ORIGINAL PAPER

Co-composting of hair waste from the tanning industry with de-inking and municipal wastewater sludges

Raquel Barrena · Estel.la Pagans · Adriana Artola · Felícitas Vázquez · Antoni Sánchez

Received: 12 July 2005 / Accepted: 15 May 2006 / Published online: 5 July 2006 - Springer Science+Business Media B.V. 2006

Abstract Production of waste hair in the leather manufacturing industry is increasing every year due to the adoption of hair-save unhairing techniques, leaving the tanners with the problem of coping with yet another solid by-product. Numerous potential strategies for hair utilisation have been proposed. However, the use of hair waste as agricultural fertiliser is one of its most promising applications due to the high nitrogen content of hair. Agricultural value of hair can be increased by composting. This paper deals with the composting of hair from the unhairing of bovine hide. Results indicated that hair cannot be either composted on its own or co-composted with de-inking sludge, a chemical complementary co-substrate. However, good results were obtained when co-composted with raw sludge from a municipal wastewater treatment plant at hair:raw sludge weight ratios 1:1, 1:2 and, 1:4 in lab scale and pilot plant scale composters. In all cases, a more stable product was achieved at the end of the process. Composting in the pilot plant composter was effectively monitored using Static Respiration Indices determined at process temperature at sampling (SRI_{T}) and at 37°C (SRI₃₇). Notably, SRI_T values were more sensitive to changes in the biological activity. In contrast, Respiratory Quotient (RQ) values were not adequate to follow the development of the process.

Keywords Biological activity indices \cdot C/N ratio \cdot Co-composting \cdot De-inking sludge \cdot Hair waste · Municipal wastewater raw sludge · Unhairing residue

Introduction

Tanning is the process of transforming animal skin to leather. Over the past 30 years global demand for leather and related products has increased by about 55% (Rivela et al. 2004). The leather tanning process is composed of several batch stages associated with the consumption of large amounts of chemicals and fresh water and with the generation of liquid and solid wastes. The unhairing of the hide is one of the most important stages of this process (Vidal et al. 2004). Traditionally, unhairing was done by dissolving the hair, with the consequent high organic pollution of wastewater. With increasingly stringent environmental requirements, it has become

R. Barrena · A. Artola · A. Sánchez Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain

E.la Pagans · F. Vázquez (\boxtimes) GIRO Centre Tecnològic, Rbla. Pompeu Fabra 1, 08100 Mollet del Vallès, Spain e-mail: felicitas.vazquez@irta.es

necessary to reduce the pollution load in wastewater as much as possible. This may be done by treating the wastewater biologically, an expensive undertaking. Moreover, wastewater treatment generates a large amount of sludge, posing disposal problems. For this reason, hair-save practices have taken on renewed importance and nowadays they are a well established practice (Rivela et al. 2004). When these methods are applied, hair can be recovered. One of the most promising possibilities for utilising this hair seems to be as a soil additive due to its high organic matter and nitrogen content.

Among the available technologies to treat organic wastes, composting is one of the most promising options to recycle organic materials into a valuable organic fertiliser, the compost. Composting is a biotechnological process by which different microbial communities decompose organic matter into simpler nutrients and, in a second stage, complex organic macromolecules such as humic acids are formed (Hsu and Lo 1999). Composting is an aerobic process which requires oxygen to stabilise organic wastes, optimal moisture and enough free air space (FAS) (Haug 1993). C/N ratio is also important and often used as design criteria (Haug 1993). Temperature plays an important role in the composting process; it is routinely chosen as the control variable because it is an indicator of the biological activity of the material. Composting process is usually carried out within the thermophilic range of temperature permitting the disinfection of the final product (Salter and Cuyler 2003). In addition to temperature, oxygen and moisture content are common control variables in the composting process. Other chemical and biochemical properties are also used but to a lesser extent.

The static respiration index (SRI) has been proposed and studied as an indicator of the biological activity in the composting process (Scaglia et al. 2000; Adani et al. 2003; Gea et al. 2004). SRI is generally determined off-line and without continuous aeration at 37° C (SRI₃₇) using a respirometric technique and is commonly used to assess compost stability (Ianotti et al. 1993). A wide range of temperatures are involved in the composting process from ambient air temperature at the beginning and the end of the process to temperatures over 65° C during the thermophilic stage. Predominant active microbial populations evolve according to composting process temperature. Thus, if SRI is estimated at process temperature (SRI_T), it can be used as an indicator of the evolution of the biological activity during composting (Barrena et al. 2005).

