

Characterisation and Composting of Tannery Sludge

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ABSTRACT

Tannery industries create serious environmental problems especially in terms of polluting organic effluent and hazardous solid waste as a result of hides and skin processing. It is very important that tannery waste in the form of sludge is managed in an environmentally sound manner. This study focuses on the characterisation of tannery sludge and its development as a composting material. The results show that electrolytic conductivity (EC) of the compost was 2.0 mS cm⁻¹, pH 6.6 and C/N ratio of 16. Total concentrations of chromium, zinc, copper, lead, and cadmium in dry compost were reduced and complied with the standards of the Canadian limits, thus classifying them excellent for making the compost suitable for use as a fertiliser and soil conditioner. The compost characteristics indicated that it was mature, and the germination index for Chinese cabbage was 82.5 %, which may suggest absence of phytotoxic compounds.

Keywords: Composting, tannery sludge, pathogens, heavy metals, germination

INTRODUCTION

The necessity to preserve natural resources and the optimisation of the use of non-renewable energy has encouraged recycling and recovery of organic waste as an alternative to dumping and incineration (ADEME 1994). Among the organic waste recycled in agriculture, residual sludge generated by wastewater treatment is a source of organic matter rich in both phosphorus and nitrogen. It can contribute to the rehabilitation of degraded soils by its fertilising and other soil-improving qualities. Sludge from leather processing, a major industry that produces up to 600 tons of sludge annually (Kenny Leather Sdn Bhd, Melaka-Malaysia), contains large concentrations of inorganic nitrogen (N) and N-rich organic residues (INE-DGMRAR 1999). Nevertheless, direct agricultural use of tannery sludge is limited by the presence of pathogens, fermentation of any unstable organic matter and the organic and inorganic pollutants it contains (Dudka and Muller 1999). To overcome the risks incurred by the direct use of this waste

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in agriculture, treatment is required to minimise and eliminate the undesirable effects and to optimise the efficiency of the materials once applied to the soil.

The process of tanning consists of the transformation of animal skin to leather. Animal skin (cow, goat, sheep and other animals) is submitted to different processes to eliminate meat, fat and hair in which different chemicals such as sodium hydroxide, sodium hypochlorite, enzymes, lime, chlorides, sulphuric acid, formic acid, ammonium salts, kerosene, and other compounds are used (Semarna 1995). The obtained hide is then treated with Cr^{+3} or tannins, mineral salts and colours to obtain leather.

Composting has long been recognised as one of the most cost effective and environmentally sound alternatives for organic waste recycling. It is considered to be the best pretreatment for overcoming these problems (Ouatmane *et al.* 2000), and the high temperatures reached, 50–70°C, destroy almost all pathogens (Dumontet *et al.* 1999). Numerous bacteria degrade the readily available organic components or transform them into stable humic components (Garcia *et al.* 1992).

A decrease in the content of organic pollutants and a reduction in the bio-availability of metal trace elements during the composting of tannery sludge has also been reported (Lau *et al.* 2003). The success of composting is linked to the quality of final product, especially its stability. Spreading immature or unstable compost can generate serious problems of hygiene and phytotoxicity (Pascual *et al.* 1997).

The reliability of individual indicators for the determination of compost maturity is debatable, so several parameters are often considered together. Numerous researchers (Ouatmane *et al.* 2000; Tomati *et al.* 2000) have suggested the use of different maturity indices (C/N ratio, humification indices, and germination indices).

The objective of this study was to determine some of the physico-chemical characteristics of tannery sludge during its composting. The evolution of compost maturity was assessed from measurement of various types of humification indices.

MATERIALS AND METHODS

Composting Sampling and Preparation of Compost Samples

The tannery sludge used in this study was collected from the Kenny Leather Sdn Bhd in Melaka, Malaysia. The sludge (100kg) was mixed with sawdust (50kg), chicken manure (30kg), beneficial organisms (1 litre), and rice bran (20kg) in a pile 2.5 m long and 1.5 m high in a composting windrow type of production. The mixture was prepared in order to optimise the composting parameters, that is, 60% humidity and a C/N ratio of about 30. Table 1 shows the main chemical characteristics of the raw materials. With the aim of maintaining aerobic conditions during the process, the pile was turned over manually every 10 days.

