Study of the organic matter contained in leachate resulting from two modes of landfilling: leachate recirculation and mechanical-biological pretreatment before landfilling

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Abstract

Landfilling remains the most widely used treatment process of Municipal Solid Wastes (MSW). Today two main landfilling approaches are developping such as Bioreactor concept and Mechanical-Biological Pretreatment (MBP) before landfilling. The purpose of this study is to compare the both methods on the acceleration of waste degradation. Measurements of global parameters (DCO, COD, UV...) and fractionations of organic matter on XAD resins were regularly carried out on leachates resulting from three experimental pilots. Comparing MBP and Bioreactor leachates, results indicate that the degradation state of Bioreactor leachate is less advanced than those of MBP leachates. Organic load (COD) is approximately 15 times higher than load observed for the MBP cells and humic substances concentration in MBP leachates is much higher than in Bioreactor leachate.

Keywords

leachate recirculation ; Mechanical-Biological Pretreatment ; waste degradation ; organic matter ; fractionation ; stabilization.

1 Introduction

For economic reasons, landfilling remains the most widely used Municipal Solid Wastes (MSW) treatment process. Various chemical and biological species, present in the MSW landfill, come from complex chemical and biological reactions, generating pollutions for the environment. The deficit of the processing capacities of MSW is often underlined by the authorities. Today, two main landfilling approaches are developed: the Bioreactor concept which consists in recirculation of leachate and the Mechanical-Biological Pretreatment (MBP) for which wastes are "stabilized" before landfilling. Many authors studied the impact of leachate recirculation (Reinhart et al., 1996; San et al., 2001; Warith, 2002; François, 2004; Sponza et al., 2005; Gachet, 2005). These studies were carried out on pilots (laboratory scale) but also on sites (in countries where the leachate recirculation is authorized: United-States, United-Kingdom and Germany. The principle of the Bioreactor consists in collecting generated leachate to reintroduce it in the mass of waste so as to accelerate the degradation of the organic matter and to decrease the lifespan of the pollutants. (Warith, 2002).

The advantages of this technique are numerous. It allows to:

- accelerate the stabilization. Reinhart et al. (1996) specify that leachate recirculation decreases the time necessary to reach the stabilization of a landfill. Indeed, it allows to bring moisture necessary to degradation. Moisture is the principal parameter affecting the degradation of the organic matter (Reinhart et al., 1996 ; Gachet, 2005).
- reduce the environmental impacts with a better control of leachates and an attenuation of rejections and contaminations of subsoil waters and surface water (Warith, 2002). It decreases the quantity of leachates to be treated.
- increase the production of biogas.The more significant water content in the solid mass of waste optimizes the growth of the population responsible for the methanogenese. This increase in production of methane is directly linked to the evolution of the waste degradation (Sponza and Agdad, 2004).
- decrease the organic load. The recirculation of the leachate increases the rate of elimination of the organic matter thanks to an acceleration of biological degradation. It brings nutriments, used by anaerobic micro-organisms, within the mass of waste. Sponza and Agdag (2004) note that, without recirculation, the quantities of phosphorus and nitrogen found in solid waste are weaker used by the anaerobic micro-organisms, which slows down the degradation of waste. Nevertheless these results were discussed by François (2004) which precises that, at the end of degradation, salting out is limited by the recirculation of leachate because of a balance between the matters constituting the leachate and those potentially relargable by waste.
- reduce the costs and maintenance due to the follow-up of aftercare period (Warith, 2002).

However it is necessary to respect certain rules to optimize the process. San et al., (2001) showed that the volume of leachate recirculated must not be too significant. Chugh et al. (1998) precise that the volume of leachate recirculated has not to exceed 30% of the initial volume of waste. Sponza and Agdad (2004) also showed that too significant volumes involve a reduction in the capacity plug of the mass of waste involving an increasing of the quantity of dissolved organic carbon, an accumulation of volatile fatty acids and a reduction in the production of methane. Morris et al. (2003) underline also the formation of preferential ways not allowing to highlight the effects of the recirculation whereas San et al. (2001) specify that the rate of recirculation must be adapted according to the season and the climate.