The respiration quotient (RQ) represents the relationship between $CO₂$ produced and $O₂$ consumed. Values of RQ are related to the biochemical composition of the organic material used as substrate and to the active microbial communities. Due to this dependence it has been routinely used in the biotechnological field (Atkinson and Mavituna 1983) although its calculation and use in composting processes has been scarce (Gea et al. 2004). Given a defined waste, the RQ value in a composting process can be considered steady under different conditions of aeration rate and moisture (Klauss and Papadimitriou 2002; Mönning et al. 2002). However, some differences in RQ values have been found when composting the same waste under different temperature regimes or composting different types of waste (Nakasaki et al. 1985; Gea et al. 2004). The determination of the exact biochemical composition of a significant number of wastes treated through composting is not always possible. This fact makes difficult to theoretically estimate RQ values.

Composting has been traditionally used as a treatment technique for the organic fraction of municipal solid waste, green waste, agricultural and farming residues and surplus sludge from municipal wastewater treatment plants (Sharma et al. 1997). However, its application to high organic matter content wastes is not widespread. This is mainly because very often these materials do not meet requirements such as C/N ratio or porosity, to be successfully composted (Jokela et al. 1997; Wakelin and Forster 1997; Charest and Beauchamp 2002). However, this fact could be overcome by the addition of a complementary substrate in a process called co-composting. Waste hair from the leather industry can be considered as an example of this type of residues. Its main characteristics are a high nitrogen content and high pH. Elevated nitrogen content produces an excessively low value of the C/N ratio to guarantee optimal composting conditions. The optimum C/N ratio should be in the range of 25–30 (Haug 1993). Excessive carbon presence slows the microbial activities (Sharma et al. 1997). Composting at very low C/N ratios that is, under excessive nitrogen, takes place at similar rates compared to optimal C/N ratios; however nitrogen losses through ammonia volatilisation are higher. The high pH value of unhairing residue associated to the rests of chemicals used in the unhairing process should also be taken into account if composting is considered for the treatment of this residue. Composting of residual hair seems to require the presence of a co-substrate for composting and nitrogen conservation. Recent works have been published on the biodegradation of animal wastes using specific microbial populations (Galarza et al. 2004 and Gousterova et al. 2005). Tiquia et al. (2005) obtained a 50% carbon conversion when composting wastes from the poultry industry with high nitrogen content. This indicated the high biodegradability of protein of animal origin under composting conditions. In this work, the authors also proposed the use of specific bacteria for enhancing keratin degradation. However, the addition of bacterial inocula did not improve the rate of composting of the material.

On these bases, the objectives of the present work are: (1) to determine the compostability of hair residues based on previous work on the biodegradability of residues of similar origin; (2) to study the suitability of different residues to be used as co-substrate, (3) to study the differences in the composting process using established control parameters, (4) to follow the evolution of the proposed biological activity parameters, SRI and RQ, during the composting process of this residue and, (5) to determine the extent of nitrogen conservation during the process.

Materials and methods

Composting materials

Hydrolysed hair produced during the hair-save unhairing of bovine hide was obtained from a tannery located in Igualada (Barcelona, Spain). This unhairing process was developed jointly by different European leather industries with the support of the European Union (Project reference ENV 4980764). Briefly, hair wastes are produced when cow hide is treated sequentially for a total period of 24 h 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%) in alkaline conditions (pH 13). Afterwards, hair in a prehydrolysed form is separated from the hide and collected by filtration.

De-inking sludge was collected from a recycled paper manufacturing industry in Spain.

Dewatered raw sludge, composed of primary and activated sludge, was obtained from the municipal wastewater treatment plant in La Garriga (Barcelona, Spain).

Wood chips were used as inert bulking agent. A semi-industrial sieve with a 10 mm mesh (Filtra Vibración) was used for the screening of the chips.

Main characteristics of the residues used in this work are shown in Table 1.

Composting mixtures

Composting mixtures were prepared as follows: hair was first mixed either with de-inking sludge or raw sludge according to the hair:sludge weight ratios 1:1, 1:2 and 1:4. These mixtures were then combined with wood chips in a 1:1 volumetric ratio as suggested by Gea et al. (2003). All mixtures were prepared by hand. These mixtures

were chosen bearing in mind combinations commonly used in composting plants. 1:1 and 1:4 mixtures can be considered as extreme values for co-composting experiments and 1:2 is an intermediate ratio normally used in this type of plants. Resulting C/N ratios were 5.5, 8.1 and, 11.6 for the 1:1, 1:2 and 1:4 mixtures respectively.

