

## PHYSICOCHEMICAL CHARACTERIZATION OF COMPOST OF THE INDUSTRIAL TANNERY SLUDGE

MAHDI AHMED<sup>1\*</sup>, AZNI IDRIS<sup>1</sup>, S. R. SYED OMAR<sup>2</sup>

<sup>1</sup>Department of chemical and environmental Engineering, Faculty of Engineering,

<sup>2</sup>Department of land Management, Faculty of Agriculture  
Universiti Putra Malaysia, 43400 UPM Serdang, MALAYSIA

\*Corresponding Author: Mahdiupm@hotmail.com

### Abstract

It is very important that tannery wastes in the form of sludge are managed in an environmentally sound manner. This study focused on the heavy metal characterization and the influence of changing the physico-chemical 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 physical and chemical properties of the composted sludge during treatment show the stability and maturity of end product. Total metal content in the final compost were much lower than the limit values of composts to be used as good soil fertilizer. Furthermore, it was observed in using a sequential extraction method in sludge compost at different phases of treatment, that a large proportion of the heavy metals were associated to the residual fraction (70– 80%) and more resistant fractions to extraction X–NaOH, X–EDTA, X–HNO<sub>3</sub> (12–29%). Less than 2% of metals bound to bioavailable fractions X–(KNO<sub>3</sub> + H<sub>2</sub>O). Bioavailable fractions of all elements tend to decrease. Mobile fractions of metals are poorly predictable from the total content.

*Keywords:* Composting, Tannery Sludge, Heavy Metals, Bioavailability, Stabilisation.

### Nomenclatures

<i>HS</i>	Humic Substances
<i>H</i>	Hour
<i>TOC</i>	Total Organic Carbon
<i>C/N</i>	Carbon Nitrogen ratio
<i>CFU</i>	Colony Formed Unit
<i>AFNOR</i>	French Association of Normalisations
<i>EC</i>	Electrical Conductivity
<i>OM</i>	Organic Matter
<i>TKN</i>	Total Kjeldahl Nitrogen
<i>Class A compost</i>	One which have no restrictions in use
<i>Class B compost</i>	One which can be used on forest lands and roadsides and for other landscaping purposes

## 1. Introduction

The agricultural utilization of tannery sludge compost implies knowing its degree of stability, as well as its content and bio geochemical forms of the heavy metals present. Not only are these elements not biodegradable and become toxic at some concentrations, they tend to accumulate along the food chain where human is the final user [1].

Many studies have been carried out on the speciation of heavy metals in soils, and soils amended with composted biosolid or raw sludge [2, 3]. One of the previous studies suggested 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 [4].

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 [5]. 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.

The treatment by composting leads to the development of microbial populations, which cause numerous physico-chemical 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 [5-7].

Some research studies showed the increase of metal concentrations during composting of swine manure and suggested that the types of composting and raw materials are of major importance to metal condensation [5]. 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 physico-chemical analyses 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 in Melaka, Malaysia. The sludge (100kg) was mixed with sawdust (50kg), chicken manure (30kg), and rice bran (20kg) in a pile 3m long and 1.5 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 physico-chemical 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 sixty 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 ten 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 points of compost heap (bottom, surface, side, and centre) at each stage of composting raw sludge mixture (0 day, sludge mixture after 10, 20, 30, 40, 50, and 60 day of composting).

On aliquots of these representative samples the following physico-chemical 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 [8], the total nitrogen (Kjeldahl method), inorganic nitrogen [9], the humic carbon extracted by 0.1 M NaOH solution was measured after oxidation by  $KMnO_4$  [10]. The rate of decomposition was calculated after ignition of the dry sample at 550°C (16 h). For the available P the Olsen method was used [11]. Available Ca, Na, K, Mg were determined using ammonium acetate. Total P, Ca, Na, K, Mg, Fe and Mn

were determined after ashing. P was measured colorimetrically and other elements were analysed in the extracts using atomic adsorption and flame photometry [12].

