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Analysis of heavy metals during composting of the tannery sludge using physicochemical and spectroscopic techniques

Mahdi Haroun [a,*], Azni Idris [a,1], Syed Omar [b,2]

[a] Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM, Serdang, Malaysia
[b] Department of land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 UPM, Serdang, Malaysia

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ABSTRACT

The major limitation of direct application of tannery sludge compost in agriculture is the total heavy metal contents and their bioavailability to the soil–plant system. This study focused on the heavy metal characterization and the influence of changing the physicochemical properties of the medium throughout the composting on the concentrations, bioavailability or chemical forms of Cr, Cu, Zn, Pb and Cd in tannery sludge. The study shows that throughout the 60 days of composting, physicochemical analysis and Fourier-transformed infrared (FTIR) spectroscopic characterization show that all parameters elaborated and reached relatively stable levels reflecting the stability and maturity of the final product, and revealed the biodegradation of components that can be easily assimilated by microorganism. The C/N ratio reaches the optimal range of stable compost; inorganic nitrogen is transformed into stable organic forms. The total concentration of Cr, Zn, Cu, Pb and Cd is very low rendering final compost acceptable for agricultural use. The germination index for both Chinese cabbage and lettuce was 97% after 60 days of composting, showing that the final compost was not phytotoxic. Furthermore, in using a sequential extraction method in sludge compost at different phases of treatment, a less than 2% of metals bound to bioavailable fractions X–($KNO_3 + H_2O$). A large proportion of the heavy metals were associated to the residual fraction (75–85%) and more resistant fractions to extraction X–NaOH, X–EDTA, X–HNO_3 (15–25%). Mobile fractions of metals are poorly predictable from the total content. Bioavailability of all fractions of elements tends to decrease.

1. Introduction

Concern over environmental toxicology and demand for safe disposal of industrial wastes are the topics of current interest [1,2]. The leather industry is associated with the generation of huge amounts of solid wastes (30–35 l/kg of raw material processed) and thus disposal of these wastes becomes a serious problem [3].

The agricultural utilization of tannery sludge compost implies knowing its degree of stability, as well as its content and bio chemical forms of the heavy metals present. These elements are not biodegradable and become toxic at some concentrations, they tend to accumulate along the food chain where human is the final user [4].

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, sulfuric acid, formic acid, ammonium salts, kerosene, and other compounds are, used [5]. The obtained hide is then treated with Cr^{+3} or tannins, mineral salts and colors to obtain leather.

Many studies have been carried out on the speciation of heavy metals in soils, and soils amended with composted biosolid or raw sludge [6,7]. A number of researcher suggest that the speciation of each metal in the tannery sludge compost depends on its initial chemical state in the tannery, the adsorption and precipitation mechanisms in sludge, and the effect of stabilization of the material and the humification process that occurs during composting on the chemical form of the metal [8].

The determination of total heavy metal content does not provide useful information about the risks of bioavailability, the capacity for remobilization and the behavior of the metals in the environment [9]. While, the chemical forms of a metal or speciation allows the estimation of heavy metal bioavailability and is related to the different natures of the metals, their bonding strength, either in free ionic form or complexed by organic matter, or incorporated in the mineral fraction of the sample.

* Corresponding author. Fax: +60 3 86567120.
E-mail addresses: Mahdiupm@hotmail.com (M. Haroun), Azni@eng.upm.edu.my (A. Idris), syedomar@agri.upm.edu.my (S. Omar).
[1] Fax: +60 3 86567120.
[2] Fax: +60 3 8946 4151.

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Composting which is a biological aerobic decomposition in which labile organic matter is degraded to carbon dioxide (CO_2), water vapour, ammonia (NH_3), inorganic nutrients and stable organic material containing humic-like substances [10], has been updated to process organic wastes of different origin, such as sewage sludge, animal manure, agro-industrial wastes [10].

The treatment by composting leads to the development of microbial populations, which causes numerous physicochemical changes within mixture. These changes could influence the metal distribution through release of heavy metals during organic matter mineralization or the metal solubilization by the decrease of pH, metal biosorption by the microbial biomass or metal complexation with the newly formed humic substances (HS) or other factors [9–11].