Hair was also composted on its own and mixed only with wood chips in a 1:1 volumetric ratio.

Lab scale experiments

Small scale composting experiments were carried out in a 4.5 l Dewar vessel adapted to be used as composter. Inside vessel dimensions were 28 cm height, 15.5 cm maximum diameter and, superficial area:volume (SA:V) ratio of 60. A plastic mesh was fitted at the bottom of the recipient to support the material and three holes were perforated through the lid to allow air inlet and outlet and, the insertion of a temperature probe. Previous experiments have shown that the most reliable parameter to follow the compostability of a mixture at this scale is temperature (Gea et al. 2003). Air supply was made via a tube passing through one of the holes on the lid right to the bottom of the recipient. A Pt-100 sensor (Desin SR-NOH, Desin Instruments, Barcelona Spain) was used for the monitoring of the temperature throughout the process. O_2 concentration in interstitial air was monitored with a portable $O₂$ detector (Oxy-ToxiRAE, RAE) connected to a portable aspiration pump. It was manually fitted to the air inlet three times a day. Air supply was adjusted by hand if oxygen concentration was below 10%. Air flow inlet varied from 0.1 to 0.2 l min⁻¹ kg⁻¹ dry matter.

Pilot scale composter

A 100 l static composter was used for pilot scale experiments. Dimensions of the vessel were length 50 cm, width 40 cm and, height 50 cm. SA:V ratio of the reactor was 14. A diagram of the rig is shown in Fig. 1. The reactor had four Pt-100 sensors (Desin mod. SR-NOH) used for the monitoring of the temperature throughout the process. Temperature in the reactor was taken as the average value from the four sensors. O_2 and $CO₂$ concentration in interstitial air were monitored with an O_2 sensor (Sensox, Sensotran Spain) and an infrared detector (Sensotran I.R., Sensotran Spain), respectively. All sensors were connected to a in-house data acquisition system. Oxygen was controlled by means of a feedback oxygen control system which automatically supplied fresh air to the reactor when oxygen concentration fell below 10%. Composter was placed on a scale (BACSA mod. 1200) for on-line weight monitoring.

Static Respiration Indices (SRI) and Respiration Quotient (RQ) estimation

Static Respiration Indices of composting samples were obtained off-line at process temperature at sampling (SRI_T) and at the fixed value of 37°C (SRI_{37}) , using a static respirometer based on that described by Ianotti et al. (1993) according to the method described by Barrena et al. (2005). SRI is expressed as the amount of oxygen consumed per unit organic matter content of the sample per hour (g O₂kg OM⁻¹ h⁻¹).

Respiration Quotient (RQ) was determined on-line from the O_2 and CO_2 concentrations according to the expression:

$$
RQ = \frac{\% CO_{2out} - \% CO_{2in}}{\% O_{2in} - \% O_{2out}} \tag{1}
$$

where $\%CO_2$ and $\%O_2$ are the respective measured percentage volume concentrations and subscript "in" and "out" correspond to the inlet and outlet concentrations. $CO₂$ _{in} was assumed as negligible and $O_{2 \text{ in }}$ as 20.9%.

Analytical methods

Moisture, dry matter (DM), organic matter (OM), N-Kjeldahl, pH, conductivity and, Dewar self-heating test were determined according to standard procedures (US Department of Agriculture & US Composting Council 2002).

FAS was estimated using an air picnometer built according to Oppenheimer et al. (1997) and Agnew et al. (2003). Air picnometers provide indirect air space measurements by relating the system's pressure and volume using Boyle's Ideal Gas Law. In these systems, a sample is placed in one chamber of known volume while a second chamber is filled with air to a known pressure. The air is allowed to equilibrate between the two chambers and the resulting pressure is used to calculate the air-space volume in the sample (Agnew et al. 2003).

Carbon content estimation

%C was estimated based on the volatile solid content (VS) of the samples and considering that for most biological materials the carbon content is between 45% and 60% of the volatile solid fraction. Assuming 55% (Adams et al. 1951), then:

$$
\% \operatorname{carbon} = \frac{(\% \operatorname{VS})}{1.8} \tag{2}
$$

where

$$
\% \text{VS} = 100 - \% \text{ash} \tag{3}
$$

Results

Lab scale experiments

First experiments were carried out with the aim of determining the feasibility of composting hair waste on the basis of its high organic matter

content, as seen in Table 1. Results indicated that it cannot be composted either on its own or combined only with bulking agent since temperature in the composter did not reach the thermophilic range. This is probably because the strong alkaline conditions that the material had been subjected to during the unhairing process eliminated all microbial flora that the material might contain, i.e. preventing the development of any biological activity.