**Table 1. Physico-Chemical Properties of Raw Materials used in Composting.**  
(results expressed on dry basis)

Characteristics	Tannery Sludge	Sawdust	Chicken Manure	Rice bran
Moisture, %	60.6±0.3	80.7± 0.1	50.6± 0.5	66.9± 1.3
pH	7.4±0.1	5.9±0.05	7.9± 0.1	7.2± 0.1
E.C. (mS cm <sup>-1</sup> )	9 ± 0.07	15± 0.07	7± 0.07	6± 0.02
Organic -C, %	20.0±0.2	57± 0.16	30.4± 0.3	49.3± 0.3
TKN %	1.0± 0.07	0.3± 0.02	4± 0.04	1.1± 0.1
C/N	20.0	190	7.6	45.7
Ash	65± 3.2	80± 2.4	45± 1.1	30± 0.4
<b>Macronutrients</b>				
K, %	0.415± 0.15	0.02± 0.04	1.2± 0.5	1.0± 0.02
P, %	0.097± 0.02	1.2± 0.1	3.02± 1.0	0.2± 0.01
Ca, %	7.7± 3.0	0.02± 0.01	1.9± 0.04	0.3± 0.001
Mg (mgkg <sup>-1</sup> )	1190	0.004	1.1	236.3
Na (mgkg <sup>-1</sup> )	1006	64	123	98
<b>Heavy metals</b>				
Fe (mgkg <sup>-1</sup> )	1062	402	1738	142.3
Cr (mgkg <sup>-1</sup> )	500± 5.4	14.6± 1.1	16.6± 1.2	6.3± 0.2
Pb (mgkg <sup>-1</sup> )	10± 0.1	16± 0.4	1.3± 0.002	1.2± 0.001
Cd (mgkg <sup>-1</sup> )	8± 0.3	6.5± 0.1	0.5± 0.02	0.2± 0.001
Cu (mgkg <sup>-1</sup> )	80± 2.1	4.8± 0.3	329.7± 4.5	24.3± 0.1
Zn (mgkg <sup>-1</sup> )	200± 5.5	8.2± 1.1	634.7± 3.2	127± 2.1
Mn (mgkg <sup>-1</sup> )	70± 4.3	4.6± 0.3	34± 2.3	24± 1.1

According to French association of normalizations [13], to obtain the total Cr, Zn, Cu, Pb, and Cd content; 1 g of each sample was mineralized for 4 h at 550°C, and then dissolved in 5 ml of hydrofluoric acid. The solution obtained was evaporated to dryness, the residue was then dissolved with concentrated HNO<sub>3</sub>/HCl (1:1) solution and the acid solution was diluted to analysis.

Heavy metal fractionation was carried out according to Sposito's procedure, which is widely applied in various studies of sludge-amended soil [3, 4]. On the samples taken from the sludge mixture at different times of composting, a series of reagents was applied with a compost/extractant ratio of about (1/4) (Table 2). However, due to fact that the final reagent (4 M HNO<sub>3</sub>) still did not extract the entire residual metal, standard test AFNOR NF X 31-151 was applied on ashed residue obtained from the last step of the extraction. The amount dosed represent "residual

fraction'' [14]. All filtered supernatants were directly analyzed by flame atomic absorption spectrometer (Varian Spectra AA220 Fast Sequential) [15].

**Table 2. Experimental Conditions used to Determine Various Extractable Heavy Metal Forms (Esposito's method).**

Extractant	Duration of shaking	Heavy metals forms
HNO <sub>3</sub> (4 M)	6 hours in 80°C	Sulfides "(Mobilisable)"
EDTA (0.5 M)	6 hours	Organically complexed or carbonates "(Mobilisable)"
KNO <sub>3</sub> (0.5 M)	16 hours	Exchangeable "(Mobile)"
H <sub>2</sub> O	2 hours, three times	Soluble "(Mobile)"
NaOH (0.5 M)	16 hours	Organically bound "(Mobilisable)"

