

Full-Scale Co-Composting of Hair Wastes from the Leather Manufacturing Industry and Sewage Sludge

Raquel Barrena^a, Estel·la Pagans^{a,b}, Felícitas Vázquez^{a,b}, Adriana Artola^{a,c} and
Antoni Sánchez^{a,c,*}

^aEscola Universitària Politècnica del Medi Ambient

Universitat Autònoma de Barcelona

Rbla Pompeu Fabra 1, 08100-Mollet del Vallès (Barcelona, Spain)

Present address:

^bGIRO Centre Tecnològic

Rbla. Pompeu Fabra 1, 08100-Mollet del Vallès (Barcelona, Spain)

^cDepartament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria, Universitat

Autònoma de Barcelona,

08193 Cerdanyola del Vallès, Barcelona, Spain.

*Corresponding Author: Dr. Antoni Sánchez

FAX: (34) 93 5812013

E-mail: antoni.sanchez@uab.es

Abstract

A full-scale co-composting experiment using hair wastes from the leather manufacturing industry and sewage sludge as co-substrates was carried out with the aim of producing compost that may be used as an organic amendment in agriculture. A 1:1 weight ratio of hair wastes and sewage sludge was used based on experiments at smaller scale. The resulting mixture was then amended with pruning wastes acting as bulking agent in a 1:1 volumetric ratio (mixture:pruning wastes). The experiment was carried out using the windrow composting technology with a weekly turning frequency. Thermophilic range of temperature was quickly achieved and maintained for more than 8 weeks. This fact ensured the sanitation of the compost according to international requirements. Additionally, the quality of the product obtained expressed in stability terms was very high (Self-heating test grade: V; respiration index: 0.83 mg O₂ per gram of organic matter per hour). The nitrogen content in the final product was also high (5.6%, dry basis). In conclusion, the recycling of hair wastes produced in the leather manufacturing industry using the composting technology is feasible and a valuable organic fertilizer may be obtained.

Introduction

The leather and hide industry in Spain plays an important role in the economy of the country. Spain is the European leader in the tanning sector with a production of 27,473 m² of cattle/calf and 16,742 m² of goat/sheep in 2003, representing more than 15% of the total European Union production (Euroleather 2005). The region with the highest tanning activity is located in Catalonia (northeast of Spain) near the city of Igualada, where an important sector is dedicated to the manufacturing of leather from cow hide (AIIICA 2005).

The tannery industry is responsible for the production of high amounts of wastewater with high levels of pollutants such as COD or Cr. There is abundant literature about the treatment of this wastewater using different technologies, such as physico-chemical treatments (Muruganathan *et al.* 2004; Song *et al.* 2004) or biological treatments (Boshoff *et al.* 2004; Farabegoli *et al.* 2004). However, to our knowledge, there are only few studies on the specific treatment of the solid wastes generated in the tannery sector, such as chrome shavings (Cabeza *et al.* 1998) or unhairing wastes. They are usually considered and treated as wastewater (Vidal *et al.* 2004).

Land application for the disposal of tannery and other leather wastes has been widely practiced, but few landfill sites willing to accept them can be found nowadays and the cost of transportation and disposal increases. From a practical, economical and environmental point of view, recycling of solid wastes from the tannery industry seems the most sustainable way to manage these materials.

These wastes are characterized by their high content of organic matter and nitrogen. Therefore, composting may be the technology of choice for the transformation of tannery solid wastes into a compost material with a high agronomical value, specially in the case of unhairing wastes, where the concentration of heavy metals is low (AIIICA 2005). Composting is a biotechnological process by which different microbial communities degrade organic matter into simpler nutrients. It is an aerobic process, which requires oxygen for microbial biodegradation, and optimal moisture and porosity. Temperature, oxygen and moisture content are often selected as the control variables in the composting process (Haug 1993). Moreover, the possibility of using a material produced by composting as an organic amendment depends on the quality of the product in relation to its nutrients content (Wong *et al.* 1999) and its maturity and stability (Wang *et al.* 2004).

The aim of this work is then to present the composting process as an alternative management technology for the treatment of hair wastes of the tannery industry generated in the leather production. Sewage sludge is selected as a complementary waste to carry out the co-composting process. Technical aspects related to the sanitation of the compost and the quality and characteristics of the final product are also discussed.