Because hair residue could not be composted alone, next step was to combine it with other residues in order to find conditions that favour the composting process. Hair residue was thus mixed with de-inking sludge, an industrial residue that had been successfully composted previously (Gea et al. 2005). De-inking sludge consists basically of cellulose and therefore, has a higher C/N ratio than hair residue, as indicated in Table 1. It was considered that a mixture between hair residue and de-inking sludge may balance the nitrogen excess of the former. However, these mixtures could not be composted at any proportion of the two residues used. A possible explanation for this may be that de-inking sludge had either a low microbial population or/and this population was not diverse enough as to be able to grow in an environment such as that provided by the hair residue (Charest et al. 2004). These results point out that for the co-composting of different residues, nutrient balance is not the only requirement that needs to be fulfilled, but an adequate initial microbial population or inoculum is also essential. This is important since co-composting recipes are usually formulated on chemical basis only and the presence of an adequate seed may not be implicit.

Conversely, hair residue could be co-composted when mixed with raw sludge at the different ratios assayed, as shown in Fig. 2. In all cases, temperature evolution curves show the typical behaviour of this type of process, i.e. a rapid increase to temperatures above 60° C at the beginning of the process, followed by a temperature decrease that was related to the amount of hair in the composting mixture. The fastest decrease was observed for the mixture with the highest proportion of hair (1:1), with mesophilic temperatures reached after 4 days of process. On the contrary, temperature of the mixture with the

Fig. 2 Temperature profile during the co-composting of hair waste and raw sludge at three different weight ratios: (a) 1:1, (b) 1:2 and, (c) 1:4 for lab scale experiments

smallest proportion of hair (1:4) was still around 40° C after 9 days of process. Table 2 summarises the main parameters obtained during the monitoring of the process. It can be observed that a highly stable material is obtained for all cases, as indicated by the Respiration Indices after 9 days of process. From these results, it is evident that raw sludge can act as a seed for the composting of hair residues. Other materials such as mature compost or even municipal solid wastes could also be useful for this purpose. The decision of using a specific waste for composting inoculation should be made on the basis of availability and/or operation of the composting plant.

In this study, because of the promising results obtained at this scale for the mixtures with raw sludge, experiments were continued at pilot scale.

Pilot scale composting

Temperature profiles obtained for the different mixtures hair:raw sludge in the 100 l composter are presented in Figs. 3–5. As expected, temperature profiles were similar to those observed at the smaller scale but thermophilic temperatures were kept for 20 days instead of 9, which is a normal behaviour since heat is better conserved at larger scale due to lower SA:V ratio. Besides, a similar pattern can be observed for all composting mixtures: temperature increased rapidly to the thermophilic stage (over 45° C) reaching values over 70° C by day 2. Temperatures were kept around this value for several days and then slowly decreased to reach around 40° C by day 20 for the 1:4 mixture (Fig. 5). A similar behaviour was observed for the 1:2 mixture (Fig. 4) although in this case, a more noticeable decrease in process temperatures was observed. Temperature profile for the 1:1 mixture was also similar to the latter (Fig. 3) however, a slight increase in temperature was observed at the end of the process.

Figures 3–5 also show the different SRI estimated along the process. These indices, indicators of microbial activity, showed that higher activities were developed during the early stages of the process because readily degradable compounds were mainly degraded during this period. As process proceeded, microbial activity declined as indicated by the fall in the respiration indices due to the depletion of readily degradable material. It can be observed that in all cases, SRI followed the same profile as temperature values inside the reactor. However, SRI_T were more sensitive to temperature changes than SRI_{37} . SRI_{37} were significantly lower than SRI_T especially at higher

Parameter	1:1 Mixture		1:2 Mixture		1:4 Mixture	
	Initial	Final	Initial	Final	Initial	Final
Dry matter $(\%)$	42.4	35.4	44.8	38.7	41.8	34.1
Organic matter (% dry basis)	76.5	74.8	72.9	60.5	70.7	67.6
N-Kjeldahl (% dry basis)	5.7	4.4	5.5	4.9	8.2	6.6
$N-Kjeldahl(g)$	4.2	2.6	3.6	2.61	3.6	1.2
Respiration Index * (mg O_2 g OM^{-1} h ⁻¹)		1.10		1.15		1.71