### 2.3 Microbial analysis

A sample from raw sludge and mixtures at each stage of composting (0, 10, 20, 30, 40, 50, and 60 day of composting) were analyzed for total aerobic mesophiles, aerobic bacilli, *Salmonella* spp. and *Shigella* spp., and yeast and moulds [16]. A sub-sample of 10 g biosolid was added to 90 ml sterile buffered peptone solution using an aseptic technique. This to allow the microorganism to migrate into the solution. A series of dilutions were prepared (10<sup>-1</sup>, 10<sup>-2</sup>... 10<sup>-6</sup>) using sterile 0.8% NaCl solutions. Microorganisms were counted after plated sterile Petri dishes with 0.1 ml from diluted liqot and incubated at the temperature in specific time as shown in Table 3[16, 17].

**Table 3. Cultural Conditions used to Characterise the Microbial Population of Raw Tannery Sludge and Compost.**

Conditions	Aerobic Bacilli	Total Aerobic Mesophile	Yeast and Moulds	<i>Salmonella</i> spp. and <i>Shigella</i> spp.
Culture medium	Plate count agar	Plate count agar	Potato dextrose agar	sulfite bismute agar
Incubation Temperature	30°C	30°C	30°C	30°C
Incubation Time	48-72h, sample heated at 80°C for 10 minutes	48-72h	24h	48-72

## 3. Results and Discussion

### 3.1 Characterization of industrial tannery sludge

The results of the physicochemical characterization of the raw sludge are presented in Table 1. The sludge showed that it was low in C/N ratio (20.02) and high in nitrogen

content (0.99). The phosphorus content of the sludge was 0.097%, while the potassium content was 0.41%. Some reported results proved that the potassium level in sludge is usually low and can range from 0.02 to 2.645%, but is enough for plant uptake and is still sufficient for crop requirement [18].

Apart from the plant nutrient the analysis of the sludge showed that it contained high amounts of trace elements especially chromium, cadmium, sodium and lead, which all have a negative impact on plant growth [19]. The level of chromium was high ( $500 \text{ mg kg}^{-1}$ ) and above the maximum level which should be present in the soil ( $100 \text{ mg kg}^{-1}$ ) [20]. Due to the low solubility of chromium, only a little (Cr) is bioavailable, which means that even when crops are grown in soils treated with sludge relatively high in Cr, phytotoxicity is rarely observed [21].

The lead content in the sludge was low ( $10 \text{ mg kg}^{-1}$ ) compared to the maximum allowable level of lead content in the soil  $15 \text{ mg kg}^{-1}$  [20]. From the above results it appears that the sludge from the tannery was at an acceptable level, except for chromium and cadmium (Table 1). The tannery sludge was alkali in nature (pH, 7.36).

### 3.2 Characterisation of compost

The main physico-chemical properties of the mixed raw materials at different times of the compost 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 [7]. Two phases of the composting process were recorded: a phase of stabilization (about 30 days), where temperature peaked at  $64^\circ\text{C}$  after 10 days of processing and pH was slightly increased to 7.5; a phase of maturation (about 30 days), characterized by a temperature plateau at  $35^\circ\text{C}$  and slight acidification of the medium (pH 6.6). The change in the C/N ratio from 24.5 to 15.7 and the amount of ash reflect microbial decomposition of organic matter and stabilization during composting (Table 4). The increase of total nitrogen during composting was caused by the decrease of substrate carbon resulting from the loss of  $\text{CO}_2$  (because of the decomposition of the organic matter which is chemically bound with Nitrogen) [22, 7]. Inorganic nitrogen,  $\text{N-NH}_4$  and  $\text{N-NO}_3$  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 [23]. Humic substances had a capacity to interact with metal ions, 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  $3 \text{ mS cm}^{-1}$  to be used as good fertilizers [24]. Available and total P, Ca, K, Mg, and Na as well Fe and Mn were more important to use this material as mineral fertilizers [24–26].