Materials and methods

Composted materials

Pre-hydrolysed hair from the leather manufacturing industry was obtained from the company *Igualadina de Depuració i Recuperació S.L.* (Igualada, Spain), which is in charge of the management of wastewater and solid waste generated in the leather manufacturing industry of the area. Briefly, hair wastes are produced when cow hide is treated sequentially for a total period of 24 hours with: 1) calcium hydroxide (1.3%) and sodium hydroxide (0.3%), 2) sodium hydrosulfide (0.4%) in alkaline conditions (pH 13) and 3) sodium sulfide (0.7%) under alkaline conditions (pH 13). After this treatment, pre-hydrolysed hair is separated from the hide and then collected by filtration. Digested sewage sludge was obtained from the wastewater treatment plant of Cambrils (Spain), which is usually processed at the composting plant of Jorba (Barcelona). Pruning wastes from the vicinity of Igualada (Spain) were used as bulking agent, since this is the typical bulking agent used in the composting plant of Jorba. Table 1 shows the main characteristics of the wastes composted.

Preliminary composting experiments

Laboratory-scale experiments were done using 4.5 L Dewar® vessels conditioned for static composting and in a 100 L static composter. A detailed description of these composters can be found elsewhere (Gea *et al.* 2005). In these reactors hair waste was composted on its own, mixed with pruning wastes in a 1:1 volumetric

ratio, and in a tertiary mixture prepared as follows: sewage sludge and hair waste were mixed first (1:1, 1:2 and 1:4 hair:sludge weight ratios were assayed) and combined then with pruning wastes in a 1:1 volumetric ratio..

Co-composting experiment at field scale

Composting was carried out at the composting plant of Jorba (Spain). A composting pile was built by mixing 10 t of hair wastes and 10 t of sewage sludge. This mixture was then blended with shredded pruning wastes in a 1:1 volumetric ratio. The pile was built on a sloped concrete floor and left in the open. It was covered from rain according to the normal operation of the plant. Approximate dimensions of the pile were: base: 2 m; height: 1.5 m; length: 10 m, in a trapezoidal shape. The composting experiment lasted from the 30th November of 2004 to the 16th February of 2005 (80 days). The pile was turned weekly using a Backhus Model 15.50 turner. Water was added to the pile on days 44 and 58 to ensure moisture content above 40%.

Pile core temperature and oxygen content were measured *in situ* at 100 cm depth in 4 points of the pile. Temperature and oxygen values are presented as average values with the standard deviation value as error bar. Temperature was measured with a portable Pt-100 sensor (Delta Ohm HD9214) and oxygen concentration was measured with a portable O₂ detector (Oxy-ToxiRAE, RAE) connected to a portable aspiration pump.

Respiration tests

Static respiration indices were determined using a previously described respirometer (Barrena *et al.* 2005). This respirometer was built according to a model previously described (Iannotti *et al.* 1993) and following the modifications and recommendations given by the U.S. Department of Agriculture and U.S. Composting Council (U.S. Department of Agriculture and U.S. Composting Council 2001). Results of the static respiration index (RI) measured at 37°C of different integrated samples are presented as an average of three replicates. The standard deviation value is also presented.

FAS measurements

Free Air Space (FAS) was measured on an integrated sample using an air pycnometer based on the works of McCartney and Chen (2001) and Agnew *et al.* (2003).

Analytical Methods

Moisture content, dry matter content, organic matter content, pH, electrical conductivity, Kjeldahl nitrogen, ammonium nitrogen (N-NH_4^+), C/N ratio and Rottegrade self-heating test were determined according to the standard procedures (U.S. Department of Agriculture and U.S. Composting Council 2001). These parameters were analyzed in the laboratory after extracting a representative solid sample of the pile. For this purpose, 4 equidistant points of the pile (two for each side of the pile at a medium height of the pile) were sampled extracting about 5 L of compost at each point. The total volume of sample (about 20 L) was

manually mixed and a final volume of 2 L (1 kg) was used to carry out the analytical procedures. An aliquot of this solid sample (250 mL, 100-150 g) was also used for the determination of the respiration index.

Results and discussion

Waste characteristics, initial mixture and preliminary composting experiments

Characteristics of the hair waste (Table 1) indicate that it may be effectively composted (Haug 1993). Particularly important are the high nitrogen content (12.1%), and the low C/N ratio (approximately 3). High nitrogen content may permit to obtain a valuable organic fertilizer. Based on these characteristics, composting was carried out at laboratory scale. However, results of experiments using hydrolysed hair alone and mixed only with pruning wastes were not satisfactory since the thermophilic range of temperatures was not reached indicating thus very low microbial activity. This was probably because the chemical treatment used for the hydrolysis of hair destroyed most of the microorganisms present in the material. Consequently, it was decided to look for a material that could act both as co-substrate and as inoculum for the degradation of the hair waste. Sewage sludge was thus chosen as complementary substrate on the basis of its characteristics, shown in Table 1, and also because it is a material easily available in most of the composting plants and contains a high amount and diversity of microbial flora. Composting experiments of hair waste mixed with sewage sludge and pruning wastes at the different weight ratios assayed indicated that they can

be effectively composted regardless of the weight ratio. Good and similar compostabilities were found for all mixtures at both scales. Therefore, mixture with higher proportion of hair was chosen for the large scale experiments.

