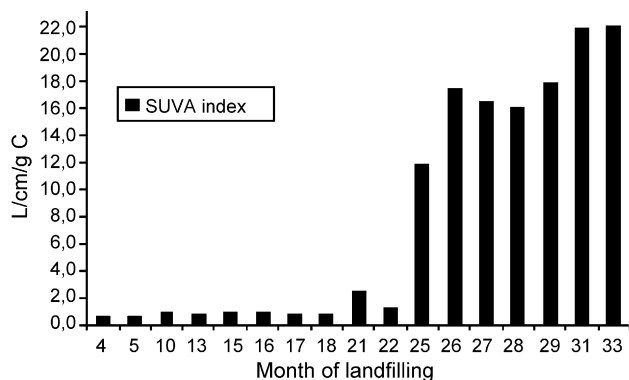


Fig. 10. Evolution of SUVA index in Bioreactor leachate.

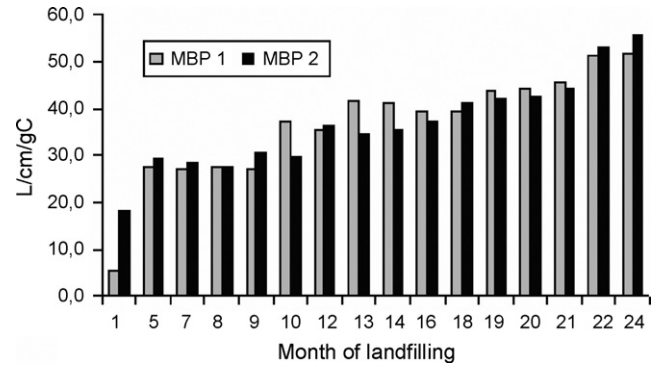


Fig. 11. Evolution of SUVA index in MBP1 and MBP2 leachates.

SUVA index corresponding to MBP leachates after 24th month of landfilling what would imply that the molecules contained in leachates resulting from pre-treated wastes would be more aromatic and hydrophobic. SUVA Index of MBP1 leachate is around 6 L/cm/g C 1 month after the landfilling whereas SUVA index of MBP2 leachate is around 18 L/cm/g C that implies that MBP leachates has different states of degradation at the time of the landfilling. However, this difference disappears quickly with relatively close SUVA index which increase until reaching values around 50 L/cm/g C translating a strong aromatic and hydrophobic character.

3.4. Fractionation of the organic matter on XAD resins

3.4.1. Fractionation of the organic matter contained in Bioreactor leachate

The proportion of HA* was 12% just after the landfilling which is high value for a leachate resulting from a fresh waste. Indeed, according to Blakey et al. [20], “young” leachates contain only 0.5–5% of HA* of the total organic carbon. These molecules are not really humic-like substances but substances which present the same properties of HS* by the means of the protocol of HA* extraction. These molecules can be carbohydrates, alcohols, amino acids or volatile fatty acids which are washed during the first phases of waste degradation. According to Hedges [21] and Weber and Huang [22], the degradation of organic biopolymer and anthropogenic compounds can generate compounds comparable to humic substances. In fact, Humic substances coming from the decomposition of waste and humic substances resulting from humification process can be observed simultaneously. This percentage in molecules called HA* should decrease due to decomposition in fulvic-like acids which in turn are decomposed in labile organic matter. Indeed It passes from 12% to 3% in 6 months indicating that these molecules were not really HS* taking into account the increase of the percentage in hydrophilic-like substances during the first 6 months (Fig. 12). It seems that these molecules initially comparable with HS* are then degraded into non humic-like substances. This first phase corresponds to a phase of washing with release of molecules initially present in waste and which did not yet have the time to degrade.