Therefore, application of material will increase the stable organic N and humic carbon and improve mineral elements necessary for plant growth.

**Table 4. Physico-Chemical Properties of Materials Mixture at Different Times of Composting. (Results Expressed in Dry Basis)**

Properties	0 day	10 day	20 day	30 day	40 day	50 day	60 day
Moisture	58.4±0.3	73.5±1.5	68.6±1.2	65.4±1.1	64.1±0.9	63.2±0.6	60.1±0.5
pH	7.3±0.1	7.4±0.2	7.5±0.3	7.5±0.3	6.9±0.2	6.7±0.2	6.6±0.1
E.C. (mS cm <sup>-1</sup> )	2.0±0.07	1.7±0.05	1.5±0.03	1.6±0.04	1.7±0.05	1.8±0.06	2.0±0.07
TOC %	19.6±0.2	18.4±0.18	17.2±0.16	16.5±0.15	16±0.14	15.6±0.12	14.8±0.11
OM %	33.8±1.1	30.5±1.0	27.6±0.8	24.4±0.6	23.6±0.4	21.7±0.3	19.8±0.1
TKN %	0.8±0.2	0.8±0.2	0.9±0.4	0.9±0.4	0.9±0.4	0.9±0.4	0.9±0.4
Ash	63±3.2	70±4.5	75±6.4	80±7.2	83±7.8	85±8.2	88±8.9
C/N	24.5	21.6	19.1	18.3	17.4	16.4	15.8
HS	19.3±0.5	17.2±0.4	20.6±0.7	22.3±0.9	23.5±1.1	24.4±1.5	26.5±1.8
NH <sub>4</sub> <sup>+</sup> -N(mgkg <sup>-1</sup> )	3.7±0.5	3.2±0.3	2.8±0.2	2.3±0.1	2.0±0.05	1.9±0.03	1.4±0.01
NO <sub>3</sub> <sup>-</sup> -N(mgkg <sup>-1</sup> )	3.4±0.4	2.9±0.2	2.6±0.1	1.8±0.09	1.5±0.05	1.03±0.03	0.1±0.01
N-org. (mgkg <sup>-1</sup> )	5.4±0.5	5.9±0.7	6.1±0.9	6.5±1.2	6.8±1.1	7.1±1.3	8.2±1.5
P total (mgkg <sup>-1</sup> )	7.5±0.7	6.5±0.6	5.9±0.5	5.5±0.5	5.0±0.3	4.5±0.2	3.9±0.1
P available (mgkg <sup>-1</sup> )	4.2±0.8	3.9±0.7	3.2±0.5	2.8±0.4	2.6±0.4	2.5±0.3	1.9±0.2
Ca total (mgkg <sup>-1</sup> )	720	680	530	330	300	210	150
Ca available (mgkg <sup>-1</sup> )	105±5.4	90±5.0	70±3.5	63±3.1	59±2.5	56±2.3	45±2.2
K total (mgkg <sup>-1</sup> )	38±1.1	27±0.9	18±0.8	15±0.6	12±0.4	10±0.2	8±0.1
K available (mgkg <sup>-1</sup> )	12±0.5	10±0.4	8±0.3	6.5±0.2	5.2±0.1	3.6±0.09	2.5±0.07
Na total (mgkg <sup>-1</sup> )	980	780	540	330	290	260	140
Na available (mgkg <sup>-1</sup> )	250	140	120	90	80	70	50
Mg total (mgkg <sup>-1</sup> )	990	740	530	340	310	260	130
Mg available (mgkg <sup>-1</sup> )	100±5.3	80±3.1	60±2.5	40±1.9	30±1.7	20±1.4	10±1.1
Mn (mgkg <sup>-1</sup> )	85±3.5	90±4.2	76±2.5	60±2.1	50±1.8	45±1.5	60±1.2
<b>Fe (mgkg<sup>-1</sup>)</b>	<b>1200</b>	<b>1345</b>	<b>2876</b>	<b>3564</b>	<b>3850</b>	<b>4543</b>	<b>5674</b>

