

The elimination of odours resulting from a process of treatment of sewage sludge by biofiltration

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ABSTRACT. Our study deals with the elimination of the odours resulting from a process of treatment of sewage sludge by biofiltration (composting is carried out at the factory site). The first phase consists of identifying the odorous compounds emitted at the time of the composting of these sewage sludges (GC-MS). After identification, the pollutants are directly eliminated, at the factory site, by biofiltration. A medium containing the compost of green waste and sewage sludge is tested. The physicochemical and bacteriological properties of the media packing have been determined and monitored during the process of biofiltration.

Results show the efficiency of elimination of ammonia by the biofilter and the molar balance of sulphur was evaluated. Particular interest is given to the biological breakdown of sulphur compounds (H_2S , DMDS, etc...), which are highly smelly, even at very weak concentrations. Removal of many reduced sulfur compounds is complete while others are higher outlet concentration than inlet of the biofilter. These compounds can be formed as an intermediate product in the degradation dimethylsulfide (DMS), dimethyldisulfide (DMDS) and/or methylmercaptan (Me-SH). Also, the phenomena of adsorption and desorption are important because the concentrations of sulphur compounds in the air are low and fluctuates periodically.

One of the interests of this work is the use of a material resulting from composting which is directly available by the industrial and this process allows him to use produced waste. Moreover, this solution saves money since it allows one to obtain a process that is far from expensive, and which in addition offers the advantage of starting without any preliminary inoculation.

1 INTRODUCTION

Tests of treatment by composting urban sludges, added of green wastes, have been realized on the industrial site of the firm R.O.M (Recyclage Organique Mobile) established in Bordères-sur-l'Echez (Hautes Pyrénées, France).

Composting is a great way to valorize sludges which so become an element like to fertilizer, directly available for agriculture, viticulture, horticulture, arboriculture... However, this production is guilty of the emission of bad smells, and particularly at the beginning of the process and during the handling of wastewaters. These ones, stemmed from the treatment of wastewaters are composed of organic matters, of nitrogenous,

sulfurous, phosphorous compounds, and can generate, through their by-products, unpleasant smells following a biological process of fermentation.

The produced gas at this aerobic fermentation is composed primarily of carbon dioxide (CO₂), ammonia (NH₃), sulphur compounds, volatile acids, aldehydic and ketonic compounds. A part of our study consisted of the physicochemical identification of the molecules volatile and odorous emitted by this exhaust gas. Among those, we followed more particularly the family of the molecules sulphur of which the principal one: the sulphide of dihydrogen (H₂S) has the nauseous odor characteristic of egg rotted and is perceptible even with very weak concentration. Then, our work was focused on the treatment by biological breakdown of this industrial gas effluent; one of the originalities was to use as packing material of the mature compost resulting from green waste and urban sludges treatment available on the factory site.

2 MATERIALS AND METHODS

2.1 Pilots of biofiltration

The biofilter, that we will describe as « research » (noted BR thereafter) was then installed with an aim of studying more precisely the various phenomena brought into biological biodegradation of pollutants, to control better operational parameters. The base of these biofilter is composed of wood chips whose role is to diffuse gas to be treated on all the surface of the filter medium, made up of compost green waste and urban sludges.

The gas flow rate measured by thermo-anemometer (KIMO). The characteristics of the air, temperature, relative humidity (using a hygrosopic transmitting sensor and temperature KIMO) were measured for both biofilters.

2.2 Exhaust air analysis

2.2.1 Method of sampling

The composting of green waste and urban sludges was carried out under a green house, the drain of the gas effluent being realized by a system which aspirates the ambient air inside this green house. Gas samples were collected and transported in Tedlar bags (3 bags of 3.8 L per sample) and were analysed within 48h after sampling.

2.2.2 Method of analysis

The necessary pre-concentration of gas sampling was developed at the time of preceding tasks of research (Tuduri *et al.*, 2003; Lestremeau *et al.*, 2003). The method used consists in pre-concentrating the sample by micro-extraction on solid phase (SPME) before analysis by gas chromatography coupled to a mass spectrometer (GC Varian 3800/MS Varian 1200 Quad). This system of analysis made it possible to identify the oxygenated, aromatic and terpenic compounds.

