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Composition of Aliphatic Hydrocarbons in Tunisian Textile Sludge and Produced Composts as a Function of Sludge Ratio

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Abstract: Aliphatic hydrocarbons are one of the most widespread contaminants in the textile wastes. In the present study, technology of windrow composting was used in order to explore a bioremediation process of these contaminants for a textile sludge restoration in Tunisia. Initially, greenwaste were added in two different proportions to the sludge received from a textile-wastewater treatment plant in the north of Tunisia, mixed thoroughly and the composting process was carried on for 3 months. The thermogenic phase improved the hygiene of the two final products. Samples of sludge and the final composts were extracted with hexane (100%), the extracts were purified on a silica gel and concentrated with evaporation. The gas chromatography analysis of the sludge sample showed the presence of a mixture of aliphatic hydrocarbons, ranging from C18 to C30. The total hydrocarbon content in the sludge was 81 mg kg⁻¹ dry weight, decreased in the 2 final composts and was lower than 27 mg kg⁻¹ dry weight in C1 and C2, respectively. The results revealed a decrease of sludge aliphatic hydrocarbon content after composting. The integration of other analytical and toxicological data is necessary to properly assess the bioremediation efficiency of the sludge composting process.

Key words: Composting, textile sludge, greenwaste, aliphatic hydrocarbons, Gaz Chromatography

INTRODUCTION

Hazardous organic materials are used widely in domestic, municipal, industrial and military activities. Organic contaminants (e.g., polychlorinated biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs)) other than pesticides can enter into the soil from fuel combustion or from sewage sludge and other feedstocks (Moorman *et al.*, 2001). In recent years, the production of physico-chemical sewage sludge has increased sharply in Tunisia due to the expansion of the textile industry and the imposition of more strict environmental laws. At the same time, the upgrading and expansion of textile wastewater treatment plants have greatly increased the volume of sludge generated. In addition, the European Community Landfill Directive (1999) seeks to minimise the quantity of waste going to landfill and to eliminate hazardous waste from landfill. It clearly states that the proportion of biodegradable solid waste disposed of to landfill must be reduced to 75% by 2002, to 50% by 2005 and 25% by 2010. The Directive also defines solid waste as household waste, together with commercial, industrial, institutional and other wastes. The identification and evaluation of biosolid waste contaminants as aliphatic hydrocarbons is based on their intrinsic properties (persistence, toxicity or other noxious properties and tendency to bio-accumulation). Generally, these characteristics are not necessarily of equal importance for the identification and evaluation of a particular or group of

toxicants. After sludge disposal, aliphatic hydrocarbons present in the sludge can contaminate soils and will inhibit seed germination and plant growth, but plants do not appear to accumulate the hydrocarbons (Wei *et al.*, 2005; Chaïneau *et al.*, 1998). In addition, land application of textile sewage sludge has been extensively used as an effective dispersive method throughout Tunisia and we tried in the last years to give more interest to sludge composting to reduce many phytotoxic substances related to the biodegradation of organic matter and pathogenic microorganisms. Composting is defined as the aerobic biological decomposition and stabilization of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to obtain a final product that is stable, free of pathogens and plant seeds (Bertran *et al.*, 2004). Composting is applied in bioremediation as a means of degrading toxic organic compounds and perhaps lessening the toxicity of some contaminants in organic residues, wastes and byproducts. In addition, composting stabilizes wastes for ultimate disposal in traditional manners in landfills or on farmland (Chaney *et al.*, 2000; Stratton and Richcug, 1998) and has many visible advantages including relatively low maintenance costs, simple design and some removal of hydrocarbon pollution (Jiang, 2001). Furthermore, bioremediation by composting become an economically attractive method for cleaning petroleum-contaminated or otherwise hydrocarbon-contaminated sludge (Allen and Gretcheu, 2002). The aim of the present study was to assess the effects of textile sludge aliphatic hydrocarbons content on two mature composts made with different sludge/greenwaste ratios. The knowledge forthcoming from these numerous measurements may allow us to have more consistent evaluation of finished compost qualities.

MATERIALS AND METHODS

A laboratory research was conducted in the Laboratory of Tunis International Center for Environmental Technologies from Mai 2006 to January 2007.

Significance and Impact of the Study

Aliphatic hydrocarbons present in textile sludge can be diminished by composting and the final compost can be resorted in agricultural activities. This work contributes to the developing of low cost and high efficient technology according to Tunisia's conditions for hydrocarbon removal.