Mechanical Biological Pretreatment (MBP) of residual municipal solid waste aims at reducing the biodegradable organic matter contained in residual waste.

The objectives of the mechanical treatment are to prepare the waste for the biological stage. Different processes can be used for the mechanical stage such as grinding, screening or magnetic separation. It is often necessary to carry out another mechanical treatment after biological treatment because it seems that threshold values, fixed by the German and Austrian regulations on the low calorific value of landfilled waste, can be only achieved if the waste gets a second mechanical treatment. This is generally a sieving.

Concerning the biological treatment, both aerobic and combined anaerobic-aerobic processes can be used. Fricke et al. (2005) precise that in comparison to aerobic process, anaerobic digestion can be ecologically advantageous, particularly with regard to exhaust emissions and energy balances.

Most MBP technologies have been developped in Germany and Austria, Switzerland and the Netherlands are also developping markets. In 2002, there are more than 70 MBP plants operating in Europe (Heerman, 2002). Indeed, this technique presents potential advantages:

- it reduces the volume of residual waste and therefore the landfill space, thus reducing the cost to the local authority of disposal (Damiecki, 2002). It reduces side-effects at the landfill site like odours, dust and windblown paper and plastics.
- it permits to eliminate potential hazardous waste contaminants of the waste stream such as batteries, solvents, paints, etc.
- it reduces the biodegradability of the waste, thus reducing the methane and leachate production (Damiecki, 2002). However, althought the biodegradability of the waste has been reduced via the biological process, the residue may not be classed as inert.

The aim of this study is to allow the comparison of these two processes and more specially to determine their efficiency on the acceleration of waste degradation and stabilization. Global parameters related to Organic Matter (OM) have been measured and fractionations of OM on XAD resins have been carried out to determine the humification state of several leachates.

2 Materials and methods

2.1 Origin of cells

Three cells were set up in august 2003 and were dimensioned on a significant scale to be the more representative of the reality of an industrial site, volume of approximately 23 m^3 which corresponds to 10 tons of wastes. All the cells were initially filled with the same fresh waste.

After a full characterization, the wastes were more and less pretreated before landfilling according to nature of cells. They were then filled thanks to a mechanical digger and inoculated by cowpat in order to accelerate the biological processes. Wastes were compressed according to a shovel on a steel plate in order to obtain densities ranging between 0.7 and 0.8. and were recovered with a PEHD-clay cover. A sprinkler simulates precipitations and a biogas collector is also installed. All around the cells a layer of compost allows a thermic isolation to preserve an optimal temperature for the degradation of waste.

2.2 Leachates characteristics

Leachates result from three different experimental cells of wastes. Their principal characteristics are as follows.

Cell 1: this cell received fresh waste coarsely crushed. This cell is exploited according to the Bioreactor concept with a daily recirculation of leachate.

Cells 2 and 3: These two cells received pretreated wastes; wastes were coarsely crushed and put in windrow during 12 or 25 weeks. An aerobic biological stabilization was carried out by a controlled aeration during 12 weeks.

The AT_4 values of wastes before they have been introduced in the cells was 29 mg O_2/g of Dry Substances (DS) for cell 2 and 16 mg O_2/g DS for cell 3. By way of comparison and according to the data of literature, a raw waste has an AT_4 from approximately 60 mg O_2/g. Then these wastes were named MBP1 (12 weeks of biological treatment) and MBP2 (25 weeks).

2.3 Leachates analysis

2.3.1 Analytical methods

Leachates was stored in a 4°C refrigerator to keep the samples characteristics unchanged. pH was measured using a pHmeter "pH M210 Meterlab" of Tacussel/radiometer provided with a combined electrode of glass Ag/AgCl.

The analyses of COD were realized according to standards methods (NFT 90-101). The measurement of the BOD_5 was facilitated by the use of oxtops WTW. Measurements of DOC and TOC were carried out by a carbon analyzer TEKMAR DOHRMANN models Apollo 9000.