### 3.3 Characterisation of microbial during composting

During composting, microbial activities are diverse [27]. Microbiological analysis of the initial mixture (tannery sludge/ sawdust/chicken manure/ rice bran) showed total aerobic mesophiles ( $5 \times 10^6$  CFUg<sup>-1</sup>fresh compost), bacilli ( $8 \times 10^9$  CFUg<sup>-1</sup> fresh compost), *Salmonella spp.*, and *Shigella spp.* (<10), and yeasts and moulds ( $4.1 \times 10^6$  CFUg<sup>-1</sup>fresh compost) (Table 5). The microbial density was significantly reduced after 60 days of composting to reach <10 total aerobic mesophile,  $9.5 \times 10^2$  basilli and <10 yeasts and moulds and for *Salmonella spp.*, and *Shigella spp.* they were not detected in the final compost.

This drop can be attributed to the exhaustion of nutrients from the medium and/or to the temperature peak during the thermogenic phase (64°C at 10 days). Maintaining the temperature at 60°C for the first month of composting caused a significant elimination of total aerobic mesophile, yeasts and moulds, and *Salmonella spp.*, and *Shigella spp.* At this temperature, only a few days are required to eliminate almost all pathogens and nematodes [28]. Although aerobic bacteria (bacilli) are very often

active between 60 and 65°C, temperatures cannot exceed 75 °C, which would irreversibly denature the bacterial enzymes [29, 30]. The intense microbial activity induced very significant transformations of the mixture of tannery sludge with other materials used in composting, the main characteristics of which are presented in Table 4.

**Table 5. Microbial Account During Composting Of Tannery Sludge (Expressed As Colony Formed Units G/Fresh Material).**

Sample	Aerobic (CFUg <sup>-1</sup> )	Total Aerob Mesophile (CFUg <sup>-1</sup> )	Yeast and Moulds (CFUg <sup>-1</sup> )	<i>Salmonel and Shige</i> (CFUg <sup>-1</sup> )
Initial tann sludge	8x10 <sup>9</sup>	5 x 10 <sup>6</sup>	4.1x10 <sup>6</sup>	<10
0 day	6.3x10 <sup>8</sup>	4x10 <sup>6</sup>	8.3x10 <sup>6</sup>	<10
10 day	4.2x10 <sup>8</sup>	3x10 <sup>6</sup>	6.3x10 <sup>6</sup>	<10
20 day	3.5x10 <sup>6</sup>	1.8x10 <sup>5</sup>	3.4x10 <sup>3</sup>	<10
30 day	7.1x10 <sup>5</sup>	2.5x10 <sup>4</sup>	2.5x10 <sup>2</sup>	<10
40 day	8.4x10 <sup>4</sup>	3.6x10 <sup>3</sup>	1.3x10 <sup>2</sup>	<10
50 day	3.8x10 <sup>3</sup>	6.7x10 <sup>2</sup>	<10	ND
60 day	9.5x10 <sup>2</sup>	< 10	<10	ND