TABLE 1
Chemical Properties of raw materials used in composting
(results expressed on dry basis)

| Characteristics | Tannery sludge | Sawdust | Chicken manure | Rice bran |
|---------------------------------|----------------|---------|----------------|-----------|
| Moisture | 60.6 | 80.7 | 50.6 | 66.9 |
| pH | 7.36 | 5.9 | 7.93 | 7.2 |
| E.C. (mS cm ⁻¹) | 9 | 15 | 7 | 6 |
| Organic -C (%) | 20.03 | 57 | 30.4 | 49.33 |
| Total nitrogen (%) | 0.9996 | 0.3 | 4 | 1.1 |
| C/ N | 20.022 | 190 | 7.6 | 45.72 |
| Ash | 65 | 80 | 45 | 30 |
| Macronutrients | | | | |
| Potassium (%) | 0.415 | 0.02 | 1.23 | 0.99 |
| Phosphorus (%) | 0.097 | 1.17 | 3.02 | 0.23 |
| Calcium (%) | 7.7 | 0.02 | 1.99 | 0.30 |
| Magnesium (mgkg ⁻¹) | 1190 | 0.004 | 1.05 | 236.33 |
| Sodium (mgkg ⁻¹) | 1006 | 64 | 123 | 98 |
| Heavy metals | | | | |
| Iron (mgkg ⁻¹) | 1062 | 402 | 1738 | 142.33 |
| Chromium (mgkg ⁻¹) | 350 | 14.6 | 16.6 | 6.3 |
| Lead (mgkg ⁻¹) | 15 | 16 | 1.3 | 1.2 |
| Cadmium (mgkg ⁻¹) | 3.23 | 6.5 | 0.5 | 0.2 |
| Copper (mgkg ⁻¹) | 60 | 4.8 | 329.67 | 24.33 |
| Zinc (mgkg ⁻¹) | 180 | 8.2 | 634.67 | 127 |
| Manganese (mgkg ⁻¹) | 70 | 4.6 | 34 | 24 |

E.C. = Electrical conductivity

Temperature was measured daily at a depth of 50 cm at different positions inside the pile. The composting cycle lasted for sixty days. Subsequently, 10 samples were taken systematically, that is, before composting (T_0), and after 20 (T_{20}), 40 (T_{40}) and 60 (T_{60}) days of composting. Each sample was air-dried for a period of ten days. The dried sample was ground down into a fine powder.

Chemical Analysis

A representative sample was taken from the homogenised compost pile for heavy metals and other analyses. Samples (250 g) were taken from 10 different points of the compost heap (bottom, surface, side, and centre) at each stage of composting, that is, 0, 20, 40, and 60 days of composting.

Physico-chemical analyses were conducted on the samples. The pH was determined in a suspension of 10 g sample in 15 mL water. Total organic carbon (TOC) was measured according to the ANNE method (Aubert 1978), while total nitrogen (Kjeldahl method) and inorganic nitrogen were measured by the method of Bremner (1965). Humic carbon extracted by 0.1 M NaOH solution was measured after oxidation by KMnO_4 (Bernal *et al.* 1996). The rate of decom-

position was calculated after ignition of the dry sample at 550°C (16 h). Available P was determined according to Olsen method (Hafidi *et al.* 1994). Exchangeable Ca, Na, K, Mg were determined using ammonium acetate. Total P, Ca, Na, K, Mg, Fe and Mn were determined after ashing. Phosphorus was measured colorimetrically and other elements in the extracts were analysed using atomic absorption and flame photometry (De Souza 1998). Total Cr, Zn, Cu, Pb, and Cd were analyzed by the method of French Association of Normalizations (AFNOR 1993). One gram of each sample was mineralised for 4 h at 550°C, and then dissolved in 5 mL of hydrofluoric acid. The solution obtained was evaporated to dryness and the residue was then dissolved with concentrated HNO₃/HCl (1:1) solution and the acid solution was diluted for analysis.