Characteristics of the composting mixture used for large scale experiments are presented in Table 1. As it can be seen, properties of the mixture seem to be optimal for composting, including a higher respiration index ($5.09 \text{ mg O}_2 \text{ g}^{-1} \text{ organic matter h}^{-1}$) than that of hydrolysed hair alone.

Field scale composting

Evolution of temperature and interstitial oxygen

Temperature profile of the composting pile is shown in Figure 1a. From this Figure it can be observed that temperature was high throughout the experiment, even when ambient temperatures were below $0 \text{ }^\circ\text{C}$, and also that temperatures over 55°C were obtained for more than 70 days. As pile turnings were carried out once a week, it may be concluded that the material in its totality was exposed to temperatures in the thermophilic range. According to this, it can be said that this material meets the international requirements on compost sanitation, which are based on time-temperature conditions (U.S. Environmental Protection Agency 1995; European Commission 2001).

Oxygen content in interstitial air was low during the composting period (Figure 1a). Nevertheless, no offensive odours typically associated to the presence of anaerobic conditions were detected. Low oxygen content can be attributed to the high activity of the material which results in a high oxygen consumption (Gea *et*

al. 2004). Moreover, it is clear that when temperature decreased at the end of the experiment (from day 70) oxygen level increased, both factors indicating a low biological activity due to the progressive diminution and exhaustion of biodegradable organic matter. Temperature rise and oxygen content clearly show the suitability of using sewage sludge as inoculum in the process of composting of hydrolysed hair. In fact, a number of studies on co-composting of wastes of complementary characteristics can be found in literature, although they are usually focused on adjusting some chemical properties such as moisture or C/N ratio (Tiquia and Tam 2000; Huang *et al.* 2004; Meunchang *et al.* 2005); however, few studies are found on the use of such wastes as inoculum in the composting process.

Chemical parameters

Monitoring of moisture and total organic matter content along the process are presented in Figure 1b. Moisture followed the typical profile of a composting process, with a sharp decrease in the first weeks and a final stabilization, which coincides with the biological activity profile. Water was added at days 44 and 58 to ensure a moisture level over 40%, which is often referred as a minimum value (Haug 1993). However, it must be pointed out that water shortage did not result in a significant decrease in the biological activity as it is shown by respiration index (Figure 2).

In reference to total organic matter content, the profile can then be considered typical of an effective composting process at full-scale (Mason *et al.*

2004), with a marked decrease in the first weeks followed by a plateau. The high level of organic matter in the final compost (57.8%, Table 1) is also an indicator of the compost quality.

Stability indices

Respiration index and self-heating test were also determined along the process. Both tests have been extensively used in the composting field to characterize the stability of composts (Iannotti *et al.* 1993; Weppen 2002; Changa *et al.* 2003). Respirometry refers to the aerobic biological activity of the material and it is generally considered that values of respiration index below $1 \text{ mg O}_2 \text{ g organic matter}^{-1} \text{ h}^{-1}$ correspond to stable compost (California Compost Quality Council 2001). Self-heating test also gives information on the stability of a compost sample. It ranges from grade I (fresh material) to grade V (compost completely stable) (U.S. Department of Agriculture and U.S. Composting Council 2001).

Results of the respiration index and self-heating test obtained in the composting experiment are presented in Figure 2. Respiration index of the composting mixture shows an important decrease throughout the process. This agrees with the progressive stabilization of organic matter, confirming the fact that important oxygen consumption takes place in the first stage. At the same time, it is evident that respiration index is a valuable indicator of the biological activity at full-scale, which indicates a significant biodegradation of hair wastes given the initial respiration indices of the composted materials (respiration indices of sewage sludge, hair wastes and initial mixture were 6.68, 3.22 and $5.09 \text{ mg O}_2 \text{ g}^{-1}$ organic

matter h^{-1} respectively, Table 1) and the final value ($0.83 \text{ mg O}_2 \text{ g organic matter}^{-1} \text{ h}^{-1}$). This is of special interest at the end of the composting process (maturation stage). In this period, thermophilic temperatures result from the thermal properties of the compost (low heat transfer rates due to low thermal conductivity) and from the biological activity of the material. Respiration index is sensitive enough as to detect the decline in the biological activity of the material.