During the following months, evolutions were observed. The percentage in hydrophilic-like substances decreases to reach

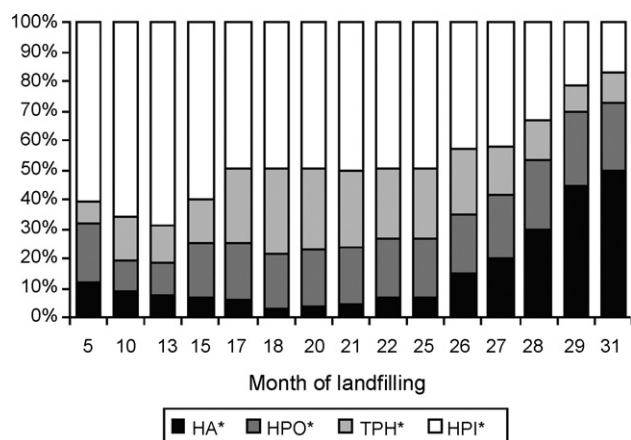


Fig. 12. Fractionation of the OM contained in Bioreactor leachate ($\pm 3\%$).

50%. This fraction, representative of an indigenous contribution, refers to a microbiological activity (bacteria). The percentage of hydrophobic-like substance, due to allochthonous contribution from soils and humus in natural waters, increases passing from 12% to 20% while remaining lower than the percentage of transphilic-like substances which correspond to intermediate compounds between HPO* and HPI* compounds. The HPO* fraction is composed of highly aromatic molecules derived from cellulose and lignin [23]. By way of comparison, the percentage of HPO* of a leachate resulting from a stabilized landfill is near 65% [6]. As for the percentage in humic-like acids, it starts to increase again slightly. These evolutions indicate the end of the washing phase and the beginning of a second phase of pre-humification. However, from the 17th month, the distribution of the OM does not seem to evolve indicating a blocking of the degradation already showed with the global parameters measurements. During the third phase, from the 28th month onwards, a great evolution of the repartition of the organic matter was observed. The percentage of humic-like acids increases considerably to reach 50% whereas the percentage of hydrophilic-like substances decreases to reach values inferior to 30%. This third phase, itself, regarded as being the humification phase knowing that this phase is known to last for several years.

By recirculating leachate, an organic load is maintained. However fractionations of the organic matter were also carried out on the recirculated leachate which was stored in a tank of recirculation. No major differences were observed concerning the distribution of organic matter. However the pH of the leachate in the tank became higher than the pH of the leachate recovered at the exit of the cell as from the 22nd month reaching values around 9. François et al. [24] showed using leaching tests that when the composition of the entering leachate was different from the leaving leachate the system evolved. On the other hand, the system seems to evolve slowly when the recirculated leachate has the same composition that the outgoing leachate. These explanations could then partly explain the blocking observed during the first 20 months for the Bioreactor cell.

The evolution of the percentage in humic-like substances ($HA^* + HPO^*$) is characteristic of these various phases of degradation in the course of time. Indeed this percentage is of 32% in

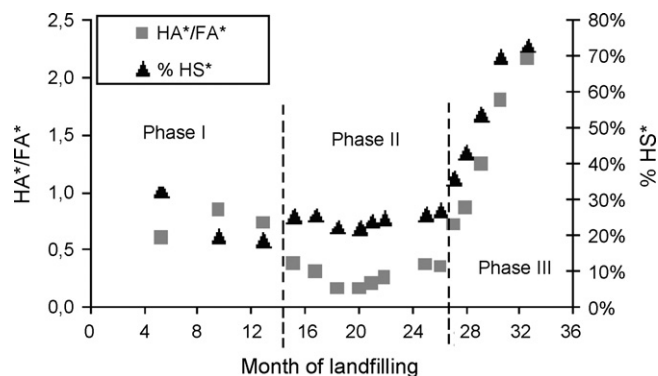


Fig. 13. Evolution of HA^*/FA^* ratio and HS^* percentage in Bioreactor leachate.

the 5th month knowing that this percentage corresponds to HS^* coming from the decomposition of wastes observed during the washing phase. A diminution is then observed during the phase of pre-humification (phase II): the percentage of HS^* is around 27%. This rate passes then from 27% to 73%, values frequently found in the literature [7]. The evolution of HA^*/FA^* ratio in the Bioreactor leachate is given in Fig. 13.