Germination Index

The germination index was used to determine the inhibitory potential of the compost water extract. Seed germination test was carried out with Chinese cabbage using compost substrate extract. Two g of oven-dried compost was placed in a test tube with screw cap and 20 mL of distilled water was added; the tube was then placed on an electric rotator at 125 rpm for 1 hour. The supernatant was decanted and centrifuged at 10000 rpm for 10 minutes and filtered through Whatman paper. Two mL of filtrate was diluted with one mL of distilled water and sprayed over a sheet of filter paper kept inside the petri dish. Ten seeds of Chinese cabbage were then placed on the filter paper; another filter paper was moistened with 3 mL distilled water and 10 seeds and was used as a control. The percentage of germination was measured after incubating the covered petri dishes in the dark at 28°C for 4 days (Matheur *et al.* 1993).

RESULTS AND DISCUSSION

Characterisation of Tannery Sludge

The results of the chemical characterisation of the sludge are presented in Table 1. The sludge showed that it was low in C/N ratio (20) and high in nitrogen content (0.99). The sludge was rich in organic matter and had a high content of sodium and calcium.

Apart from the plant nutrients, the analysis of the sludge showed that it contained high amounts of trace elements like chromium, cadmium, and lead, all of which have a negative impact on plant growth (Lisk *et al.* 1992). From the above results, it appears that the sludge from the tannery was at an acceptable level according to Canadian limits (CCME 1995), except for chromium and cadmium (Table 2).

The tannery sludge was alkali in nature (pH, 7.36) (Table 1). More than 83% of the sludge had a particle size fraction <50µ. The wet bulk density was close to that of mineral soil but when dry, it was relatively light with a bulk density equal to 0.14g cm⁻³ (Table 3).

TABLE 2
Total heavy metal contents in the final compost (60 day) and allowable limit for different class compost according to Canadian limit (CCME 1995) (results expressed in dry basis)

| Heavy metal | Raw Tannery Sludge (mgkg ⁻¹) | Final mature compost content (mgkg ⁻¹) | Allowable limit (mgkg ⁻¹ dry wt) Class A | Allowable limit (mgkg ⁻¹ drywt) Class B |
|-------------|--|--|---|--|
| Cr | 350 | 100 | 210 | 1060 |
| Zn | 180 | 148 | 500 | 1850 |
| Cu | 60 | 54 | 100 | 757 |
| Pb | 15 | 2.2 | 150 | 500 |
| Cd | 3.23 | 1.6 | 3 | 20 |

Class A compost (which have no restrictions in use).

Class B Compost (which can be used on forest lands and roadsides and for other landscaping purposes).

TABLE 3
Physical properties of the tannery sludge

| Parameters | Sludge | Typical tropical soil * |
|------------------|--------|-------------------------|
| Bulk density | 0.140 | 1.3 |
| Total pore space | 94.72 | - |
| Available water | 8.93 | 5.3 |

Water retention at pressure (Kpa) (%w/w, dry basis):

| | | |
|------|--------|-------|
| 0 | 153.41 | 33.40 |
| 1 | 117.5 | 32.20 |
| 10 | 89.50 | 22.80 |
| 33 | 78.50 | 21.20 |
| 1500 | 69.57 | 15.90 |

* Mokhtaruddin *et al.* (2001)

Characterisation of Compost

The main physico-chemical properties of the composting mixtures at different times of the process are presented in Table 4. The pH values were within the optimal range for the development of bacteria 6–7.5 and fungi 5.5–8.0 (Zorpas *et al.* 2003). Two phases of the composting process were recorded: a phase of stabilisation (about 30 day), where temperature peaked at 64°C after 30 days of processing and pH was slightly increased (7.5); a phase of maturation (about 30 days), characterised by a temperature plateau at 35°C and slight acidification of the medium (6.6). The change in the C/N ratio from 23 to 16 and the amount of ash reflect microbial decomposition of organic matter and stabilisation during composting.