CFU=Colony Formed Unit

### 3.4 Heavy metals content of compost

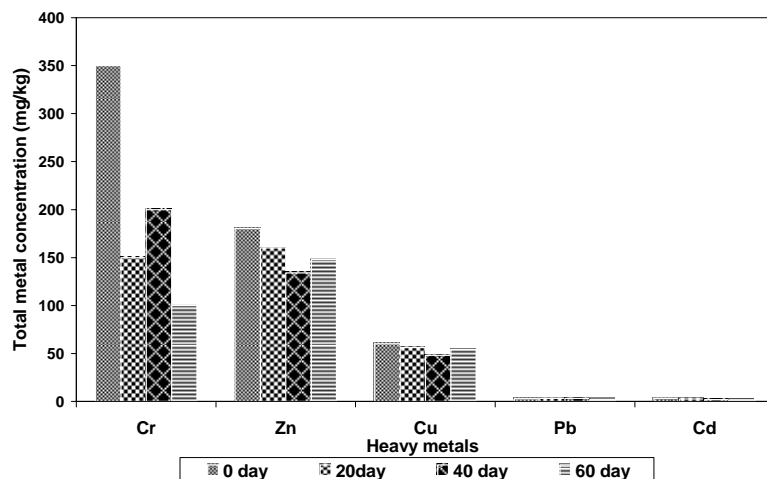
Composting can concentrate or dilute heavy metals present in tannery sludge [7]. Lowering the amounts of heavy metal depends on metal loss through leaching. The increase of metal level is due to weight loss in the course of composting following organic matter decomposition, release of carbon dioxide and water and mineralization processes [31].

Figure 1 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, 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 and could be related to metal release from decomposed organic matter, an increase of moisture from 58.4% to 73.5%, a change in other oxidizing and anionic conditions in the medium and therefore increasing the solubility of metals [5, 7, and 24]. Some authors suggest that where the potential toxic metal concentrations of compost are high, the leachability of metal associated with compost is of concern [5].

It should consider the role of composting as important environmental sink to eliminate the most labile fraction of metal, mainly during active decomposition phase. Indeed, after stabilization phase, metal total concentration is steady indicating that



leachability is stopped; this demonstrates the interest of land application of mature compost.



**Fig.1. Total Amount Of Heavy Metals During Composting Of Tannery Sludge.**

For each metal, the sum of the amounts extracted by sequential extractions is almost four times lower than the total amount of metal extracted by the AFNOR method. Therefore, even 4 M HNO<sub>3</sub> digestions at 80°C were not effective to extract total metal content, especially from the silicate phase. Almost, 70–80% of metals were bound to this residual fraction occurred as silicate forms. The total metal content of the final compost was lower than the values of sludge composts, which have no restrictions for use and are considered good soil fertilizer according to the Canadian Council of Ministers of the Environment (Table 6) [32] as available recommendation for sludge compost, as well as from the values obtained for other sludge composts [7].

Furthermore, the largest proportion of metal was found associated to the residual fraction (70–80%) and fractions more resistant to extraction X–NaOH, X–EDTA, X–HNO<sub>3</sub> (12–29%). This indicates that the metals were in more stable forms and can consequently be considered unavailable for plant uptake. A less than 2% of metals were bound to bioavailable fractions X–(KNO<sub>3</sub> + H<sub>2</sub>O). Similar results have been reported in previous studies [7, 24]. A good correlation coefficient (R = 0.97) was found at each stage of composting between total metal amount and total amounts extracted by sequential extractions, in spite of the later is about four times lower than the former wherever the metal and step of composting. To follow up the metal distribution during composting, each metal fraction was referred to % of total extractable amounts.

$$\% \text{ of total extractable metal} = (\text{X-fraction} / \text{total extractable metal}) \times 100 \quad (1)$$

X-fraction = amount of metal in form KNO<sub>3</sub> or X–H<sub>2</sub>O, or X–NaOH or X–EDTA or X–HNO<sub>3</sub>,

