



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

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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<sub>3</sub> + H<sub>2</sub>O). 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<sub>3</sub> (15–25%). Mobile fractions of metals are poorly predictable from the total content. Bioavailability of all fractions of elements tends to decrease.

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### 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 biochemical 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<sup>+3</sup> 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.

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Composting which is a biological aerobic decomposition in which labile organic matter is degraded to carbon dioxide (CO<sub>2</sub>), water vapour, ammonia (NH<sub>3</sub>), 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<sup>-1</sup> 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<sup>-1</sup> HNO<sub>3</sub>. 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<sub>4</sub> [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 <sup>-1</sup> )	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
<b>Macronutrients</b>				
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 <sup>-1</sup> )	1190	0.004	1.05	236.33
Sodium (mg kg <sup>-1</sup> )	1006	64	123	98
<b>Heavy metals</b>				
Iron (mg kg <sup>-1</sup> )	1062	402	1738	142.33
Chromium (mg kg <sup>-1</sup> )	500	14.6	16.6	6.3
Lead (mg kg <sup>-1</sup> )	10	16	1.3	1.2
Cadmium (mg kg <sup>-1</sup> )	8	6.5	0.5	0.2
Copper (mg kg <sup>-1</sup> )	80	4.8	329.67	24.33
Zinc (mg kg <sup>-1</sup> )	200	8.2	634.67	127
Manganese (mg kg <sup>-1</sup> )	70	4.6	34	24

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

**Table 2**

Conditions for determination of heavy metals according to French association of normalizations (AFNOR NF X 31-151) [21].

Conditions	Weight of metal (g)	Mineralization time (h)	Temperature (°C)	Dissolved in 5 ml	Redissolved in (1:1)
Chromium	1	4	550	HCl	HNO <sub>3</sub> /HCl
Copper	–	–	–	–	–
Zinc	–	–	–	–	–
Lead	–	–	–	–	–
Cadmium	–	–	–	–	–

method was used [19]. 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 calorimetrically and other elements were analyzed in the extracts using atomic absorption and flame photometry [20].

FTIR spectra were recorded on a FTIR PerkinElmer 1600 spectrophotometer (Metrohm Ltd., CH.-9101 Herisau, Switzerland), on potassium bromide (KBr) pellets, which were prepared by pressing a mixture of a 2-mg sample with 400 mg KBr under vacuum. To limit moisture interference, both samples and KBr were separately dried at 105 °C before making pellets. Spectra were determined by exposing samples to a frequency ranging from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> at a rate of 16 nm s<sup>-1</sup>.

According to French association of normalizations (AFNOR NF X 31-151) [21], to obtain the total Cr, Zn, Cu, Pb, and Cd content; a series of reagents were used and the final acid solution was diluted to analysis (Table 2).

Heavy metal fractionation was carried out according to Sposito's procedure, which is widely applied in various studies of sludge-amended soil [7,8]. On the samples taken from the sludge mixture at different times of composting, a series of reagents were applied with a compost/extractant ratio of about (1/4) (Table 3). However, due to fact that the final reagent (4 M HNO<sub>3</sub>) still did not extract the entire residual metal, standard AFNOR test was applied on ashed residue obtained from the last step of the extraction. The amount dosed represents "residual fraction" [22]. All filtered supernatants were directly analyzed with a flame atomic absorption spectrometer (Varian Spectra AA220 Fast Sequential) [23].

### 2.3. Microbial analysis

A sample from raw sludge and mixtures at each stage of composting (0, 10, 20, 30, 40, 50, and 60 days of composting) were analyzed for total aerobic mesophiles, aerobic bacilli, *Salmonella* spp. and *Shigella* spp., and yeast and moulds [24]. A sub-sample of 10 g biosolid was added to 90 ml sterile buffered peptone solution using an aseptic technique 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. Microorganism was counted after plated sterile Petri dishes with 0.1 ml from diluted liquot and incubated at the temperature in specific time as shown in Table 4 [24].

**Table 3**

Design of experiment used for determination of various extractable heavy metal forms (Esposito's method).