The compounds with low molecular mass, such as ammonia and the hydrogen sulphide could not be detected by this method. Moreover, amines are also not easily identifiable by GC/MC, because of their strong capacity with being retained by the column used. This is why the inlet and outlet concentration of ammoniac are determined by colorimetric tubes (Dräger). As for the sulphur compounds, they are measured using a specific chromatographic analyzer (electrochemical cell, Airmédor). In the case of an analysis carried out on site and a follow-up of process, it was more adapted to follow the families of odorous chemical compounds rather than the compounds alone. Also, we followed the family of sulphur (including H₂S) and ammonia.

2.3 Packing material

The studied filter medium consists of a compost containing green waste and urban sludge (6 months of age) produced by the company R.O.M.

Physicochemical and bacteriological analysis were carried out on these medium at the beginning, at the middle and at the end of the treatment by biofiltration (cf. Table 2).

2.4 Experimental conditions

To design a biofilter, several parameters must be taken into account, the air flow rate, the biofilter layer height and the residence time of the pollutants (τ):

$$\tau = \frac{V_f}{Q} \quad (1)$$

where Q is the air flow rate ($\text{m}^3 \text{h}^{-1}$) and V_f the filter bed volume (m^3).

The time of residence corresponds to time that the gas puts to across the porous medium. Typical values of τ are lower than 1 minute (Kennes *et al.*, 2001), the process of biofiltration not being more economic on a large scale for higher time of residence. Important values can moreover lead to low removal efficiency and accumulation of toxic intermediate products.

The height of the filter medium in general does not exceed 1 to 1,5 m to limit the energetic costs necessary to counter the strong pressure losses (clogging).

In our study, the residence time is 60 s, the biofilter layer height is 0.5 m and the air flow rate is $15 \text{ m}^3 \text{h}^{-1}$.

3 RESULTS AND DISCUSSION

3.1. Physicochemical characterisation of waste exhaust air

The production of compost containing urban sludges is in the beginning strong odorous emissions. As for the odors related to the operations of composting of green residues (sheets, grass, branches of tree), a study carried out in Quebec (Odotech, 2001) announces that at the 20th of composting, the odorous compounds make mainly party of the family of terpenes (limonene, pinene, camphene), under aromatic products characteristic of the decomposition of lignin, abundant in the matters derived from wood the such barks of pine. Later, during the process (at approximately 50 days), others compounds of the family of the ketones (acetone, methyl ethyl ketone) as well as dimethylsulphur appear in larger quantity.

These results show also the presence and a more important concentration of some compounds released under conditions of anaerobic digestion: pinenes, hexenes, camphenes, hexadiene and ethanol inter alia, as well as butanoic and propanoic acids.

In Table 1 and Figure 1, we gathered the odorous and/or volatile molecules analyzed by family. The quantitative analysis of the oxygenated, aromatic and terpenic compounds comes from an estimate of the concentration of these compounds compared to the response given by the GC/MS to toluene. Then, that carried out on the sulphur compounds results from the specific chromatographic analyzer. For ammonia, the concentrations were given thanks to colorimetric tubes.

According to Table 1 and Figure 1, it is clear that the ammonia is the emitted majority compound. With regard to the families of compounds, we can note that the family of sulphur is majority, the Me-SH and the DMS being the most abundant compounds.

Moreover, all the concentrations in sulphur compounds higher than the odour threshold value (OTV) are indexed but, nevertheless lower than the threshold limit value (TLV), except for NH_3 .

Considering the important quantity of NH_3 and emitted sulphur compounds (Figure 1), we decided more particularly to follow these compounds at the time of the biological breakdown of this industrial effluent.

3.2 Ammonia

3.2.1 Removal efficiency

Two consecutive operations of composting were carried out using the same bed filter. Only results of the 2nd operation of composting are presented, results of first operation showing similar tendencies.

The NH_3 emissions vary between 10 and 70 ppmv (saturation of the measuring apparatus beyond 70 ppmv, Figure 2). The inlet concentration of the biofilter gradually decreases, which corresponds to the end of fermentation of composting process.

The removal efficiency RE (equation 2) is the operational parameter generally used to judge good or faulty operation of the biofilter :

$$RE(\%) = \frac{C_i - C_o}{C_i} \times 100 \quad (2)$$

where C_i = inlet concentration (ppmv); C_o = outlet concentration (ppmv)

Varying with the concentration of the pollutants, the air flow and the size of the biofilter, it reflects only the specific conditions under which were measured concentrations of pollutants in a point and at a time given in the filter medium.