Table 2 Characteristics of the hair:raw sludge co-composting mixtures at the beginning and at the end of the composting process (9 days) in lab scale composter

Corresponds to the Static Respiration Index at 37°C

temperatures, indicating that at this stage SRI_{37} may be underestimating the microbial activity within the reactor. A reason for this could be that at higher temperatures microbial population may be largely thermophilic. If this population is placed at lower temperatures as for the SRI_{37} assay, its activity would then be considerably reduced. As temperature in the reactor decreased, differences between SRI_T and $SRI₃₇$ would be reduced, as shown in Figs. 3–5. Therefore, it can be said that, because of their sensitivity, SRI_T is more appropriate for the monitoring of the composting activity. On the contrary, SRI_{37} should be used only for the estimation of the final compost stability or with mesophilic samples (Gea et al. 2004; Barrena et al. 2006). Figures $3-5$ also indicate that SRI_T cannot be directly calculated from SRI_{37} using an Arrenhius type temperature correlation because other factors such as oxygen transfer limitations and/or microbial community changes (mesophilic/ thermophilic) are also influencing this index. These findings are in agreement with those reported by Barrena et al. (2005).

Figures 3–5 also display RQ obtained for the different composting mixtures. From these figures it can be observed that these values did not show a clear tendency throughout the process for any mixture. This is, the stage of the process, either thermophilic or mesophilic, and mixture composition did not seem to have a direct influence on RQ values. These results agree with those obtained when working with different sludge and organic fraction of municipal solid waste (Gea et al. 2004). This may suggest that composting is a process where catabolic and anabolic reactions take place at the same time and not as a series of sequential reactions. If the latter were the case, higher RQ values should be expected at the beginning of the process, since readily degradable materials such as proteins and glucose and its associated complex compounds have elevated RQ values (Cronjé et al. 2004). As process continued, RQ values would tend to decrease because less oxidised material would be degraded, and also because there would be different microbial communities. However, in our case this behaviour is not observed, probably because the composting process involves the hydrolysis and synthesis of different compounds at the same time. Moreover, RQ values are considerable higher for the mixture with higher hair content. This may be because hair is composed mainly of proteins. Total protein content of the mixture will be then higher and could significantly contribute to the RQ value. However, it should also be borne in mind that many of the estimated RQ values were above 1 thus indicating that in those moments the system could be working under oxygen limitations. Consequently under these conditions RQ estimation would be of no use.

Table 3 shows the main characteristics of the composting mixtures at the beginning and after 20 days of process. As it can be seen, the highest organic matter degradation corresponded to the mixture with the highest initial organic matter content. This degradation agreed with weight reduction that took place during the process. Hair decomposition was also visually observed for all mixtures. Table 3 also shows that pH rose during the process in all cases. This was probably due to ammonia production as a consequence of organic nitrogen ammonification, solubilisation of ammonia led to the formation of ammonium and an increase

Fig. 3 Co-composting of the mixture hair waste:raw sludge 1:1 weight ratio. (a) Average temperature profile (T), Static Respiration Index at process temperature SRI_T and Static Respiration Index at 37° C (SRI₃₇). (b) O₂ concentration, $CO₂$ concentration. (c) Respiratory Quotient (RQ)

in the pH values. No significant differences were found amongst the three mixtures. Conductivity also increased during the process. This increase was more noticeable for the 1:1 mixture. It was probably due to the release of mineral salts such phosphates and ammonium ions through decomposition of organic substrates (Sánchez-Monedero et al. 2001; Venglovsky et al. 2005).

Fig. 4 Co-composting of the mixture hair waste:raw sludge 1:2 weight ratio. (a) Average temperature profile (T), Static Respiration Index at process temperature SRI_T and Static Respiration Index at 37° C (SRI₃₇). (b) O₂ concentration, $CO₂$ concentration. (c) Respiratory Quotient (RQ)

Regarding total nitrogen content of the mixtures, a comparison between the initial and final values, expressed as N-Kjeldahl is shown in Table 3. The values indicate that for all mixtures total nitrogen increased as the process progressed due to the concentrating effect caused by the weight loss associated with mineralisation of organic matter. However, this increase seemed to