Results of self-heating grade (Figure 2) confirm the results obtained for the respiration index. Thus, it took 11 weeks for the composting material to become very stable (grade V), which is a typical time in the windrow composting process (Haug 1993).

Final compost characteristics

Both self-heating test and respiration index of the final compost (Table 1) confirmed that the final compost can be considered stable (grade V and respiration index of $0.83 \text{ mg O}_2 \text{ g organic matter}^{-1} \text{ h}^{-1}$, respectively). This is of special interest for the application of this compost to soil. However, specific plant growth tests would be required to assess the actual agronomical value of the compost. On the other hand, FAS slightly increases during the process to reach a final value of 63.5% (Table 1), whereas pH is relatively steady and electrical conductivity shows a marked trend to increase, as it is usual in composting processes due to organic matter mineralization (Guerra-Rodríguez *et al.* 2003).

In reference to nitrogen conservation, it must be borne in mind that the open windrow process does not allow to perform a nitrogen balance, since losses due to

gas emissions are difficult to account. Nevertheless, contents of Kjeldahl nitrogen and N-NH_4^+ have been determined in some samples (Table 2). Kjeldahl nitrogen showed an important decrease at the beginning of the process (from day 0 to 27) and a progressive stabilization and conservation in the following weeks. In fact, some authors have proposed the use of the nitrogen losses as an indicator of the biological activity of the material, although it implies a loss of the agronomical value of compost (Liao *et al.* 1995). The final nitrogen content can be considered high when compared with compost produced from other wastes, such as organic fraction of municipal solid wastes or sewage sludge (Barrington *et al.* 2002). This is because hair waste has a higher content of nitrogen. This is one of the main indications that composting of hair residue results in a final product with potential agricultural value.

N-NH_4^+ increased considerably during the active stage of the process (from day 27 to 63) to end up in a progressive decrease at the end of the process. Final N-NH_4^+ value can be considered as high (0.5%, Table 2) when compared with typical values for Spanish organic fraction of municipal solid wastes, around 0.1-0.2% (Grau, 2000). This results from the high nitrogen content of the hair waste. Nevertheless, it is probable that a final curing stage of the compost at mesophilic temperature would produce a transformation of N-NH_4^+ to nitrate form via the nitrification process (Shi *et al.* 1999; Sánchez-Monedero *et al.* 2001).

In any case, the nitrogen and organic matter content confers this compost a high agronomical value, which can be properly used to recycle this material from the tannery industry.

Conclusions

From the results obtained, it can be concluded that:

- 1) Hair wastes from the leather manufacturing industry can be successfully composted using sewage sludge as a co-substrate for inoculation. A 1:1 weight ratio mixture of hair wastes and sewage sludge has proven to be an adequate blend for the process when it is mixed with pruning wastes in a 1:1 volumetric ratio to provide the adequate porosity. A measure of porosity in form of FAS appears necessary to carry out composting experiments at full-scale with new mixtures.
- 2) Composting mixture reaches and maintains the thermophilic range of temperature long enough as to fulfil the international requirements on compost sanitation (U.S. Environmental Protection Agency 1995; European Commission 2001).
- 3) The compost obtained has a high nitrogen content and optimal grade of stability, which are key parameters for its utilization as an organic fertilizer. However, plant growth tests are still required to determine the actual agronomic value of the product.
- 4) The composting technology appears as a sustainable and environmentally friendly method to recycle one of the main solid wastes produced in the Spanish tannery industry.

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Tables

TABLE 1: Main characteristics of the wastes composted and of the final product.

Parameter	Sewage sludge	Hydrolysed hair	Mixture*	Final product
Moisture (%)	81.8	62.1	67.7	43.2
Dry Matter (%)	18.2	37.9	32.2	56.8
Organic Matter (% dry basis)	57.7	88.7	76.6	57.8
N-Kjeldhal (% dry basis)	2.5	12.1	8.5	5.6
N-NH ₄ ⁺ (% dry basis)	0.47	1.53	0.77	0.55
C/N ratio	13.0	3.3	5.0	6
pH	8.1	8.8	8.1	8.4
Electrical conductivity (mS/cm)	1.8	2.8	2.7	8.17
Respiration index (mg O ₂ g ⁻¹ organic matter h ⁻¹)	6.68	3.22	5.09	0.83
Free Air Space (%)	42.3	45.3	54.4	63.5
Self-heating test				V

* Mixture includes hydrolysed hair and sewage sludge (weight ratio 1:1) and pruning wastes (volume ratio 1:1 with mixture hydrolysed hair-sewage sludge)

TABLE 2: Kjeldahl nitrogen and N-NH₄⁺ in some samples during the composting experiment.