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

### 2.4. Germination index

The germination index was used to determine the inhibitory potentials of water extract. Seed germination test was carried out with both Chinese cabbage and Lettuce using compost extract. Two grams of oven-dried compost was placed in test tube with screw cap and 20 ml of distilled water was added, then the tube was placed on electric rotator at 125 rpm for 1 h. The supernatant was decanted and centrifuged at 10,000 rpm for 10 min and filtered through Whatman paper. Two milliliters of filtrate was diluted with 1 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 moisten 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 [25,26].

### 2.5. Statistical analysis

All the physical and chemical analyses were repeated three times and the statistical analyses were performed according to SAS program [27]. Correlation was explored between all metal fractions and selected variables: pH, ash, organic matter (OM) and HS content, and between the various metal fractions among themselves.

## 3. Results and discussion

### 3.1. Characterization of 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%. Sommers [28] 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.

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 [29]. The level of chromium was high (500 mg kg<sup>-1</sup>) and above the maximum level which should be present in the soil (100 mg kg<sup>-1</sup>) [30]. Alloway [31] reported that 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.

The lead content in the sludge was low (10 mg kg<sup>-1</sup>) compared to the maximum allowable level of lead content in the soil 15 mg kg<sup>-1</sup> [30].

The concentration levels of the following elements in the sludge were as follows: cadmium (8 mg kg<sup>-1</sup>); copper (80 mg kg<sup>-1</sup>); iron (1062 mg kg<sup>-1</sup>); manganese (70 mg kg<sup>-1</sup>); and zinc (200 mg kg<sup>-1</sup>) (Table 1). From the above results it appears that the sludge from the tannery was at an acceptable level, except for chromium and cadmium.

**Table 4**  
Cultural condition used to characterized the microbial population of raw tannery sludge and compost.

Conditions	<i>Salmonella</i> spp. and <i>Shigella</i> spp.	Aerobic bacilli	Yeast and moulds	Total aerobic mesophile
Incubation temperature	30 °C	30 °C	30 °C	30 °C
Incubation time	48–72	48–72 h, sample heated at 80 °C for 10 min	24 h	48–72 h
Culture medium	Sulfite bismute agar	Plate count agar	Potato dextrose agar	Plate count agar

The tannery sludge was alkali in nature (pH, 7.36). The sludge was rich in organic matter.

The nitrogen content was high; it also had a high content of sodium and calcium.

### 3.2. Characterization of compost

Two phases of the composting process were recorded: a phase of stabilization (about 30 days), where temperature peaked at 64 °C after 10 days of processing and pH was slightly increased (7.5); a phase of maturation (about 30 days), characterized by a temperature plateau at 35 °C and slight acidification of the medium (6.6).

The main physicochemical properties of the materials mixtures composted at different times of the process are presented in Table 5. The change in the C/N ratio from 23.06 to 15.78 and the amount of ash reflect microbial decomposition of organic matter and stabilization during composting (Table 5). The pH values were within the optimal range for the development of bacteria 6–7.5 and fungi 5.5–8.0 [11]. The increase of total nitrogen during composting was caused by the decrease of substrate carbon resulting from the loss of CO<sub>2</sub> [11,32]. Inorganic nitrogen, N-NH<sub>4</sub> and N-NO<sub>3</sub> 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 [33]. Humic substances had 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<sup>-1</sup> to be used in good fertilizers [34]. Available and total P, Ca, K, Mg, and Na as well Fe and Mn were more important to use this material as mineral fertilizers [34]. Therefore, application of material will increase the stable organic N and humic carbon and improve mineral elements necessary for plant growth. The differences in results for elements and various samples were likely the result of leaching. Infrared spectra of the compost at various stages of treatment are illustrated in Fig. 1. FTIR spectra exhibit the same absorbance area at different stages of composting, but they differ in the intensity of some peaks, such as a remarkable decrease of aliphatic structures and lipids (2922 and 2855 cm<sup>-1</sup>), peptidic structures (1540 cm<sup>-1</sup>), and carbohydrates (1140–1090 cm<sup>-1</sup>); in parallel the increase of intensity of aromatic structures occurred with phenolic OH and carboxylates extrimity COO<sup>-</sup> around 1384 cm<sup>-1</sup>, and sharply of etherified aromatic structures around 1034–1027 cm<sup>-1</sup>. This shows that sludge decomposition during composting begins by the lipid, protein, and carbohydrate components, with a relative increase of more resistant and stable aromatic structures such as oxidized lignin degradation products and etherified/esterified aromatic structures [33].