Fig. 5 Co-composting of the mixture hair waste:raw sludge 1:4 weight ratio. (a) Average temperature profile (T), Static Respiration Index at process temperature SRI_T and Static Respiration Index at 37° C (SRI₃₇). (b) O₂ concentration, $CO₂$ concentration. (c) Respiratory Quotient (RQ)

be smaller for the 1:1 mixture probably because its higher nitrogen concentration led to higher ammonia volatilisation. Ammonia emissions in the pilot scale experiments ranged from 1,000 to 1,500 mg NH₃ m⁻³ for the 1:1 mixture and from 500 to 1,000 mg NH₃ m⁻³ for the 1:4 mixture. The total contribution of these emissions to nitrogen losses was below 10% according to results recently obtained with wastes with high nitrogen content (Pagans et al. 2006). Moreover, an estimation of nitrogen content indicates that more than 90% of the total nitrogen is conserved for all mixtures. Nitrogen content of the different mixtures was used to estimate their corresponding C/N ratios at the beginning and at the end of the process. As expected, initial C/N ratios can be considered as low, with the smallest value corresponding to the mixture with the highest nitrogen content. However, this ratio did not affect composting kinetics since high temperatures were reached practically at the same time for the three mixtures. After 20 days, C/N ratio was reduced in all cases. Similar results have been reported for the co-composting of other high nitrogen content residues such as fish offal (Laos et al. 2002). Decrease in C/N ratio during composting is considered as optimal (US Department of Agriculture & US Composting Council 2002). In fact, C/N ratio has been proposed as a stability indicator of finished compost (US Department of Agriculture & US Composting Council 2002). However, in order to be a valuable indicator, the initial C/N ratio must be at or near the optimum value of 30, which is not the case of hair:raw sludge mixtures. Nevertheless, C/N ratio results suggest that an important part of the nitrogen contained in the composting material was preserved along the process. These results suggest that final C/N ratio of compost would ultimately depend on the initial C/N ratio of the material. This is particularly important if agricultural use is considered as the final destination of the compost. Nevertheless, it should be kept in mind that there are no data on bioavailability of C and N; although nitrogen availability should be high because of the strong alkaline conditions the hair was subjected to prior to composting.

FAS values estimated for all composting mixtures, were around 60–65%, i.e. remarkably higher than the optimum range (30–35%) reported for the composting process (Haug 1993; Madejón et al. 2002). This did not seem to have a negative impact on the process. Nevertheless, obtained FAS indicated that less bulking agent could have been used. However, if scaling-up of the process was considered, high FAS values would ensure that no compaction of the materials

Parameter	1.1 Mixture		1:2 Mixture		1:4 Mixture	
	Initial	Final	Initial	Final	Initial	Final
Dry matter $(\%)$	42.6	50.7	43	50.4	44.4	50.7
Organic matter (% dry basis)	60.1	48.7	80.2	77.8	82.7	66.1
pH	8.20	8.53	7.66	8.63	7.58	8.60
Conductivity (mS/cm)	3.42	8.29	3.25	5.54	3.16	5.43
N-Kjeldahl (% dry basis)	6.1	6.7	5.5	8.9	4.0	5.1
$N-Kjeldahl$ (kg)	1.19	1.15	0.90	0.96	0.55	0.51
C/N	5.5	4.0	8.1	4.9	11.6	7.2
FAS $(\%)$	60.4		66.5		61.9	
Weight loss $(\%)$		10.8		12.2		20.4
Dewar self-heating test		IV		IV		IV
Respiration index [*] (mg O ₂ g OM ⁻¹ h ⁻¹)	3.22	1.95	2.43	1.28	1.72	1.42

Table 3 Characteristics of the hair:raw sludge co-composting mixtures at the beginning and at the end of the composting process (20 days) in the pilot scale reactor

* Corresponds to the Static Respiration Index at 37C

would take place when processing at larger scale. It must be noticed that there are few studies that relate FAS with the composting process and, most of them deal with typical and well characterised residues. Optimal FAS of other type of residues such as hair waste might be different.