Composting and Sampling

The experiment was carried out by mixing sludge from a textile-wastewater treatment plant in Ras Jebel (in the north of Tunisia) with garden waste collected selectively from CITET garden. Two piles were built and contained different volumetric sludge/greenwaste ratios (1:1 v/v volume/volume (pile 1) and 1:3 volume/volume (pile 2) ratios). The well progress of composting and microbial activities were followed by measuring the pile and external temperature during the composting process with a portable thermometer. The composting process of the two piles with different sludge-green waste ratios was monitored for 3 months. The mixture was turned over periodically to ensure aerobic conditions. Numerous samples from various points of the compost heaps were collected and mixed thoroughly. The two selected times of sampling were T = 0 (initial mixture) and after 90 days. The samples were kept deep frozen until analysis.

Compost Parameters

Nitrogen was determined by the Kjeldahl method (Anonymous, 1995), the organic matter by Gravimetry. Total organic carbon is measured according to Colorimetry method (Anonymous, 1998). The C/N ratio was calculated from contents of Total Organic Carbon (TOC) and total nitrogen (Kjeldahl) in air-dried samples. The pH was determined with a glass electrode. The elements Cd, Cu and Cr were analyzed by emission spectrometry-ICP (Anonymous, 1997).

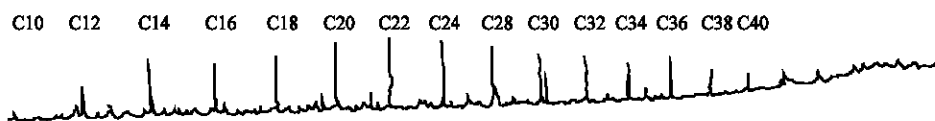


Fig. 1: Gas chromatographic profiles of the external standards

Hydrocarbons Extraction

A sample of about 20 g of compost and sludge were used. Hydrocarbons extraction was performed on this amounts of matter with hexane (100%). The organic phases were taken, dried on Na_2SO_4 , concentrated and purified on a silica catridge. Hydrocarbon were determined and quantified by Gas Chromatography.

GC Analysis

Individual hydrocarbons were analysed by Perkin Elmer series gas chromatograph. The column used for analysis was a HP-5 type (30 mL, 0.25 mm I.D., 320 μm film thickness). As carrier gas, high-grade helium was used at a flow rate of 1 mL min^{-1} . For hydrocarbon analysis, the oven temperature was increased from 50 to 300°C over a 20 min run time. The injection volume was 1 μL . Samples were analysed for GC profiles. The hydrocarbon concentrations were calculated by comparing the peak areas of samples with external standard (Fig. 1).

RESULTS AND DISCUSSION

The presented data is obtained from hydrocarbon extraction of sludge and compost samples at $T = 0$ and after 90 days of composting. The Table 1 presented the different physical and chemical features of the mixtures during the composting process. Table 2 shows the results of the experiment obtained by applying the gas chromatographic method and give the final concentrations of aliphatic hydrocarbons in the sludge and the different compost samples. In addition, the chromatograms gave qualitative information on the composition of the hydrocarbons in the sludge and compost samples. Some of the peaks seen in the sludge chromatogram were originating from aliphatic hydrocarbons and they disappeared with most of the other peaks in the compost chromatograms. In the initial sludge, the alkanes detected are in the range of C18-C30 (Fig. 2) and the most important alkane was C18. In addition, the peak of C18 was taller than those of C22, C28 and C30.

In the study of Wei *et al.* (2005), the alkanes in the range of C13-C29 were found to be major compounds in the initial sludge and the C18 was the most represented. In our study, the highest hydrocarbon ratio in the sludge was for the C18 and the total sludge hydrocarbon content was 81 mg kg^{-1} DW.

On the other hand, the GC data of the different compost samples showed an enhanced decrease of total hydrocarbon content compared to the sludge. The results of the analysis showed that hydrocarbons were not significant presence in the compost mixture at $T = 0$ in the two piles (Fig. 3). These differences may be due to mixing and subsequent dilution with greenwastes (Harrison *et al.*, 2006).

Comparing these results with study previously carried out by (Righetti *et al.*, 2003), their results showed that some aliphatic hydrocarbons were present in the initial mixture. In the final composts, the contents of these hydrocarbons groups increased to 26 and 24 mg kg^{-1} DW for the final composts 1 and 2, respectively (Fig. 4). It have been noted in other studies that the degradation of hydrocarbons is mainly of aerobic in nature (Filauro *et al.*, 1998; Tamburini, 1997) and that some hydrocarbon homologues have been shown to be inhibitory to the majority of hydrocarbon degraders and tend to

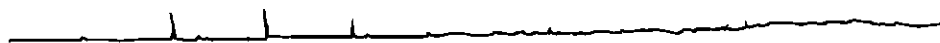


Fig. 2: Gas chromatographic profile of the hydrocarbons extracted from the textile sludge