UV-visible absorbances were measured using a spectrophotometer Agilent 8453. Measurements are carried out at 254 nm wavelength which is characteristic of polyphenols compounds. This measurement allows to determine the SUVA index (absorbance 254 nm/DOC) which gives information on the aromaticity and the hydrophobicity of the leachates. This index increases with the aromaticity and the molecular weight of the molecules.

2.3.2 Determination of the percentage in humic acids

Humins are eliminated by filtration on nitrate cellulose membrane (porosity 0.45 µm). Fulvic acids and Humic acids have been isolated by using their capacity of solubilisation in function of pH (protocol of Schnitzer and Khan (1972)).

2.3.3 Fractionation of the organic matter

The method of fractionation of humic substances proposed by Aiken et al. (1992) and Croué et al. (1993) depends of the properties of solubility of the organic compounds. The protocol makes it possible to obtain three different fractions gathering compounds with homogeneous physicochemical properties. To carry out these fractionations it is necessary to determine a capacity factor called k' who corresponds to the mass of organic compound retain on the resin versus the mass of compound in the mobile phase. According to the literature the most used values are 100, 50, 25 and 5. A first study carried out in the laboratory on leachate fractionation has showed thaht the best valueof the capacity factor was equal to 25 for this work. The volume of sample is given thanks to the following formula: Vech = 2*V0 * (1+k ') with V0: the dead volume of the resin column (60% of the volume of the bed) and Vech: the volume of sample filtered.

Leachate sample was filtered by gravity through the DAX-8 and XAD-4 resins which are hard and insoluble balls containing polymers macroporous and noncharged. The DAX-8 resin is of acrylic nature and present a light polarity whereas XAD-4 resin has a structure of the styrene-divinylbenzène type and is regarded as nonpolar. After to be filtered (pH2), the sample is successively passed on the DAX 8 resin and on the XAD 4 resin. It makes it possible to separate the compounds considered as hydrophobic (HPO*), adsorbed on DAX-8 resin, and represented essentially by humic substances, the compounds transphilic (TPH*) adsorbed on XAD-4 resin and the compounds says hydrophilic (HPI*) which include the DOC not adsorbed on these resins. The higher the percentage of hydrophobic substances will be, the more the leachate will have an advanced state of humification.

3 Results and discussion

3.1 Analyses of global parameters related to OM

A regular follow-up of global parameters related to OM was carried out during time since the cells set-up.

3.1.1 Case of Bioreactor leachate (Table 1)

Table 1 parameters related to the OM of the Bioreactor leachate

parameters	12/03	02/04	06/04	09/04	11/04	01/05	03/05	evolution
pH	6	6.1	6	6	5.8	5.9	6	=
COD (mg O_2/L)	81 680	81 600	86 400	98 160	97 000	111 360	95 045	↗
"Hard" COD (mg O_2/L)	/	/	/	/	28 320	45 600	60 000	↗
"Hard"COD/COD	/	/	/	/	0.29	0.41	0.63	≈
BOD_5 (mg O_2/L)	/	/	/	5 000	4 000	4 000	2 000	↘
BOD_5/COD	/	/	/	0.05	0.04	0.035	0.02	=
TOC (mg C/L)	24 250	24 100	25 850	31 050	27 900	31 600	32 100	↗
DOC (mg C /L)	21 958	21 750	23 384	27 900	25 130	28 512	28 962	↗
COD/TOC	3.4	3.4	3.3	3.2	3.5	3.5	3	=
UV 254 nm	/	10.5	21.53	21.64	20.33	20.50	21.55	=
SUVA index($L.gC^{-1}.cm^{-1}$)	/	0.5	0.9	0.8	0.8	0.7	0.7	=