Stabilities of the final products estimated by means of the SRI_{37} obtained at the end of the process are shown in Table 3. According to the literature (California Composting Quality Council 2001), composts with SRI_{37} values between 0.5 and 1.5 mg O_2 g OM^{-1} h⁻¹ can be considered as stable, while $\overline{\text{SRI}_{37}} > 1.5$ mg O_2 g OM^{-1} h⁻¹ corresponds to unstable materials. Therefore, 1:2 and 1:4 hair:raw sludge mixtures were stable, with SRI_{37} values of 1.28 and 1.42 mg O₂ g OM⁻¹ h⁻¹ respectively, while 1:1 hair:raw sludge mixture was moderately unstable $(SRI_{37} 1.95 \text{ mg } O_2 \text{ g})$ OM^{-1} h⁻¹). This last result seems to agree with the slight increase observed in the reactor temperature at the end of the process (Fig. 3), probably resulting from an increase in microbial activity due to the degradation of more complex organic substrates. Results from Dewar Self-Heating Test are also shown in Table 3. According to this method, all mixtures had a maturity grade of IV (in a scale from I to V, where I corresponds to a fresh material and V to a very mature compost), which indicated that they were effectively cured at the end of the process. Therefore, according to the Respiration Indices and Dewar Self-heating test, composts from mixtures 1:2 and 1:4 obtained after processing were stable, while compost from the 1:1 mixture can be considered as reasonably stable. This is of special interest if soil application is considered.

Conclusions

Hair resulting from the unhairing of the hide used for leather manufacturing can be successfully composted if the right conditions are found, as in the case of mixtures with wastewater treatment sludge. Failure in composting of the residue alone or mixed with de-inking sludge demonstrated the importance of having an adequate initial microbial population or inoculum.

Composting activity and hence organic matter decomposition can be monitored using Static Respiration Indices, especially those estimated at process temperature at sampling (SRI_T) throughout a composting process, because they provide information on the real situation of the material and the rate limiting step for biodegradation. Conversely, RQ was not sensitive enough as to be used for process monitoring.

Co-composting of hair:raw sludge mixtures produced stable and cured products with high nitrogen content. These characteristics increase the value of hair waste in agriculture.

Although hair:raw sludge mixtures could be composted at all the different proportions

assayed, more work should be done to optimise the composting mixture, especially in terms of the amount of bulking agent used.

Composting may be considered as a sustainable and environmentally friendly technology for the recycling of a solid residue that is produced in large amounts in the tannery industry in Spain.

Acknowledgments The authors thank the interest of Miquel Vila from Igualadina de Depuració i Recuperació S.L: in the development of this work. The financial support from the Spanish Ministerio de Ciencia y Tecnología (Project REN2003-00823) is also acknowledged.