In this test, the effectiveness of elimination reaches an average of 94%. It was deferred in the literature that for high NH_3 concentrations (50 ppmv), biofiltration is not the process adapted best taking into account the sensitivity of the nitrifying micro-organisms. But, it was also recognized that, in the case of biofilter composed of organic materials (compost, peat..), the removal efficiency could reach 100% with an inlet concentration of 213 ppmv (Choi *et al.*, 2003).

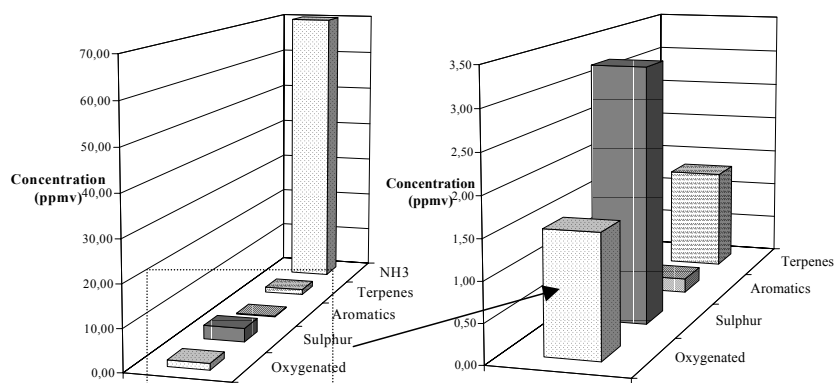


Figure 1. Distribution of exhaust compound.

Table 1. Analysis of compounds in waste gas.

	Compounds	Odor	Concentration (ppmv)	OTV (ppmv)	TLV ¹ (ppmv)
Sulphur (Airmédor)	Dimethylsulphure (DMS)	vegetables in decomposition	1,34	0,001-0,26	-
	Dimethyldisulphure (DMDS)	putrid	0,15	0,008-0.004	10
	Disulphure de carbone (CS ₂)		0,01	< 0,1 ⁽²⁾	-
	Methanethiol (Me-SH)	cabbages, garlic	1,78	0,02-0,025	5,1 ⁽³⁾
	Ethanethiol (Et-SH)	cabbages	0	0,001-0,012	3,94 ⁽³⁾
	Hydrogene sulphide (H ₂ S)	egg rotted	0	0,0007-0,036	107 ⁽³⁾
	Total			4,1	
Oxygenated (GC/MS)	Acetona	Soft fruit	0,73	13 ⁽²⁾	750
	2-Butanone	Strong sweetened odor	0,75	5,4 ⁽²⁾	200
	2,3-Butadione		0,01		
	3-Pentanone		0,01		200
	3-hydroxybutanone		0,02		
	Methyl acetate		0,02	4,6 ⁽²⁾	200
	3-methylfurane	Fruity pleasant odor	0,02		
Total			1,56		
Aromatics (GC/MS)	Toluene		0,05	2,94 ⁽⁴⁾	50
	Phenol		0,13	0,049 ⁽⁴⁾	
Total			0,18		
Terpenes (GC/MS)	Terpenes (C ₁₀ H ₁₆)		0,13		
	Camphène		0,01	5,02 ⁽⁵⁾	25 ⁽⁵⁾
	□-phellandrene		0,01		
	□-pinène		0,06	0,7 ⁽⁵⁾	25 ⁽⁵⁾
	3-carene		0,14		
	o-cymene		0,11		
	limonene		0,07	0,45 ⁽⁵⁾	25 ⁽⁵⁾
	eucalyptol		0,03		
	thujone		0,66		
	isomer of thujone		0,10		
Total			1,32		
Tubes Dräger	Ammoniac		> 70	10-100	25

¹Handbook, 1996-1997²INRS, toxicological card³VME (Valeur Moyenne d'Exposition): Average concentration over one 8 hours period⁴<http://www.cdc.gov/niosh/ipcs/iscpd6.html>⁵<http://www.mst.dk/chemi/01082909.htm>

3.2.2 Evolution of nitrates and ammonium within the packing material

The physicochemical properties of the medium during the process of biofiltration are differed in Table 2. The water content, the pH, the organic matter and organic carbon don't change significantly. On the contrary, nitrates and ammonium strongly vary.