pH of Bioreactor leachate is about 6, remains constant during time and correspond to values obtain during acidogenic phase, where pH decreases up to 5-6. For a methanogenic phase pH is stabilized around 7-8, these values are not obtained during the study. Bioreactor leachate is still in the first phases of waste degradation. Organic load contained in leachate is very significant and gradually increases until 95 000 mg O_2/L for COD and around 28 000 mg C/L for DOC which accounts for approximately 90% of TOC. BOD_5 seems to decrease and then BOD_5/COD ratio gradually decreases to reach a value of 0.02 which corresponds to a very low biodegradability of leachate. The measurement of "Hard" COD, considering organic non biodegradable fraction of the sample, represents approximately 50% of the total COD. "Hard" COD/COD ratio gradually increases during time showing an organic matter which becomes less and less biodegradable. Index SUVA is very weak what means that the molecules present in the Bioreactor leachate have a weak aromaticity and hydrophobicity. COD/TOC ratio can also be used as indicator of waste degradation. Millot (1986) and Lo (1996) consider that this ratio is higher than 4 for young leachates and decreases gradually up to 2 for leachates close to a stabilization state. In the case of Bioreactor leachate this ratio is nearly constant and around 3.3 what would classify this leachate among the young leachate. However, the evolution of this ratio is not always significant ; the measurements carried out on sites in Hong Kong (M.C. LO, 1996) indicate values much less low for old sites because of a strong proportion of nonoxydable organic compounds. The important organic load as well as weak index SUVA lets to us suppose that Bioreactor leachate is still in the first phases of degradation.

3.1.2 Case of MBP1 leachate (Table 2)

Table 2 parameters related to the OM of MBP1 leachate

parameters	06/04	09/04	11/04	12/04	01/05	03/05	evolution
pH	6.5	7	7.4	7.5	7.5	7.5	=
COD (mg O_2/L)	19 200	5 500	7 440	8 256	6 720	6 048	=
"Hard" COD (mg O_2/L)	/	/	6 336	7 344	6 624	/	=
"Hard" COD/COD	/	/	0.85	0.89	0.98	/	➚
BOD_5 (mg O_2/L)	5 000	900	650	650	450	350	➘
BOD_5/DCO	0.26	0.16	0.087	0.08	0.07	0.06	➘
TOC (mg C/L)	6 000	2 400	2 350	2 300	1 940	1888	=
DOC (mg C /L)	5 470	2 225	2 125	2 102	1 734	1690	=
COD/TOC	3.2	2.3	3.1	3.6	3.5	3.2	
UV 254 nm	31.22	61.06	57.05	58.12	47.07	62.80	=
SUVA index($L.gC^{-1}.cm^{-1}$)	6	27	27	28	27	37	=

pH increases from 6.5 to 7.5. The pH is higher than the one of Bioreactor leachate, what already makes it possible to think that waste is not at the same degradation stage. Generally, the parameters do not significantly involve as it was the case for Bioreactor leachate. Salted out organic pollution confirms this tendency. COD seems stabilized around 6 000 mg O_2/L; this value is approximately 15 times less significant than for recirculated leachate. Robinson *et al.*, (2005) showed that MBP can considerably reduce the organic strength of leachates, avoiding the acetogenic phase, and more rapidly producing leachates similar to those from MSW landfills in methanogenic phases of decomposition. COD/TOC ratio varies slightly and is equal to that observed for Bioreactor leachate. SUVA index is higher than in the case of Bioreactor leachate (30 $L.gC^{-1}.cm^{-1}$), which means that the molecules present in this leachate have an aromaticity and an hydrophobicity much more important than the recirculated leachate. In term of biodegradability, BOD_5/COD ratio decreases during time and stabilizes around 0.07 what represents a low biodegradability of the leachate. It would seem that the organic fraction quickly biodegradable has already been degraded during the phase of pretreatment and in the first phases of degradation after landfilling. The measurement of the "Hard" COD confirms this assumption. Indeed the biodegradable fraction represents only a very small percentage. However this measurement of hard COD (carried out at 28 days), makes possible to estimate the quantity of OM quickly biodegradable and not OM slowly biodegradable even recalcitrant. MBP1 leachate appears in a state of degradation more advanced than Bioreactor leachate with an organic load much weaker and a SUVA index higher.