References

- Adani F, Gigliotti G, Valentini F, Laraia R (2003) Respiration index determination: a comparative study of different methods. Compost Sci Util 11:144–151
- Agnew JM, Leonard JJ, Feddes J, Feng Y (2003) A modified air picnometer for compost air volume and density determination. Can Biosyst Eng 45:6.27–6.35
- Adams, RC, MacLean FS, Dixon JK, Bennett FM, Martin GI, Lough RC (1951) The utilization of organic wastes in N.Z.: second interim report of the interdepartmental committee. New Zealand Engineering November 15:396–424
- Atkinson B, Mavituna F (1983) Biochemical engineering and biotechnology Handbook. Nature Press, NY
- Barrena Gómez R, Vázquez Lima F, Gordillo Bolasell MA, Gea T, Sánchez Ferrer A (2005) Respirometric assays at fixed and process temperatures to monitor composting process. Biores Technol 96:1153–1159
- Barrena Gómez R, Vázquez Lima F, Sánchez Ferrer A (2006) The use of respiration indices in the composting process: a review. Waste Management Res 24:37–47
- California Compost Quality Council (2001) Compost maturity index. URL: http://crra.com/ccqc/ccqchome. htm
- Charest MH, Beauchamp CJ (2002) Composting of deinking paper sludge with poultry manure at three nitrogen levels using mechanical turning: behavior of physico-chemical parameters. Biores Technol 81:7–17
- Charest MH, Antoun H, Beauchamp CJ (2004) Dynamics of water-soluble carbon substances and microbial populations during the composting of de-inking paper sludge. Biores Technol 91:53:67
- Cronje AL, Turner C, Williams AG, Barker AJ, Guy S (2004) The respiration rate of composting pig manure. Compost Sci Util 12:119–129
- Galarza BC, Goya LM, Cantera CS, Garros ML, Reinos HE, López LMI (2004) Fungal biotransformation of bovine hair Part 1: isolation of fungus with keratinolitic activity. partial characterization of crude fungal extracts. J Soc Leather Technologists Chemists 88:93– 98
- Gea T, Barrena R, Artola A, Sanchez A (2004) Monitoring the biological activity of the composting process: Oxygen Uptake Rate (OUR), Respirometric Index (RI), and Respiratory Quotient (RQ). Biotechnol Bioeng 88:520–527
- Gea Leiva T, Artola Casacuberta A, Sánchez Ferrer A (2003) Application of experimental design techniques to the optimization of bench-scale composting conditions of municipal raw sludge. Compost Sci Util11:321–329
- Gea T, Artola A, Sánchez A (2005) Composting of deinking sludge from the recycled paper manufacturing industry. Biores Technol 96:1161–1167
- Gousterova A, Braikova D, Goshev I, Christov P, Tishinov K, Vasileva-Tonkova E, Haertle T, Nedkov P (2005) Degradation of keratin and collagen containing wasted by newly isolated thermoactinomycetes by alkaline hydrolysis. Letters Appl Microbiol 40:335–340
- Haug RT (1993) The practical handbook of compost engineering. Lewis Publishers, Boca Raton, Fl
- Hsu J, Lo S (1999) Chemical and spectroscopic analysis of organic matter transformation during composting of pig manure. Environ Pollut 104:189–196
- Iannotti DA, Pang T, Toth BL, Elwell DL, Keener HM, Hoitink HAJ (1993) A quantitative respirometric method for monitoring compost stability. Compost Sci Util 1:52–65
- Jokela J, Rintala J, Oikari A, Reinikainen O, Mutka K, Nyronen T (1997) Aerobic composting and anaerobic digestion of pulp and paper mill sludges. Water Sci Technol 36:181–188
- Klauss M, Papadimitriou EK (2002) Determining the degree of aerobiosis in composting material. Bioprocessing Solid Waste Sludge 2:37–47
- Laos F, Mazzarino MJ, Walter I, Roselli L, Satti P, Moyano S (2002) Composting of fish offal and biosolids in northwestern Patagonia. Biores Technol 81:179–186
- Madejón E, Díaz MJ, López R, Cabrera F (2002) New approaches to establish optimum moisture content for compostable materials. Biores Technol 85:73–78
- Mönning K, Kuhne M, Bidlingmaier W (2002) Composting of municipal bio-waste: the influence of temperature, $O₂$ and $CO₂$ content and the respiratory quotient in the thermophilic stage. In: Michel FC, Rynk RF, Hoitink HAJ (Eds) Proceedings of the 2002 international symposium composting and compost utilization. JG Press, Emmaus, Pa
- Nakasaki K, Shoda M, Kubota H (1985) Effect of temperature on composting sewage sludge. Appl Environ Microbiol 50:1526–1530
- Oppenheimer J, Martin J, Walker L (1997) Measurements of air-filled porosity in unsaturated organic matrices using a pycnometer. Biores Technol 59:241–247
- Pagans E, Barrena R, Font X, Sánchez A (2006) Ammonia emissions from the composting of different organic wastes. Dependency on process temperature Chemosphere 62:1534–1542
- Rivela B, Moreira MT, Bornhardt C, Méndez R, Feijoo G (2004) Life cycle assessment as a tool for the environmental improvement of the tannery industry in

developing countries. Environ Sci Technol 38:1901– 1909

- Salter C, Cuyler A (2003) Pathogen reduction in food residuals composting. Biocycle 44:42–50
- Scaglia B, Tambone F, Genevini PL, Adani F (2000) Respiration Index determination. Dynamic and static approaches. Compost Sci Util 8:90–98
- Sharma VK, Canditelli M, Fortuna F, Cornacchia G (1997) Processing of urban and agroindustrial residues by aerobic composting: Review. Energy Conversion Manage 38:453–478
- Sánchez-Monedero MA, Roig A, Paredes C, Bernal MP (2001) Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. Biores Technol 78:201–308
- Tiquia SM, Ichida JM, Keener HM, Elwell DL, Burttt EH, Michel FC (2005) Bacterial community profiles on feathers during composting as determined by terminal

restriction fragment length polymorphism analysis of 16S rDNA genes. Appl Microbiol Biotechnol 67:412– 419

- US Department of Agriculture & US Composting Council (2002) Test Methods for the examination of composting and compost (TMECC). Edapho International, Houston, USA
- Venglovsky J, Sasakova N, Vargova M, Pacajova Z, Placha I, Petrovsky M, Harichova D (2005) Evolution of temperature and chemical parameters during composting of the pig slurry solid fraction amended with natural zeolite. Biores Technol 96:181–189
- Vidal G, Nieto J, Cooman K, Gajardo M, Bornhardt C (2004) Unhairing effluents treated by an activated sludge system. J Hazardous Mat B112:143–149
- Wakelin NG, Forster CF (1997) An investigation into microbial removal of fats, oils and greases. Biores Technol 59:37–43