It allows the identification of the three phases of degradation in a very distinct way. During the first phase, the ratio is ranging between 0.5 and 0.8. This report decreases during the second phase because of the decrease of HS^* of decomposition. Then this ratio increases very quickly reaching a value of 2.2 showing the prevalence of the humic-like acids compared with the fulvic-like acids. The increase of the HA^*/FA^* ratio translates an advanced state in the humification process.

3.4.2. Fractionation of the organic matter contained in MBP1 leachate

The MBP1 wastes were landfilled in the pre-humification phase. The washing phase was not observed because it probably took place during the aerobic treatment (Fig. 14). From the 7th month, a significant evolution is observed. In fact, the percentage in HPO* increases from 17% to approximately 40% compared with 20% for the Bioreactor leachate at the 10th month. The proportion of hydrophobic-like substances is superior to the one of transphilic-like substances indicating a more advanced state. The

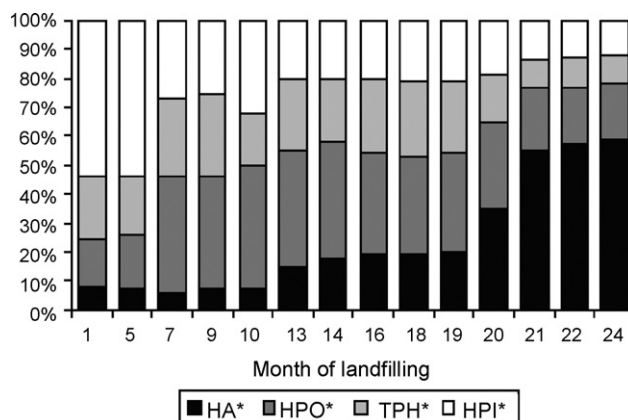


Fig. 14. Fractionation of the OM contained in MBP1 leachate ($\pm 3\%$).

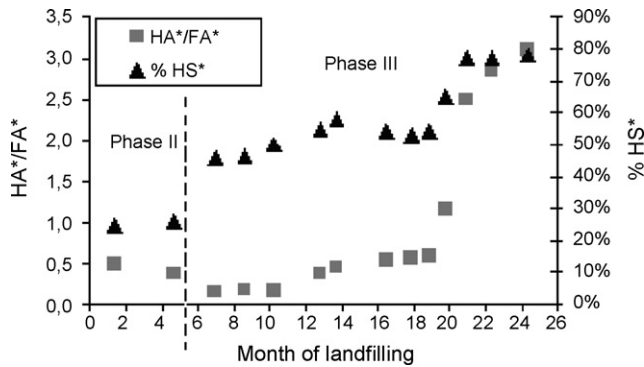


Fig. 15. Evolution of HA^*/FA^* ratio and HS^* percentage in MBP1 leachate.

percentage of hydrophilic-like substances decreases over time to reach values inferior to 30%. The percentage of HA^* remains constant until the 10th month and increases considerably from the 13th month to reach 59%.

The percentage in humic-like substances ($HA^* + HPO^*$) raises from 25% to 78% (Fig. 15) that shows an evolution rather similar to the evolution of the Bioreactor leachate. The evolution of HA^*/FA^* ratio in MBP1 leachate is also given in Fig. 15.

It is ranged between 0.4 and 0.5 during the phase of pre-humification (from the 1st month to the 5th month). During the following months, this ratio decreases around 0.15 and then increases gradually for finally reaching a value of 3.1 (compared to a value of 2.2 for the Bioreactor leachate). The evolution of HA^*/FA^* ratio allows to identify the different phases of the biological degradation; namely there are two stages: a phase of pre-humification during which the ratio decreases and a second phase which conveys the humification process. This last phase can last for several months. During it, the ratio remains constant and then increases. This last stage is conveyed by the increase in the humic-like acids which become majority.