Day of process	Kjeldahl nitrogen (%, dry basis)	N-NH ₄ ⁺ (%, dry basis)
0	8.5	0.3
27	4.9	1.2
63	5.5	1.4
78	5.6	0.5

Figure Legends

Figure 1: Large scale co-composting of hair waste and sewage sludge with pruning wastes as bulking agent. a) Temperature and interstitial oxygen profiles. b) Moisture and organic matter content during the course of the experiment.

Figure 2: Respiration index and Self-heating test determined during the course of the composting experiment.

Figure 1: Barrena et al.

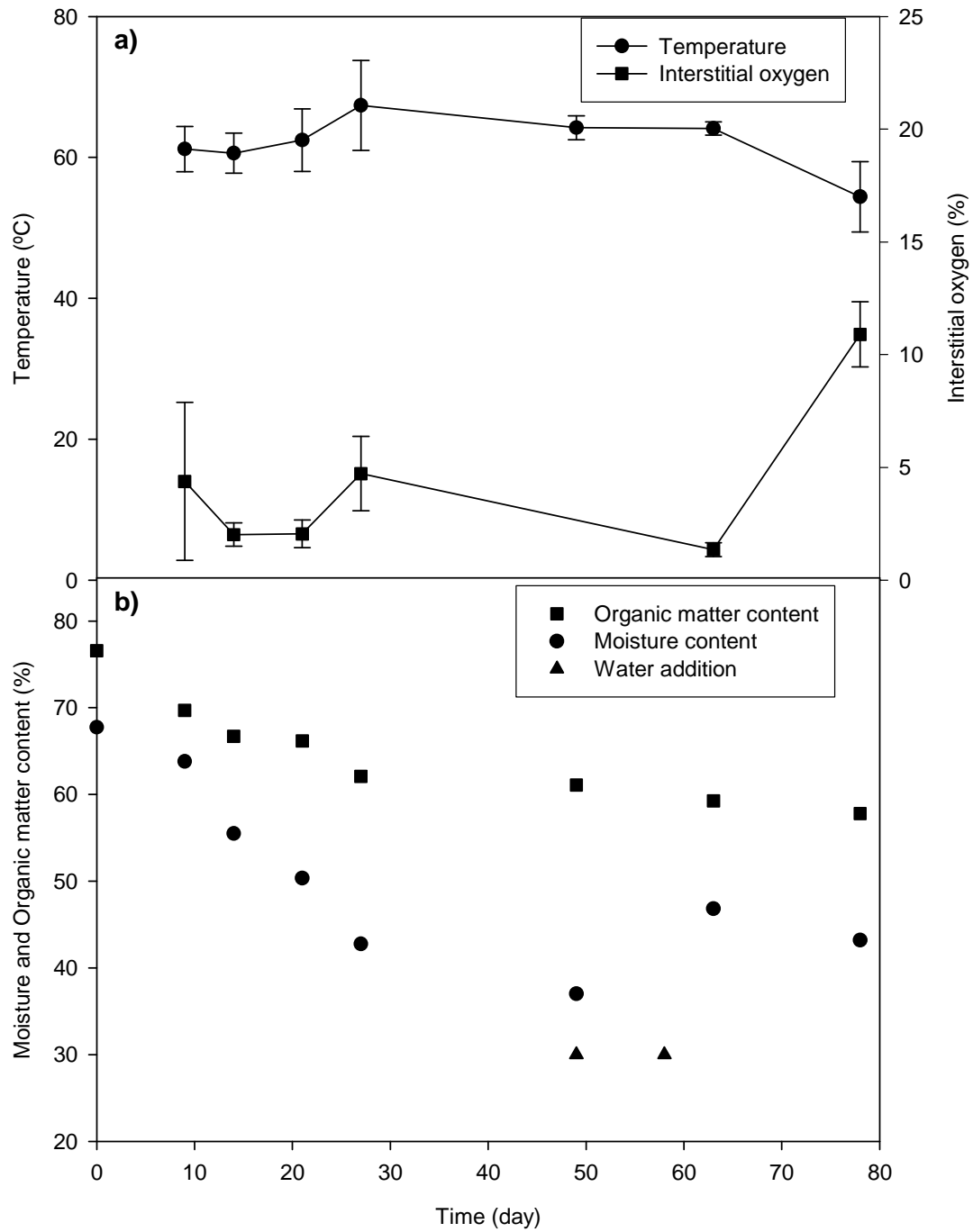


Figure 2: Barrena et al.