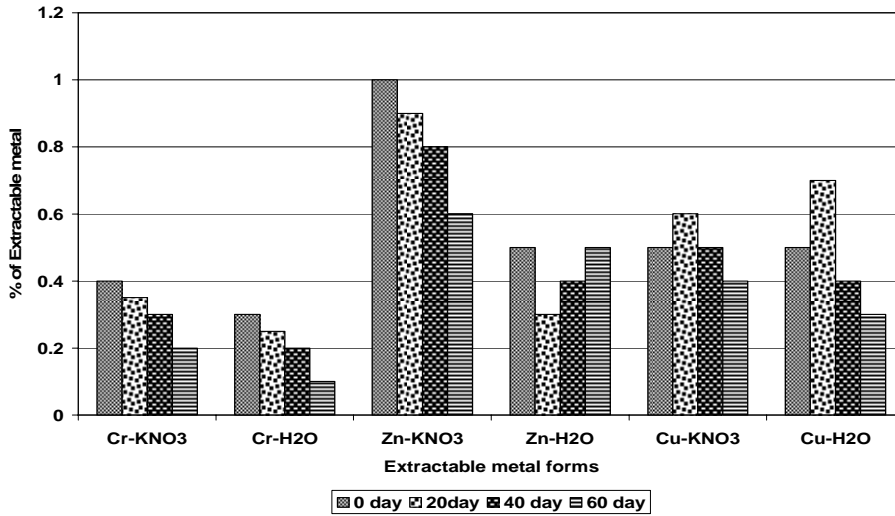
$$\text{Total extractable metal} = \text{X–KNO}_3 + \text{X–H}_2\text{O} + \text{X–NaOH} + \text{X–EDTA} + \text{X–HNO}_3.$$

During composting, the mobile fractions X-KNO<sub>3</sub> and X-H<sub>2</sub>O of Cr, Zn, and Cu tended to decrease (Figure 2). The elements Pb and Cd were not detected in the easily mobile class at any time of composting; indeed Pb and Cd are known to be almost insoluble in water [4].

**Table 6. Total Heavy Metal Contents In The Final Compost (60 Day) And Allowable Limit For Different Class Compost According To Canadian Limit [32]**

Heavy metal	Final mature compost content (mgkg <sup>-1</sup> )	Allowable limit (mgkg <sup>-1</sup> dry wt)	
		Class A	Class B
Cr	100	210	1060
Zn	148	500	1850
Cu	54	100	757
Pb	2.2	150	500
Cd	1.6	3	20

Class A compost (which have no restrictions in use), and Class B Compost (which can be used on forest lands and roadsides and for other landscaping purposes).



**Fig.2. Percentage of Extractable Metal Forms Change [X-KNO<sub>3</sub> (Exchangeable) and X-H<sub>2</sub>O (Soluble)] During Composting Tannery Sludge.**