3.4.3. Fractionation of the organic matter contained in MBP2 leachate

At the beginning the percentage in HA^* was identical to that found in the MBP1 leachate (Fig. 16). It follows the same evolution with a significant increase from the 13th month to reach 57% of humic-like acids. However, the percentage of hydrophobic-like substances just before landfilling was equal

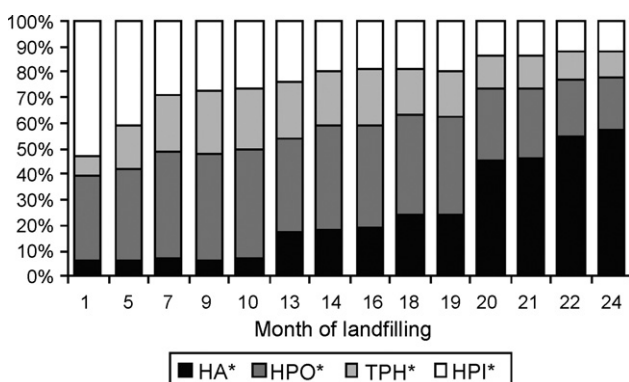


Fig. 16. Fractionation of the OM contained in MBP2 leachate ($\pm 3\%$).

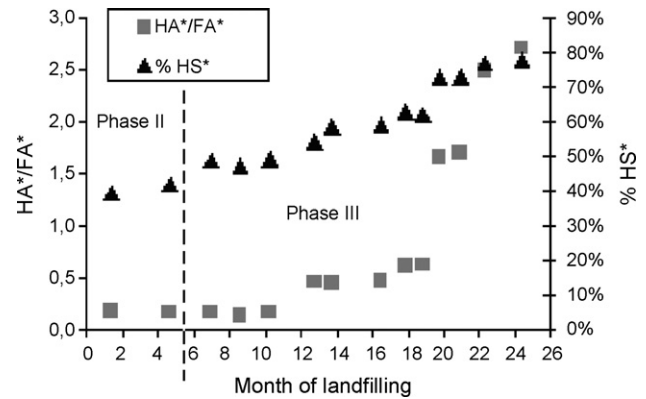


Fig. 17. Evolution of HA^*/FA^* ratio and HS^* percentage in MBP2 leachate.

to 34% compared with 18% for MBP1 leachate. MBP2 wastes would appear to be in the third phase of humification from the beginning of landfilling. Consequently the duration of the pre-treatment seems clearly to accelerate the speed of waste degradation during the first months. The more the pre-treatment is pushed, the quicker waste is humified before landfilling. The percentage in HPO^* increases over time to finally stabilize near 40%, a value very close to MBP1 value. As for MBP1, the percentage of hydrophilic-like substances reaches values inferior to 30%. From the 7th month the distribution of the organic matter were not different between the both cells in comparison to the beginning of the study. Waste resulting from the two pre-treated cells seems to tend towards the same state of humification.

The percentage in humic-like substances passes from 40% to 78%, this initial proportion indicating an advanced state of humification at the moment of the landfilling. Artiona-Fully and Fuller [7] found approximately 60% HS^* for leachate considered as stabilized. The evolution of HA^*/FA^* and the quantity of HS^* in MBP2 leachate is given in Fig. 17.

Contrary to the Bioreactor and MBP1 leachates, the decrease in HA^*/FA^* ratio is not observed for MBP2 leachate. This result confirms the total absence of the first phases of degradation. The ratio is 0.18 until the 10th month. Then it increases gradually up to values of 2.7, values slightly lower than those found for MBP1 leachate but higher than the values obtained for Bioreactor leachate. In addition, no significant evolution of the distribution of the OM is noted during the last 2 months in the case of MBP leachates, what could mean that the stabilization of waste is close. Only the follow-up of the fractionation of the OM of the leachate during the next month will allow to confirm or to cancel this assumption.