3.1.3 Case of MBP2 leachate

The same study has been carried out with the MBP2 leachate. The results obtained are not presented in this paper but they show some differences between MBP1 and MBP2, less important than with Bioreactor leachate. pH varies weakly with time until a value between 7 and 7.5. Organic load is lower than the load measured in MBP1 leachate . According to SUVA index, the molecules present in MBP2 leachate also present a strong aromaticity and hydrophobicity. COD/TOC ratio is near 2.7, value would indicate a more advanced state of degradation according to Millot (1986). In term of biodegradability, BOD_5/COD ratio gradually decreases to 0.06 and "Hard" COD/COD ratio is about 0.9 ; the same conclusion which has been done for MBP1 leachate can be formulated. This follow-up of global parameters allows to highlight differences, more or less marked, between the different ways of landfilling. The Bioreactor leachate, with a still low pH, a very high organic load and a very weak index SUVA appears to be in a state of degradation less advanced compared to both leachates resulting from MBP wastes.

3.2 Fractionation of the organic matter

The organic matter fractionation was carried out so as to determine the humification state of each leachate in relation to time.

3.2.1 Case of Bioreactor leachate (figure 1)

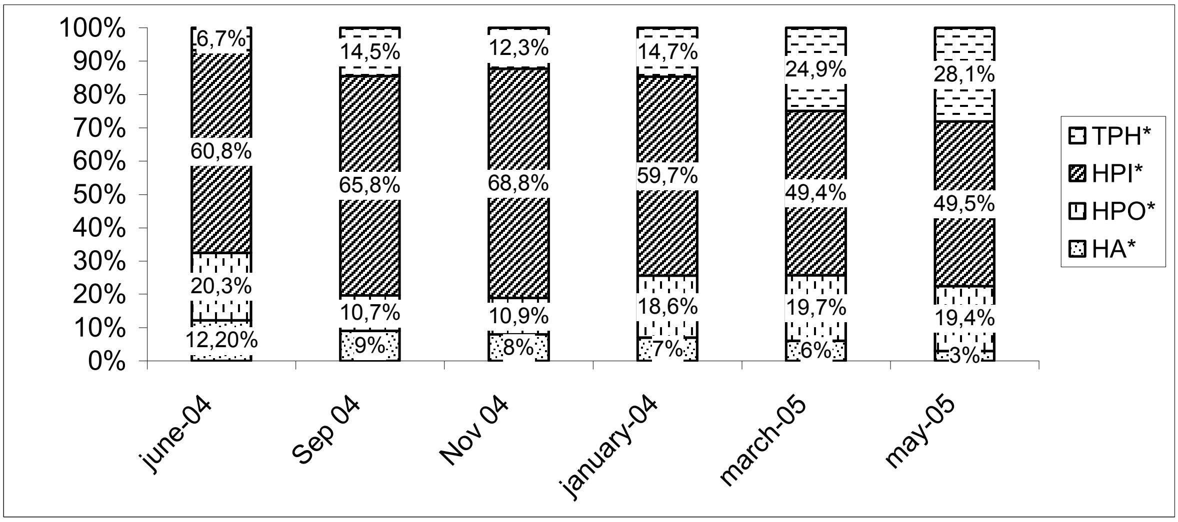

Figure 1 OM fractionation in Bioreactor leachate

The percentage of Humic Acids (HA*) in Bioreactor leachates decreases from the value of 12% to 3% one year later. This very low percentage is charasteristic of a weak humification. This decrease can be explained by the assimilation of proteins to humic acids during precipitation with pH 2. The percentage in HPO* are weak too, about 19%. This percentage has increased of approximatively 60% since the startup of cell. By way of comparison, the percentage in HPO* of a leachate resulting from a stabilized landfill situated near Limoges (France) is about 65% (Labanowski, 2004). The evolution of the other percentages are linked to the evolution of HPO*, with a decrease of the hydrophilic substances and an increase of transphilic substances considered like intermediate substances.