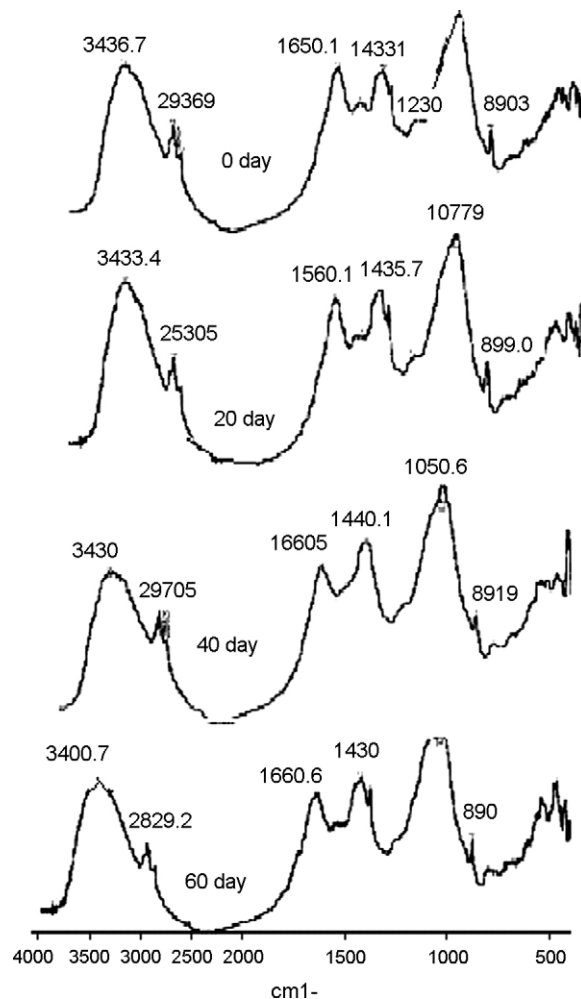
Likewise, Hsu and Lo [35] found an increase in aromatic character and a decrease in carbohydrates as composting of swine manure proceeded. Accordingly, all these physicochemical changes and spectroscopic characteristics are similar to the results of other studies and could reflect the stability and maturity of the final product [35,36].

### 3.3. Characterization of microbial during composting

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 5.

During composting, microbial activities are diverse [37]. Microbiological analysis of the initial mixture (tannery sludge/sawdust/chicken manure/rice bran) showed total aerobic mesophiles ( $5 \times 10^6$  CFU g<sup>-1</sup> fresh compost), bacilli ( $8 \times 10^9$  CFU g<sup>-1</sup> fresh compost), *Salmonella* spp., and *Shigella* spp. (<10), and yeasts and moulds ( $4.1 \times 10^6$  CFU g<sup>-1</sup> fresh compost) (Table 6). 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 thermo-



**Fig. 1.** Fourier-transformed infrared spectra of compost mixture at four different phases of composting.

**Table 5**  
Physicochemical properties of materials mixture at different times of composting (results expressed in dry basis).