For the three leachates, significant evolutions of the distribution of the OM were observed during the last months whereas the COD seemed constant. This implies that the system can always evolve in spite of a constant COD. This also highlights the importance of the fractionation to analyse more precisely the OM.

3.5. Fractionation of the organic matter by ultrafiltration

The distribution of the apparent molecular weight of the compounds contained in leachates at different month is shown in

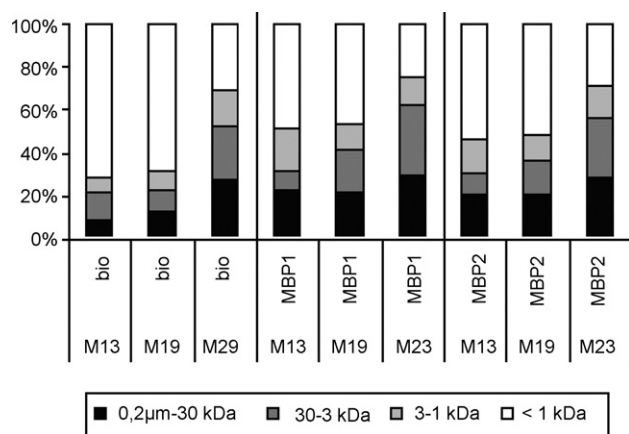


Fig. 18. OM fractionation of leachates by ultrafiltration in function of time ($\pm 5\%$).

Fig. 18. Fractionations were carried out after 13, 19 and 29 month of landfilling for Bioreactor leachate and after 13, 19 and 23 month for MBP leachates.

These results confirm those observed with fractionation on XAD resins. Differences are observed between bioreactor and MBP leachates. The MBP leachates contain approximately 20% of high molecular weight molecules after 13 and 19 month of landfilling whereas the percentage of high molecular weight was only of 10% for bioreactor leachate. This is explained by the greater presence of HA^* in MBP leachates than in Bioreactor leachate. The percentage of molecules having a molecular weight inferior to 1 kDa was around 70% for Bioreactor leachate. These results were linked to those observed for organic matter fractionation according to the hydrophobic character of molecules. The greater the percentage in HS^* , the higher the apparent molecular weight is. They are also in accordance with literature results [14–25] for which the molecular distribution over a wider range increases with the increasing age of landfill leachates and therefore with the humification state. Few differences are observed between MBP1 and MBP2 leachates showing that molecules tend to the same state of humification. Evolutions can be observed during time for the three leachates as in the case of fractionation on XAD resins. For bioreactor leachate, the percentage of molecules having an apparent molecular weight superior to 30 kDa increases slightly reflecting the increase in HA^* whereas in the case of MBP leachates it can be seen that the percentage of high molecules remains constant in spite of the increase in the percentage of HA^* . On the other hand the proportion of molecules with molecular weights ranging between 30 and 3 kDa increases, what shows that HA^* could also be found in this fraction. Li et al. [26] have shown that the apparent molecular weight of HA^* can change depending on their heterogeneous structural and compositional characteristics. They precise that the HA^* s with smaller molecular weight may derive from lignin materials and that the HA^* s with greater molecular weight may be originated from lipid-rich biopolymers. It suggests that, even though the biogeochemical and environmental conditions remain the same, different source materials can lead to the formation of very different HA compounds (chemically, structurally, and molecularly).

4. Conclusion

This work concerns the study of the impact of leachate recirculation and Mechanical Biological Pre-treatment before landfilling on waste degradation by using the organic matter as an indicator of the biological degradation and stabilization. Fractionations of the organic matter were carried out over time according to the hydrophobicity and to the apparent molecular weight of molecules contained in leachates resulting from several treatment schemes.

This study initially showed the interest to use the fractionation of the organic matter as an indicator of degradation and stabilization because it was observed, for all the leachates, that even if the total parameters like the DOC or COD are constant, the system can always be in evolution.