3.2.2 Case of MBP1 leachate (figure 2)

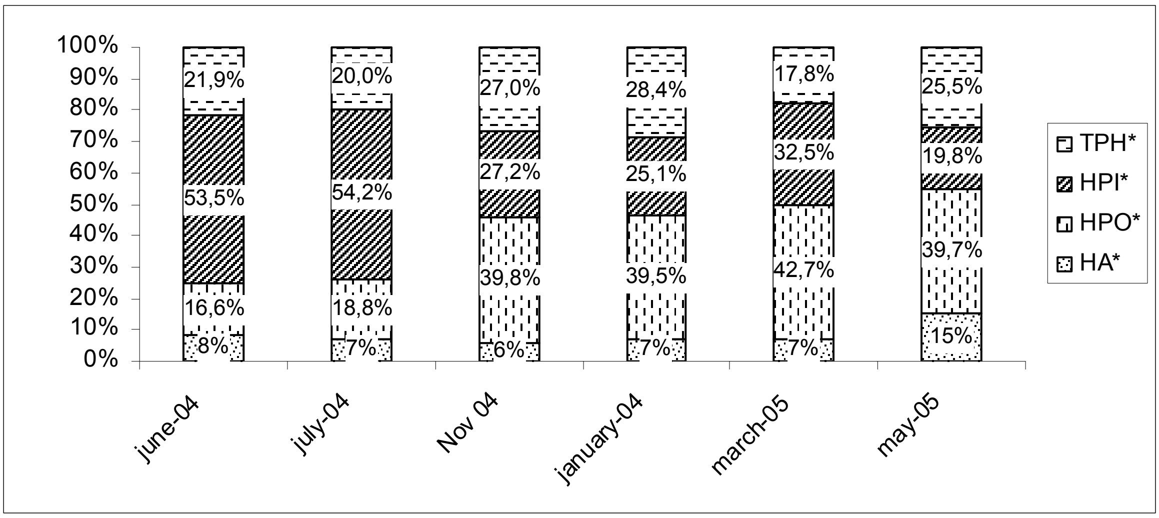

Figure 2 Figure 2: OM fractionation in MBP1 leachate

The percentage in HA* is quasi constant (7%) untill march 2005 and an increase is observed for finally reach 15% ie a value 5 times higher than in the case of Bioreactor leachate, indicating a state of humification more advanced. These values are close to the values found in the literature for a leachate considered as stabilized (Labanowski, 2004). The percentage in HPO* is doubled and pass from 17% to approximately 40% (20% for Bioreactor leachate). The percentage of hydrophilic substances decreases with time whereas the percentage of transphilic substances remains about constant. These results show that the state of waste degradation is advanced in the case of the cell constitutes of pretreated wastes. The landfilling of pretreated wastes seems more effective in term of acceleration of the waste degradation compared with the leachate recirculation.

3.2.3 Case of MBP2 leachate

The percentage in AH * is identical to that found in MBP1 leachate. It follows the same evolution with a significant increase in March 2005 to reach 17% of humic acids. This percentage does not make it possible to differentiate MBP1 from MBP2. However the percentage in substances of the hydrophobic type of MBP2 is equal to 36% at the beginning of the study compared with 18% for MBP1 leachate. Pretreatment length thus seems clearly influence the speed of degradation of waste during the first phases. The more the pretreatment is pushed, the more waste is degraded quickly. The percentage in HPO* increases during time for finally stabilizing itself around 40%, a value very close to the value of MBP1.

4 Conclusion

This study has initially consisted in determining global parameters of different leachates. These results showed a great difference between the leachate resulting from the bioreactor cell and the leachate resulting from the cells containing pretreated wastes before landfilling with in particular a COD approximately 15 times more significant for Bioreactor leachate. SUVA index show that MBP leachates contains molecules with a strong aromaticity and hydrophobicity what could mean a state of more advanced degradation of waste. Fractionations of OM on resins were carried out in order to have more intrinsic information on the humification state and the evolution of OM contained in each leachate. Determination of humic acids percentage and fractionations of OM have showed that the landfilling of pretreated waste seems to be more advanced in term of degradation. It is also observed that, in the first steps, MBP1 and MBP2 leachates have different characteristics, but they tend to be at the same humification state today.

5 Literature

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