The bacteria present in the biofilm uses ammonium and degrades it out of nitrite reducing the pH of the system (Baquerizo *et al.*, 2005; Sheridan *et al.*, 2002). At the same time, the nitrite is oxidized out of nitrates. Moreover, the NH_3 oxidation in NO_2^- generates H^+ ions, NH_3 added can be eliminated via a reaction acid-bases and transformed into ammonium. With regard to the decrease in nitrates (Table 2), it can have with their chemical reduction to ammonium. These various reactions explain the high increase in NH_4^+ . According to Joshi *et al.*, (2000), under these conditions there, the pH decreases; what is not the case in our study. According to Chung *et al.* (2000), this phenomenon represents a neutralization of ammonia and sulphates (cf. following paragraph). Such values mean that it is thus not necessary to add buffer solutions to maintain the pH of the filter medium near to 7.

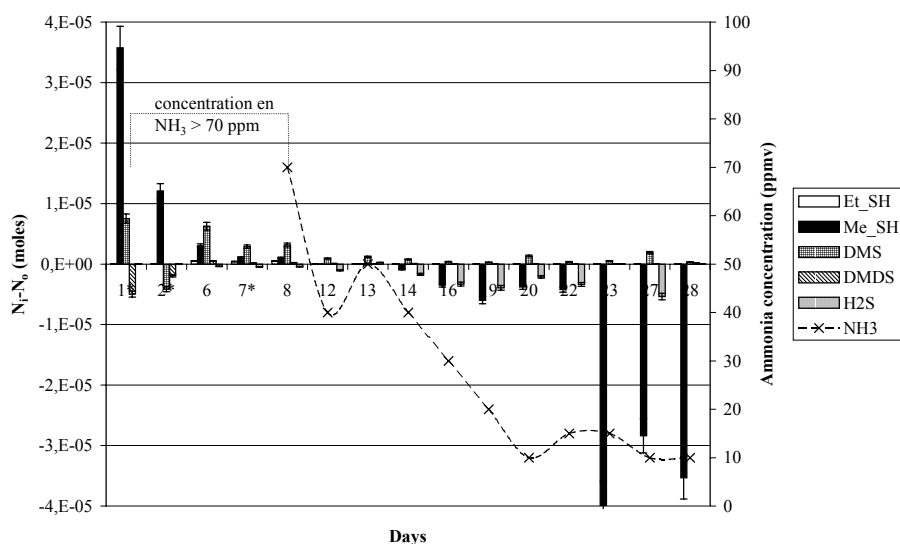


Figure 2. Molar balance of sulphur and concentration of ammonia during 28 days.

3.3 Sulphur compounds

3.3.1 Evolution of the sulphur compounds

The majority sulphur compounds emitted by urban sludge and green waste composting are the Me-SH and the DMS with a maximum concentration respectively (C_{\max}) of 1780 ppb and 1335 ppb first day of composting, H_2S with C_{\max} of 62 ppb the 27th days. Composting releases a smaller quantity of Et-SH and DMDS.

Table 2. Physicochemical properties of the medium.

Days	0	13	28
Aerobic microorganisms			
30°C (UFC ⁶ .g ⁻¹)	8.3.10 ⁷	3.4.10 ⁷	4.5.10 ⁷
pH (±0.2)	6.3	6.1	6,2
Water content (%)	54.8	48.96	54,33
Organic matter (±3%)	45.59	42.35	50,64
Organic carbon (±3%)	22.17	21.17	25,32
Nitrate NO ₃ ⁻ (mg.kg ⁻¹)	16396,1	14733,1	9067,8
Ammonium NH ₄ ⁺ (mg.kg ⁻¹)	24,35	156,74	298,63
P ₂ O ₅ (±0.2%)	2,15	2,55	1,77
K ₂ O (±0.2%)	3,87	0,64	3,35
CaO (%)	2,41	0,33	5,88
MgO (±0.3%)	2,14	0,13	1,37
Na ₂ O (%)	0,21	0,39	0,17
SO ₄ ²⁻ (moles) medium	2.48	2.61	1.47