Properties	0 day	10 days	20 days	30 days	40 days	50 days	60 days
Moisture	58.4 ± 0.3a	73.5 ± 0.5b	68.6 ± 0.9c	65.4 ± 0.7d	64.1 ± 0.4e	63.2 ± 0.3f	60. ± 0.5g
pH	7.3 ± 0.3a	7.4 ± 0.3a	7.50 ± 0.3a	7.51 ± 0.3a	6.9 ± 0.1 b	6.7 ± 0.2 b	6.6 ± 0.3b
E.C. (mS cm <sup>-1</sup> )	2.0 ± 0.2a	1.7 ± 0.1a	1.5 ± 0.2b	1.6 ± 0.2b	1.7 ± 0.2ab	1.8 ± 0.2ab	2.0 ± 0.2a
TOC (%)	19.6 ± 0.3a	18.4 ± 0.4b	17.2 ± 0.3c	16.5 ± 0.4d	16.0 ± 0.1d	15.6 ± 0.3d	14.8 ± 0.4e
OM (%)	33.8	30.5	27.6	24.4	23.6	21.7	19.8
TKN (%)	0.80 ± 0.2a	0.85 ± 0.3a	0.90 ± 0.05b	0.90 ± 0.1b	0.92 ± 0.1b	0.95 ± 0.2c	0.95 ± 0.02c
Ash	63 ± 1.2a	70 ± 2.2b	75 ± 1.2c	80 ± 4.2d	83 ± 2.2e	85 ± 1.2f	88 ± 3.2g
C/N	24.5 ± 0.5a	21.65 ± 0.7b	19.11 ± 0.2c	18.33 ± 0.4d	17.4 ± 0.3e	16.42 ± 0.6f	15.78 ± 0.7g
HS	19.3 ± 0.4a	17.2 ± 1.5b	20.6 ± 0.5c	22.3 ± 1.1d	23.5 ± 0.1e	24.4 ± 0.5f	26.5 ± 0.7g
RD	–	20.3 ± 1.5a	28.5 ± 0.6b	36.3 ± 1.2c	38.4 ± 0.8d	40.4 ± 0.9e	45.7 ± 1.1f
NH <sub>4</sub> <sup>+</sup> -N (mg kg <sup>-1</sup> )	3.7 ± 0.4a	3.2 ± 0.3a	2.8 ± 0.5ab	2.3 ± 0.2b	2.0 ± 0.1b	1.9 ± 0.3b	1.4 ± 0.1c
NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	3.4 ± 0.4a	2.9 ± 0.3a	2.6 ± 0.5ab	1.8 ± 0.1c	1.5 ± 0.1c	1.03 ± 0.4d	0.09 ± 0.1e
N-org. (mg kg <sup>-1</sup> )	5.4 ± 0.6a	5.9 ± 0.1ab	6.1 ± 0.2b	6.5 ± 0.1bc	6.8 ± 0.1c	7.1 ± 0.1c	8.2 ± 0.5d
P total (mg kg <sup>-1</sup> )	7.5 ± 0.5a	6.5 ± 1.5b	5.9 ± 0.5c	5.5 ± 0.5c	5.0 ± 0.5c	4.5 ± 0.5c	3.9 ± 0.5d
P available (mg kg <sup>-1</sup> )	4.2 ± 0.5a	3.9 ± 0.2a	3.2 ± 0.2b	2.8 ± 0.5b	2.6 ± 0.1bc	2.5 ± 0.1c	1.9 ± 0.3d
Ca total (mg kg <sup>-1</sup> )	720 ± 1.5a	680 ± 0.9b	530 ± 0.8c	330 ± 0.7d	300 ± 1.5e	210 ± 0.5f	150 ± 0.3g
Ca available (mg kg <sup>-1</sup> )	105 ± 0.5a	90 ± 0.9b	70 ± 0.5c	63 ± 0.5d	59 ± 0.6e	56 ± 0.8f	45 ± 0.2g
K total (mg kg <sup>-1</sup> )	38 ± 0.9a	27 ± 0.5b	18 ± 0.5c	15 ± 0.6d	12 ± 0.8e	10 ± 0.9f	8 ± 0.5g
K available (mg kg <sup>-1</sup> )	12 ± 0.7a	10 ± 0.5b	8 ± 0.6c	6.5 ± 0.3d	5.2 ± 0.2e	3.6 ± 0.1f	2.5 ± 0.3g
Na total (mg kg <sup>-1</sup> )	980 ± 0.8a	780 ± 0.5b	540 ± 0.5c	330 ± 0.9d	290 ± 0.8e	260 ± 0.6f	140 ± 0.4g
Na available (mg kg <sup>-1</sup> )	250 ± 0.4a	140 ± 0.5b	120 ± 0.5c	90 ± 0.3d	80 ± 0.3e	70 ± 0.2f	50 ± 0.2g
Mg total (mg kg <sup>-1</sup> )	990 ± 0.5a	740 ± 0.9b	530 ± 0.7c	340 ± 0.6d	310 ± 0.5e	260 ± 0.8f	130 ± 0.5g
Mg available (mg kg <sup>-1</sup> )	100 ± 0.9a	80 ± 0.5b	60 ± 0.4c	40 ± 0.5d	30 ± 0.6e	20 ± 0.5f	10 ± 0.4g
Mn (mg kg <sup>-1</sup> )	85 ± 0.1a	90 ± 0.4b	76 ± 0.3c	60 ± 0.2d	50 ± 0.1e	45 ± 0.1f	60 ± 0.5d
Fe (mg kg <sup>-1</sup> )	1200 ± 0.5a	1345 ± 0.5b	2876 ± 0.7c	3564 ± 0.8d	3850 ± 0.8e	4543 ± 0.9f	5674 ± 0.9g