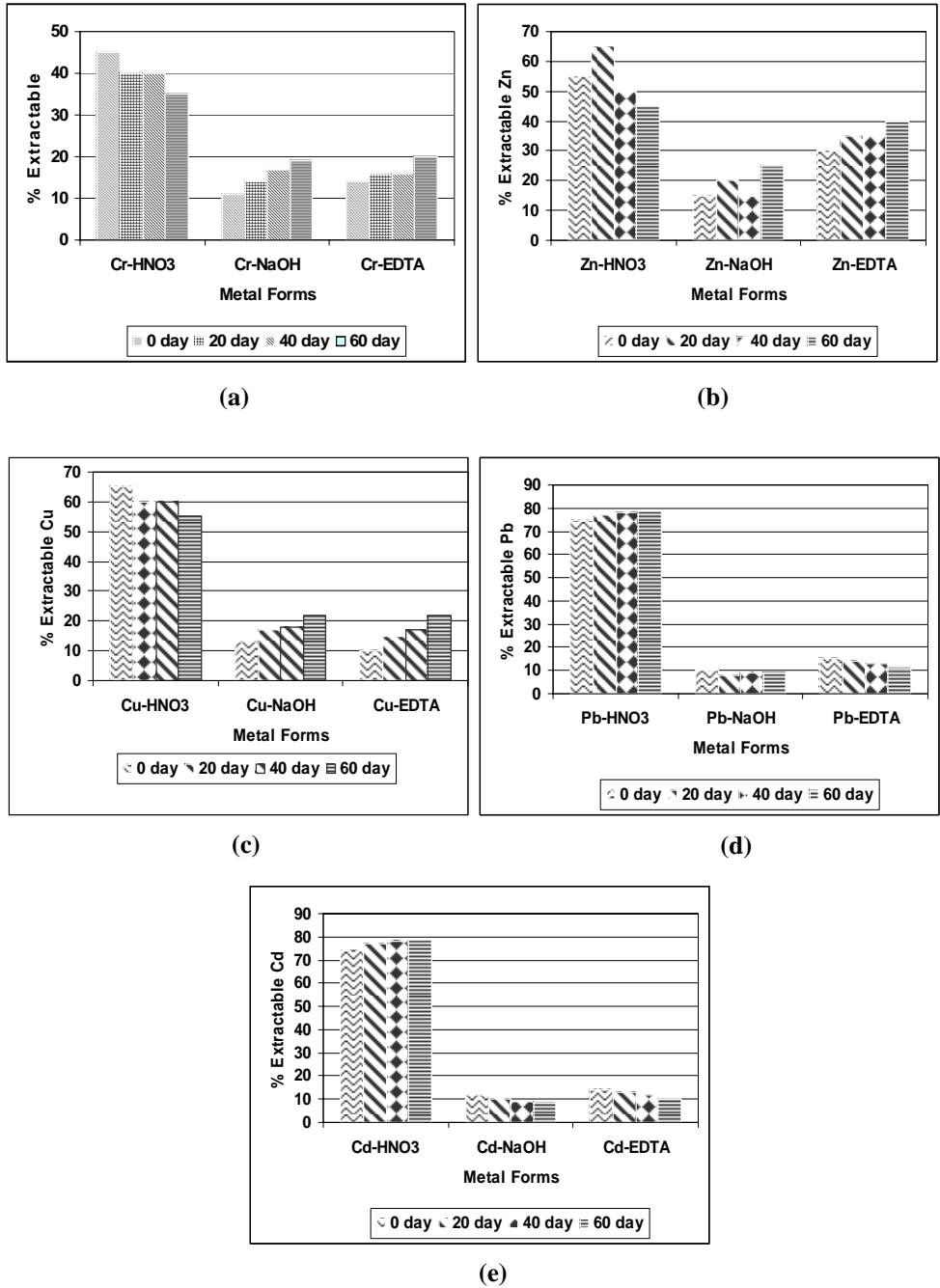


Fig 3. Percentage of Variation of Extractable Metal Forms During Composting of Tannery

For mobilisable fractions (Figure 3 a – e), of Cr, Zn and Cu during composting there was a decrease of the X–HNO<sub>3</sub> fraction with an increase of X–EDTA, and X–NaOH forms. In contrast, Pb and Cd presented a slight increase of X–HNO<sub>3</sub> with a decrease of NaOH and EDTA soluble forms. In the course of composting, in the thermophilic phase, intense microbial decomposition of organic matter was achieved, and could involve the release of Pb and Cd from organic sites. These elements are later bound in less extractable forms in EDTA and HNO<sub>3</sub> fractions respectively. Pb and Cd were preferentially bound to sulfide forms X–HNO<sub>3</sub>. In contrast, during composting the formation of humic substances seems to transform Cr, Zn and particularly Cu from sulfide fractions to organic fractions X–NaOH and X–EDTA. One of the authors reported that during composting of swine manure, Cu was primarily in the organically bound fraction and Cr and Zn were concentrated in the organically complexed fraction [5].

#### 4. Conclusions

The study concludes that throughout the 60 days of tannery sludge composting, physicochemical analysis show that all parameters 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 compost can supply all micro and macronutrients necessary for plant growth. The total concentration of Cr, Zn, Cu, Pb and Cd is very low rendering final compost acceptable for agricultural use. Monitoring of heavy metal characterization during composting shows that mobility and bioavailability of heavy metals are dependent on other physico-chemical properties of the medium besides total metal contents such as decomposition of organic matter, humic substance content, and pH; as well as to the affinity of metals for various chemical forms. The largest proportion of metal was found in the residual fraction and fractions more resistant to extraction indicating that the metals were in more stable forms and is consequently considered unavailable for plant uptake. The amount of potentially bioavailable metals was less than 2%.

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