TABLE 4
Physico-chemical properties of composting mixture at different times
(results expressed in dry basis)

| Properties | Day 0 | Day 20 | Day 40 | Day 60 |
|---|-------|--------|--------|--------|
| Moisture | 58.4 | 68.6 | 64.1 | 60.1 |
| pH | 7.3 | 7.50 | 6.9 | 6.6 |
| E.C. (mS cm ⁻¹) | 2.0 | 1.5 | 1.7 | 2.0 |
| TOC % | 19.6 | 17.2 | 6.0 | 14.8 |
| OM % | 33.8 | 27.6 | 23.6 | 19.8 |
| Total nitrogen (%) | 0.80 | 0.90 | 0.92 | 0.95 |
| Ash (%) | 63 | 75 | 83 | 88 |
| C/N | 23 | 19.11 | 17.4 | 16 |
| HS | 19.3 | 20.6 | 23.5 | 26.5 |
| NH ₄ -N(mgkg ⁻¹) | 3.7 | 2.8 | 2.0 | 1.4 |
| NO ₃ -N(mgkg ⁻¹) | 3.4 | 2.6 | 1.5 | 1.5 |
| N-org. (mgkg ⁻¹) | 5.4 | 6.1 | 6.8 | 8.2 |
| P total (mgkg ⁻¹) | 7.5 | 5.9 | 5.0 | 3.9 |
| P available (mgkg ⁻¹) | 4.2 | 3.2 | 2.6 | 1.9 |
| Ca total (mgkg ⁻¹) | 720 | 530 | 300 | 150 |
| Ca exchangeable (mgkg ⁻¹) | 105 | 70 | 59 | 45 |
| K total (mgkg ⁻¹) | 38 | 18 | 12 | 8 |
| K available (mgkg ⁻¹) | 12 | 8 | 5.2 | 2.5 |
| Na total (mgkg ⁻¹) | 980 | 540 | 290 | 140 |
| Na available (mgkg ⁻¹) | 250 | 120 | 80 | 50 |
| Mg total (mgkg ⁻¹) | 990 | 530 | 310 | 130 |
| Mg available (mgkg ⁻¹) | 100 | 60 | 30 | 10 |
| Mn (mgkg ⁻¹) | 85 | 76 | 50 | 60 |
| Fe (mgkg ⁻¹) | 1200 | 2876 | 3850 | 5674 |

OM= Organic Matter, HS= Humic Substances

The increase in total nitrogen during composting was caused by the decrease in substrate carbon resulting from the loss of CO₂ (Soumare *et al.* 2002; Zorpas *et al.* 2003). Inorganic nitrogen, N-NH₄ and N-NO₃ are usually affected by the action of proteolytic bacteria and partly incorporated into stable organic forms such as amide and heterocyclic nitrogen. Organic matter is decomposed and transformed to stable humic compounds (Amir *et al.* 2004, in press). Humic substances (HS) have a capacity to interact with metal ions, and the ability to buffer pH and to act as a potential source of nutrients for plants. Electrical conductivity in a water extract of final product did not exceed the salinity limit value of 3 mS cm⁻¹ to be used in good fertilisers (Soumare *et al.* 2003). Available and total P, Ca, K, Mg, Na as well Fe and Mn were more important for use in this material as mineral fertilisers (Soumare *et al.* 2003). Therefore, application of this material will increase the stable organic N and humic carbon and improve mineral elements necessary for plant growth.

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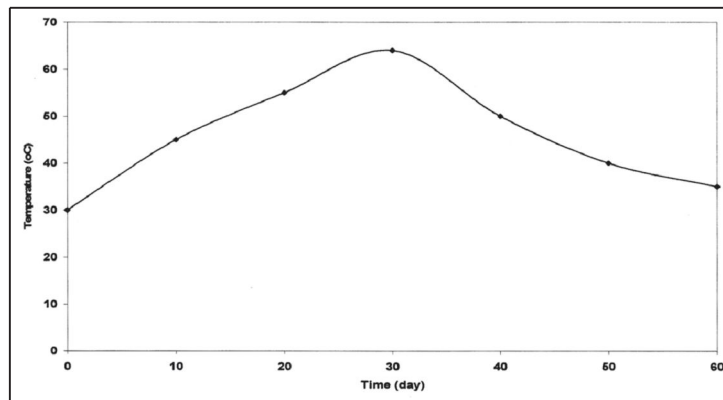