All values are reported as mean ± standard deviation between three replicates; values in the same row with different letters are significantly different ( $P < 0.05$ ).

genic 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 [38]. 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 [39,40].

#### 3.4. Characterization of heavy metals during composting

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 and could be related to metal release from decomposed organic matter, an increase of moisture from 58.4% to 73.5%, change of other oxidic and anionic conditions in the medium increasing so the solubility of metals [9,11,34].

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. Although some authors suggest that where the potential toxic metal concentrations of compost are high, the leachability of metal associated with compost is of concern [9].

Composting can concentrate or dilute heavy metals present in tannery sludge [11]. 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 [41].

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.

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 values of sludge composts which have no restrictions of use and are considered as soil fertilizer with good quality according to the limitation of the Canadian Council of Ministers of the Environment (Table 7) [42] as available recommendation for sludge compost, as well as from the values obtained for other sludge composts [11]. Furthermore, the largest proportion of metal was found associated to the resid-

**Table 6**  
Microbial account during composting of tannery sludge (expressed as colony formed units g/fresh material).

Sample	<i>Salmonella</i> spp. and <i>Shigella</i> spp. (CFU g <sup>-1</sup> )	Aerobic bacilli (CFU g <sup>-1</sup> )	Yeast and moulds (CFU g <sup>-1</sup> )	Total aerobic mesophile (CFU g <sup>-1</sup> )
Initial tannery sludge	<10	8 × 10 <sup>9</sup>	4.1 × 10 <sup>6</sup>	5 × 10 <sup>6</sup>
0 day	<10	6.3 × 10 <sup>8</sup>	8.3 × 10 <sup>6</sup>	4 × 10 <sup>6</sup>
10 days	<10	4.2 × 10 <sup>8</sup>	6.3 × 10 <sup>6</sup>	3 × 10 <sup>6</sup>
20 days	<10	3.5 × 10 <sup>6</sup>	3.4 × 10 <sup>3</sup>	1.8 × 10 <sup>5</sup>
30 days	<10	7.1 × 10 <sup>5</sup>	2.5 × 10 <sup>2</sup>	2.5 × 10 <sup>4</sup>
40 days	<10	8.4 × 10 <sup>4</sup>	1.3 × 10 <sup>2</sup>	3.6 × 10 <sup>3</sup>
50 days	ND	3.8 × 10 <sup>3</sup>	<10	6.7 × 10 <sup>2</sup>
60 days	ND	9.5 × 10 <sup>2</sup>	<10	<10

CFU: colony formed unit.

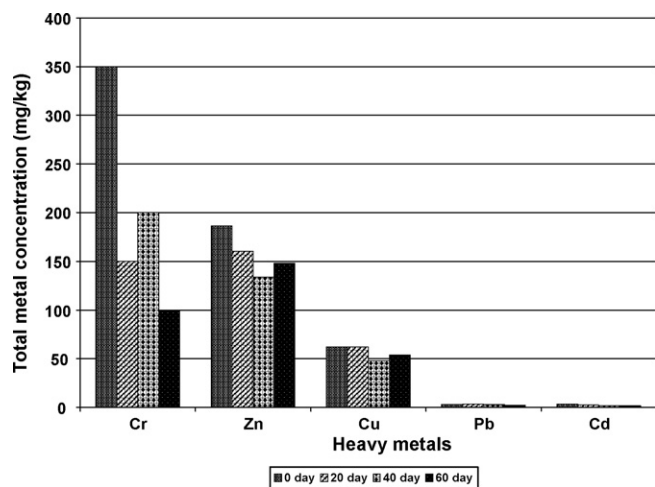


Fig. 2. Total amount of heavy metals during composting of tannery sludge.