Different diagrams of waste degradation have been determined for bioreactor leachate, MBP1 leachate (12 weeks of pre-treatment with an $AT_4 = 29 \text{ mg O}_2/\text{g DS}$) and MBP2 leachate (25 weeks of pre-treatment with an $AT_4 = 16 \text{ mg O}_2/\text{g DS}$). Three phases have been determined. The first phase corresponds to the washing of molecules initially present in wastes. These substances are humic-like substances of decomposition but not humic-like substances emerging from humification process. This phase was only observed for bioreactor leachate and not for MBP leachates because of the washing of these molecules during the pre-treatment stage of MBP. The second phase is a phase of pre-humification observed for the three leachates. It corresponds at the set-up of humification process with the disparition of humic-like substances of decomposition and the formation of humic-like substances of humification. An increase of fulvic-like acids can particularly be observed. This second phase has been longer for MBP1 than for MBP2 leachate (MBP2 wastes were landfilled with a humification state more advanced than MBP1 wastes), showing the impact of the duration of the pre-treatment. The third phase conveys the humification process characterized by an increase of humic-like acids and hydrophobic compounds and it has been observed for all the leachates.

MBP1 and MBP2 wastes were at different phases of degradation during the first months. Nevertheless they tend to be at the same humification state today. Indeed, the distribution of the organic matter highlights that the humification process is advanced and nearly identical for MBP leachates, showing that the duration of the pre-treatment is not very significant after few months of landfilling. The degradation of Bioreactor wastes seems to be less rapid than MBP wastes. These results are confirmed by ultrafiltration tests. Differences observed between Bioreactor and MBP processes could be explained by the accumulation of volatile fatty acids which prevent the methanogenic phase. However, despite of the blocking of the degradation in the case of the bioreactor cell, leachate recirculation allows a quicker degradation of wastes in comparison to conventional landfilling.

A low cost MBP processes have potential to reduce organic strength in leachates and the easily biodegradable fraction could be targeted, avoiding all of the problems due to the production of volatile fatty acids during the early phase of the landfill (i.e.,

acidogenesis). However, the timescale over which leachates will not require management remains to be determined.