Fig. 1: Temperature profile throughout the composting process

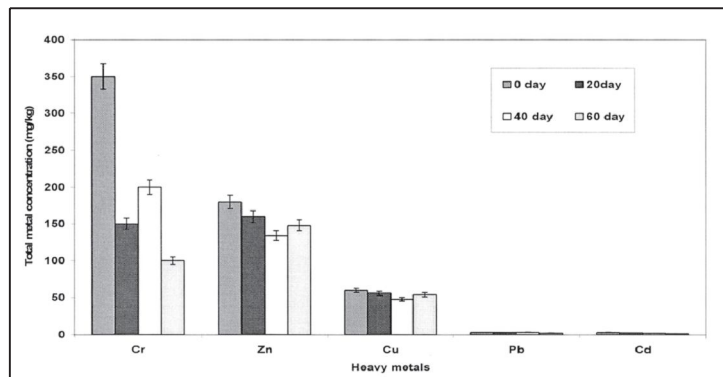


Fig. 2: Total amount of heavy metals during composting of tannery sludge

Fig. 1 shows the temperature profile with time for compost development. It was characterised by increasing the temperature up to 64°C, and then decreasing it to 35°C, which indicated the end of the composting process. It was found that tannery sludge compost was able to reach high thermophilic temperatures due to its high content of nutrients from organic materials (Mays and Giordano 1989). To maintain a high temperature within the windrow, the compost heap should be large enough to allow heat generated by metabolic processes to exceed the heat loss at the exposed surfaces (Eweis *et al.* 1998).

Heavy Metals Content of Compost

Composting can concentrate or dilute heavy metals present in tannery sludge (Zorpas *et al.* 2003). Lowering the amounts of heavy metal depends on metal loss through leaching. The increase in metal level is due to weight loss in the course of composting following organic matter decomposition, release of carbon dioxide and water and the mineralisation processes (Canarutto *et al.* 1991).

Fig. 2 shows the total concentration of metals (Cr, Zn, Cu, Pb, Cd) during composting. The order of total metal content in the final composted sludge was

Zn > Cr > Cu > Pb > Cd. During composting, all total metal content decreased. This could be explained by metal loss through leaching in the course of composting. This loss mainly occurred during the thermophilic phase which could be related to metal release from decomposed organic matter, an increase in moisture from 58.4 to 73.5%, and change of other oxidic and anionic conditions in the medium increasing so too the solubility of metals (Hsu and Lo 2001; Soumare *et al.* 2003; Zorpas *et al.* 2003). Although some researchers suggest that when the potential toxic metal concentrations of compost are high, the leachability of metal associated with compost is of concern (Hsu and Lo 2001).

The determination of the total content of heavy metals in the tannery sludge compost showed values significantly lower than those of compost authorised for agricultural use as determined by the Canadian limits, thus classifying them as excellent (CCME 1995)(Table 2). However, knowledge of the total content of heavy metals remains insufficient to estimate the mobility risk, and metal bioavailability for plants. The results of the metals analysis on the compost at different stages of composting show that the main part of the metal elements concentrated in the most resistant fractions are either not bioavailable or weakly bioavailable to plants, and only a weak proportion represents the unstable fraction that is easily bioavailable (exchangeable + soluble).

Aqueous compost extracts had a germination index of 82.5 %. A germination index value of above 50% indicates that maturity is sufficient (Zucconi *et al.* 1981; Mathur *et al.* 1993) and phytotoxic compounds such as acetic, propionic, butyric and isobutyric acid might have not been metabolised, inhibiting germination (Epstein 1997).

CONCLUSION

The study concludes that the initial concentrations of chromium, cadmium, lead, copper and zinc decreased as the composting process progressed. The total concentrations of heavy metals in the compost complied with the standards of the Canadian Limits (CCME 1995), making the compost suitable for use as a fertiliser and soil conditioner. The composting process significantly produced stable and mature compost and the germination index of Chinese cabbage significantly encourages the utilisation of the compost.

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