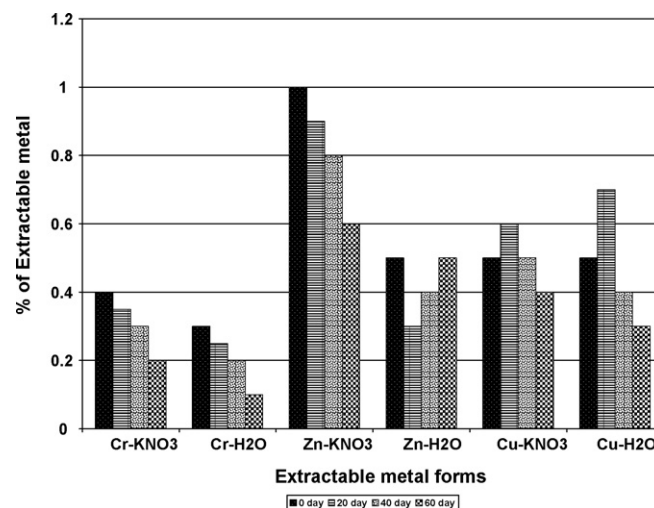


Fig. 3. Extractable metal forms change percentage during composting of tannery sludge [X-KNO<sub>3</sub> (exchangeable) and X-H<sub>2</sub>O (soluble)].

ual 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 [11,34]. 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.

% of total extractable metal

$$= (X\text{-fraction} / \text{total extractable metal}) \times 100, X\text{-fraction}$$

$$= \text{amount of metal in form KNO}_3$$

or X-H<sub>2</sub>O, or X-NaOH or X-EDTA or X-HNO<sub>3</sub>,

Total extractable metal

$$= X\text{-KNO}_3 + X\text{-H}_2\text{O} + X\text{-NaOH} + X\text{-EDTA} + X\text{-HNO}_3.$$

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 (Fig. 3). 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 [8].

For mobilisable fractions (Fig. 4a–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.

Table 7

Total heavy metal contents in the final compost (60 day) and allowable limit for different class compost according to Canadian limit (CCME, 1995).

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

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).

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 involving 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. Hsu and Lo [9] found 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.

### 3.5. Germination index

The germination index of both Chinese cabbage and lettuce exceeded 50% at 40 days and reached 97% after 60 days of composting, revealing loss of phytotoxicity and achievement of compost maturity (Table 8). A germination index value above 50% indicates that the maturity was sufficient and phytotoxic compounds such as acetic, propionic, butyric and isobutyric acid might have not been metabolized, inhibiting germination [25,26,43–45].

### 3.6. Statistical analysis and influence of change of selected variables on metal distribution

Correlation matrices of metal fractions with pH, ash, humic substances and organic matter content were investigated to determine the influence of these selected variables on the changes of metal distribution during composting (Table 9). The metal rearrangement between the fractions could also be approached by the correlation between the changes of metal fractions during composting.

The Cr-H<sub>2</sub>O fraction shows a significant decrease highly correlated with the decrease of pH ( $R=0.99^{***}$ ), the decrease of organic matter content ( $R=0.76^*$ ) and the increase of the amount of ash ( $R=0.90^{**}$ ). According to Henry and Harrison [46], Cr is recognized as a relatively mobile and low water-soluble metal. Kiekens [47] suggests that a large percentage of Cr could be leached in the organic form. Chirenje and Ma [48] suggested the high affinity of Cr to dissolved organic matter. Indeed, the increase of Cr-NaOH shows a weak correlation with the decrease of organic matter ( $R=0.69^*$ ) and the decrease of ash ( $R=0.45$ ), while the increase