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References

- [1] R. Damiecki, Mechanical-Biological Pre-treatment of MSW, *Bioprocess. Solid Waste Sludge* 2 (2002) 31–36.
- [2] H.D. Robinson, K. Knox, B.D. Bone, A. Picken, Leachate quality from landfilled MBT waste, *Waste Manag.* 26 (2005) 383–391.
- [3] D.R. Reinhart, A.B. Al-Yousfi, The impact of leachate recirculation on municipal solid waste landfill operating characteristics, *Waste Manag. Res.* 14 (1996) 337–346.
- [4] C. Gachet, R. Bayard, M. Singh, R. Gourdon, Effects of water content and leachate recirculation on anaerobic degradation of landfilled waste, in: *Proceedings Sardinia 2003, Ninth International Waste Management and Landfill Symposium*, Cagliari, Italy, 6–10 October, 2003.
- [5] J.B. Christensen, D.L. Jensen, C. Gron, Z. Filip, T.H. Christensen, Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater, *Water Res.* 32 (1) (1998) 125–135.
- [6] J. Labanowski, C. Gauthier, G. Feuillade-Cathalifaud, Fractionation of the organic matter from a stabilised MSW landfill leachate, in: *Proceedings Sardinia 2003, Ninth International Waste Management and Landfill Symposium*, S. Margherita di Pula, Sardinia, Italy, 6–10 October, 2003.
- [7] J. Artiola-Fortuny, W. Fuller, Humic substances in landfill leachates—Humic acid extraction and identification, *J. Environ. Qual.* 11 (1982) 663–668.
- [8] K.H. Kang, H.S. Shin, H. Park, Characterization of humic substances present in landfill leachates with different ages and implications, *Water Res.* 36 (16) (2002) 4023–4032.
- [9] S.T.S. Yuen, Bioreactor landfills promoted by leachate recirculation: a full-scale study, Thesis, University of Melbourne, 1999.
- [10] R. Lornage, E. Redon, T. Lagier, I. Hébé, J. Carré, Performance of a low cost MBT prior to landfilling: study of the biological treatment of size reduced MSW without mechanical sorting, *Waste Manag.* 27 (12) (2007) 1755–1764.
- [11] D. Von Felde, H. Doedens, Mechanical-biological pre-treatment: results of full scale plant, in: *Proceedings Sardinia 97, 6th International Landfill Symposium*, Cagliari, Italy, vol. 1, 1997, pp. 531–542.
- [12] *Richlinie für die MBA (Guidance for the MBT)*. BMLFUW, Vienna, Austria, 2002.
- [13] G.R. Aiken, D.M. McKnight, K.A. Thorn, E.M. Thurman, Isolation of hydrophilic organic acids from water using non-ionic macroporous resins, *Org. Geochem.* 18 (1992) 567–573.
- [14] J.P. Croué, B. Martin, A. Deguin, B. Legube, Isolation and characterization of dissolved hydrophobic and hydrophilic organic substances of a water reservoir, in: *Proceedings of Workshop on NOM in Drinking Water*, Chamonix France, 1993, pp. 43–51.
- [15] F.H. Frimmel, M. Weis, Ageing effects of high molecular weight organic acids which can be isolated from landfill leachates, *Water Sci. Technol.* 23 (1991) 419–426.
- [16] N. Calace, A. Liberatori, B.M. Petronio, M. Pietroletti, Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals, *Environ. Polut.* 113 (2001) 331–339.
- [17] A. De Guardia, S. Brunet, D. Rogeau, G. Matejka, Fractionation and characterisation of dissolved organic matter from composting green wastes, *Bioresour. Technol.* 83 (2002) 181–187.
- [18] S.R. Qasim, W. Chiang, *Sanitary Landfill Leachate: Generation, Control, and Treatment*, Technomic Publishing, Lancaster, 1994.
- [19] J.O. Tränkle, C. Visvanathan, Mechanical-biological pre-treatment in south-east Asia—Results of a first practical approach, *Proceedings Sardinia 2003, Ninth International Landfill Symposium*, Cagliari, Italy, D2, 2003, p. 334.
- [20] N. Blakey, R. Cossu, P. Maris, F. Mosey, Anaerobic lagoons and UASB reactors: Laboratory experiments, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), *Landfilling of Waste: Leachate*, Elsevier Applied Science Publisher, Amsterdam, 1992, pp. 245–263.
- [21] J.I. Hedges, Polymerization of humic substances in natural environments, in: F.H. Frimmel, R.F. Christman (Eds.), *Humic Substances and Their Role in the Environment*, Life Sciences Research Report 41, Wiley Interscience, Chichester, 1988, pp. 45–58.
- [22] W.J. Weber, Q. Huang, Inclusion of persistent organic pollutants in humification processes: Direct chemical incorporation of phenantrene via oxidative coupling, *Environ. Sci. Technol.* 37 (18) (2003) 4221–4227.
- [23] L. Labouyrie-Rouillier, Extraction et caractérisation des matières organiques naturelles dissoutes d'eaux de surface: étude comparative des techniques de filtration membranaire et d'adsorption sur résines macro poreuses non ioniques, Thèse de doctorat, université de Poitiers, 1997.
- [24] V. François, G. Feuillade, N. Skhiri, T. Lagier, G. Matejka, Indicating the parameters of the state of degradation of Municipal Solid Waste, *J. Hazard. Mater.* 137 (2) (2006) 1008–1015.
- [25] E.S.K. Chian, Stability of organic matter in landfill leachates, *Water Res.* 11 (1977) 225–232.
- [26] L. Li, Z. Zhenye, H. Weilin, P. Ping'an, S. Guoying, F. Jiamo, Characterization of humic acids fractionated by ultrafiltration, *Org. Geochem.* 35 (2004) 1025–1037.