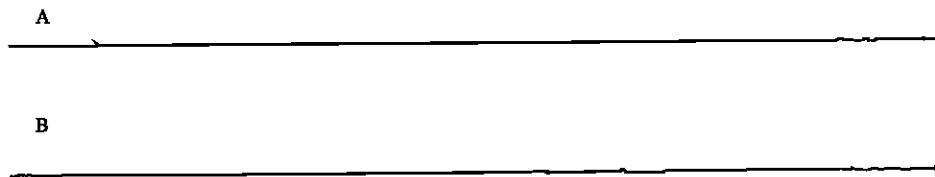


Fig. 3: Gas chromatographic profiles of the Hydrocarbons extracted from the initial mixtures (T = 0)
A: Initial mixture (pile 1) and B : Initial mixture (pile 2)

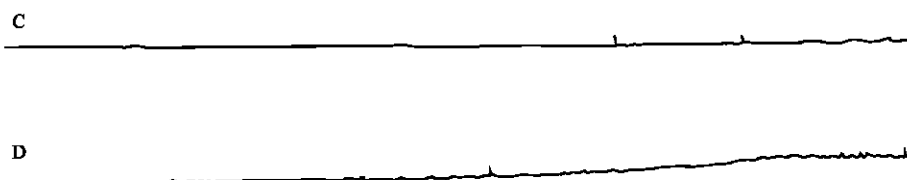


Fig. 4: Gas chromatographic profiles of the Hydrocarbons extracted from the mature composts,
C: Final compost (pile 1) and D: Final compost (Pile 2)

Table 1: Evolution of physico-chemical parameters during composting

Parameters	Pile 1		Pile 2	
	T = 0	Mature compost	T = 0	Mature compost
pH	8.40	7.58	8.1	7.50
C org ^a	285.00	179.00	265.8	166.00
TKN ^{ab}	21.80	14.20	22.7	11.30
DM ^c	33.80	80.00	43.2	70.70
OM ^a	599.00	344.00	763.0	364.00
C/N	13.07	12.60	11.7	14.69
<i>E. coli</i>	>1.1×10 ⁶	7.5×10 ³	2.4×10 ⁵	9.3×10 ²

^a: Results expressed in g kg⁻¹ of dry matter, ^b: TKN: total Kjeldahl nitrogen, ^c: Results expressed in (%) dry weight

Table 2: Hydrocarbon contents in the sludge and during composting (results expressed in mg kg⁻¹ of dry matter)

Materials	Hydrocarbon content
Sludge	81
Pile 1	
First mixture (T = 0)	<0.22
Mature compost	26
Pile 2	
First mixture (T = 0)	<0.22
Mature compost	24

destroy lipid membrane structures of Microorganismes as alkanes in C5-C10 and C20-C40 ranges (Okoh, 2006). Additionally, these homologues contents can rise above those observed in previous weeks due to the concentrating effect caused by the weight loss (Sanchez-Mondero *et al.*, 2001). In this study, the removal rate of the total aliphatic hydrocarbons present in the initial sludge after composting was 67.9 and 70.37%, respectively in C1 and C2. A net drop was observed; this means

that the level of hydrocarbon contamination in the sludge is brought down to low levels and this means that there would not be an hydrocarbon problem in our case when the textile sludge mixed in a composting field. In other studies, the total hydrocarbon removal rate were from 50 and 90% (Dott *et al.*, 1989). Filauro *et al.* (1998) reported 48% degradation of the initial total hydrocarbon concentration in the case of biopiles with wood chips as bulking agent (Tamburini, 1997) experiments showed a more effective degradation of 80%. Altogether, application of compost at agronomic rates should not deliver high amounts of these compounds to cause phytotoxicity and subsequent hydrocarbon application to land has been suggested to generate problems of phytotoxicity (Chaîneau *et al.*, 1998). Generally, users must allow sufficient lead time in the case of hydrocarbon contamination between applications of composts to land and planting of crops to avoid phytotoxicity (biological degradation in the soil generally alleviates any potential toxicity of compounds generated during composting), but this research provides a treatment option that allows textile sewage sludge to be directly used as a soil fertilizer. From an agricultural point of view, the results obtained in this study may contribute to the prevention of hydrocarbon environmental damage, although they cannot be extrapolated directly for making predictions about other contaminants behaviour in the soil.

CONCLUSIONS

The composting of textile sewage sludge with green waste under a Mediterranean climate reached maturity after 90 days. The analysis carried out on samples of compost which were taken from two piles with different sludge-green waste ratios after the end of the process showed that the contents of hydrocarbons were largely lower than the initial contents of the sludge. This means that it is possible to dispose of the aliphatic hydrocarbons by using composting and that the process produced a very sufficient reduction of hydrocarbons of mineral origin. Furthermore, composting the textile sludge with green matter at about 1/2 of the initial volume becomes a possible method for its disposal without hydrocarbon environmental damage.

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