The Me-SH is the majority compound in the exhaust gas, this can be explained by the degradation of the amino acids containing sulphur (cysteine, methionine, homocysteine and taurine) under anaerobic and aerobic conditions. In the field of food, more precisely in the case of the cheeses fermentation, the degradation of methionine recently was the subject of studies (Bonnamme *et al.*, 2000). According to the biogeochemical cycle of the DMS, H₂S and the Me-SH can also be formed (The University of Minnesota Biocatalysis/ Biodegradation Database). Evolutions of the sulphur pollutants emitted by the composting of urban sludge are different. Some decrease gradually during the process of composting such as the Et-SH and the DMDS which are not present any more in the gas effluent at the 10th day of composting. The DMS also follows this tendency with a concentration at the end of the composting of ppb range concentration. On the contrary, H₂S concentration increase during composting to reach on average of 50 ppmv. As for the Me-SH, it is very strongly emitted with the starting of composting. In the case of H₂S and Me-SH, we cannot speak about removal efficiency because the effluent at outlet of the biofilter is more charged. To understand this phenomenon, we established the molar balance of sulphur.

3.3.2 Molar balance of sulphur

The molar balance of sulphur was carried out thanks to calculations of the number of moles of sulphur brought by the various sulphur compounds in the following way :

$$N_{i/o} = Q \times \frac{P \times C_i \times 10^{-9}}{R \times T} \times (j_n - j_{n-1}) \times 24 \quad (3)$$

with $N_{i/o}$ the inlet or outlet number of moles of sulphur, P atmospheric pressure (Pa), C_i concentration of compound i (ppb), R the molar gas constant (J mol⁻¹ K⁻¹), T the temperature of the gas (K), j_n a number of days. Figure 2 shows 2 distinct phases : during the first 10 days of biofiltration, there is degradation of the sulphur compounds whereas the following days, an increase at outlet biofilter is observed. The total balance being negative, we were then interested in the phenomena of adsorption being able to explain a possible desorption. The tests carried out indicate very low capacity of adsorption of the packing material : about 10⁻⁸ g g⁻¹ of medium (Ruthven *et al.*, 1998).

⁶ Unité Formation Colonies

By way of comparison, the capacities of adsorption of an activated carbon felts and fabric are about $0,2 \text{ g g}^{-1}$ of activated carbon, for an ethyl acetate concentration of 2000 mg m^{-3} (Fournel, 2000). The adsorption of medium cannot thus explain this salting out of the sulphur compounds.

3.3.3 Participation of sulphates

The results of the analysis of sulphates on the support are deferred in Table 2. During the first 10 days, we can note an increase in the quantity of sulphates caused by biodegradation of sulphur compounds. Indeed, sulphur-oxidizing bacteria likely to develop in the biofilter (*Thiobacillus thioparus*) use, amongst other things, H_2S to form sulphates (Chung *et al.*, 2000). With regard to the reduction in sulphates, it can be correlated with the metabolism of the sulphate-reducing bacteria transforming sulphates into thiosulphates and then into H_2S . In addition, according to Figure 2, we can note that the production of Me-SH is more important than that of H_2S evoked previously. According to Lomans *et al.* (1997), the degradation of lignin and amino acids (constantly present in large quantities in the organic supports) involves the formation of methoxylated aromatic compounds then, of methyl group causing the methylation of H_2S , from where formation of Me-SH.

3.3.4 Ammoniac concentration and biodegradation of sulphur compounds

Figure 2 makes it possible to highlight a correlation between the concentration in the inlet concentration of NH_3 and the production and/or the degradation of H_2S and Me-SH, sulphur compounds concerned. Thus, for important NH_3 concentrations (higher than 30 ppmv), it is easy to see that H_2S and the Me-SH are degraded ($N_i - N_o > 0$). This can be explained by a nitrogen contribution supporting the development of micro-organisms *T thioparus CH11* (Chung *et al.*, 2000). On the contrary, when the NH_3 concentrations are lower than 30 ppmv, the conditions appear unfavourable at their development. One then attends the formation of H_2S and Me-SH which can correspond to the renewal of activity of the sulphate-reducing bacteria as evoked previously.

4 CONCLUSIONS

The originality of this study comes from the use of a support containing mature compost of green waste and urban sludges produces by company R.O.M and consequently, available on factory site. The NH_3 , DMS, DMDS et Et-SH biodegradation is effective (respectively of 94%, 78%, 75% and 100%). However, a quantity of sulphates on this support is reduced in Me-SH and H_2S . We can hope that, day after day, SO_4^{2-} quantity on the packing material decreases. It is thus necessary to plan to make improvements to the packing material (stratification, increase in the quantity of green waste...)

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