Contreras-Ramos et al. [12] study the composting of Tannery effluent with cow manure and wheat straw for 90 days to reduce pathogens and toxic organic compounds and monitored. The compost was characterized by an electrolytic conductivity (EC) of 28.1 mS cm^{-1} and C:N ratio 7:1 with a germination index for cress (*Lepidium sativum*) of 48% after 90 days.

Hsu and Lo [9] show the increase of metal concentrations during composting of swine manure and suggest that the types of composting and raw materials be of major importance to metal condensation.

Ghaedi et al. [13] report a method for preconcentration of trace elements, viz., Co, Ni, Cu, and Pb on a activated carbon modified with 4,6-dihydroxy-2-mercaptopyrimidine (DHMP). The sorbed elements were eluted with 5 mL, 2 mol L^{-1} HNO_3. The effluents were further analyzed by AAS for evaluating.

Shokrollahi et al. and Ghaedi et al. [14,15] develop a sensitized and selective spectrophotometric method for trace ion determination in the presence of dodecyltrimethylammonium bromide (DTAB) using eriochrome cyanine R (ECR), and on activated carbon modified with bis salicyl aldehyde, 1,3 propan diimine (BSPDI). Accordingly, the objective of this work was to determine agronomic value of tannery sludge compost and the evolution of the bioavailability of heavy metals in course of composting by following their chemical forms. The main physicochemical analyses and Fourier-transformed infrared (FTIR) spectroscopic characterization were carried out and a sequential extraction was applied on sludge compost in the course of different steps of treatment.

2. Materials and methods

2.1. Composting

The tannery sludge used in this study was collected from the Kenny Leather Sdn Bhd (Melaka, Malaysia). The sludge (100 kg) was mixed with sawdust (50 kg), chicken manure (30 kg), beneficial organism (1 l), and rice bran (20 kg) in a pile 5 m long and 2 m high on a composting windrow type. The mixture was prepared so as to optimize the composting parameters, i.e. 60% humidity and a C/N ratio of about 30. Table 1 shows the main physicochemical characteristics of the raw materials. With the aim of maintaining aerobic conditions during the process, the pile was turned manually every 10 days.

Temperature was measured daily at a depth of 50 cm at different positions inside the pile. The composting cycle lasted for 60 days. Subsequently, samples were taken systematically before composting (T_0), after 10 days of composting (T_{10}), and at T_{20}, T_{30}, T_{40}, T_{50} and T_{60}). Each sample was air-dried for a period of 10 days. The dried sample was ground down into a fine powder.

2.2. Chemical analysis

A representative sample was taken from the homogenized compost pile for the sequential extraction of heavy metals and other analyses. Sub-samples (250 g) were taken from 10 different point of compost heap (bottom, surface, side, centre) at each stage of composting raw sludge mixture (0 day, sludge mixture after 10, 20, 30, 40, 50, and 60 days of composting.

On aliquots of these representative samples the following physicochemical analyses were made: the pH was determined on a suspension of sample in water (10 g/15 ml), the total organic carbon (TOC) was measured according to the ANNE method [16], the total nitrogen (Kjeldahl method), and inorganic nitrogen [17], the humic carbon extracted by 0.1 M NaOH solution was measured after oxidation by $KMnO_4$ [18]. The rate of decomposition was calculated after ignition of the dry sample at 550 °C (16 h). For P available the Olsen

Table 1
Physicochemical 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
TKN (%)	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 (mg kg^{-1})	1190	0.004	1.05	236.33
Sodium (mg kg^{-1})	1006	64	123	98
Heavy metals				
Iron (mg kg^{-1})	1062	402	1738	142.33
Chromium (mg kg^{-1})	500	14.6	16.6	6.3
Lead (mg kg^{-1})	10	16	1.3	1.2
Cadmium (mg kg^{-1})	8	6.5	0.5	0.2
Copper (mg kg^{-1})	80	4.8	329.67	24.33
Zinc (mg kg^{-1})	200	8.2	634.67	127
Manganese (mg kg^{-1})	70	4.6	34	24

E.C.: electrical conductivity; TKN: total kjeldahl nitrogen.