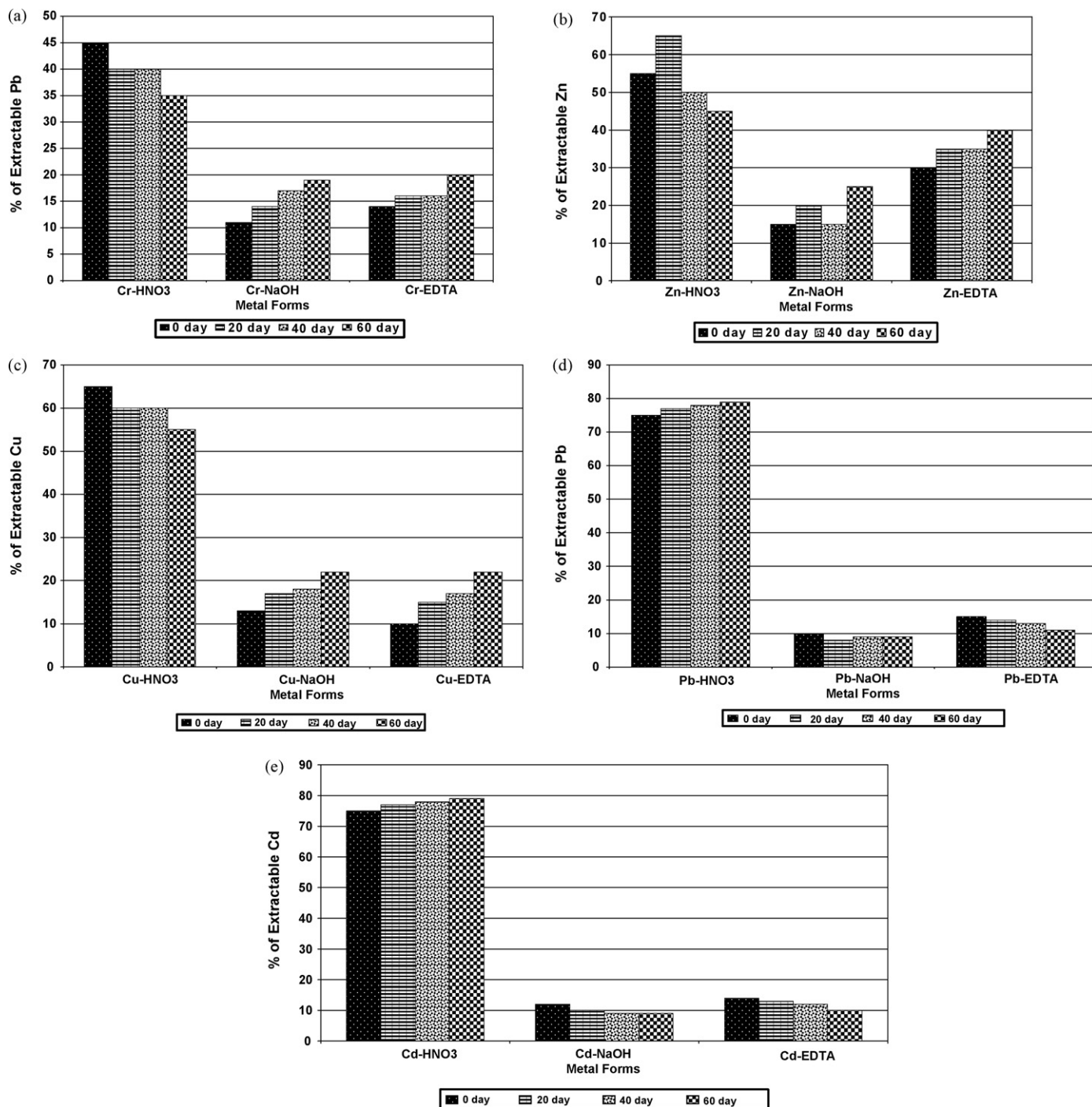


Fig. 4. Percentage of variation of extractable metal forms during composting of tannery sludge (a) Cr; (b) Zn; (c) Cu; (d) Pb and (e) Cd.

of Cr-EDTA presents a good correlation to humic substances and pH. The Cr seems to have high affinity for new-formed humic substances during the maturation phase, or could be attached to organic compounds contributing to the humic substances network.

The decrease of Zn-KNO<sub>3</sub> was significantly positively correlated with the decrease of organic matter content ( $R=0.89^{**}$ ) and the increase of ash ( $R=-0.88^{**}$ ), and Zn-NaOH and Zn-EDTA were well correlated with humic substances. Therefore, the transformation of raw organic matter to stable humic substances during composting process allows the transformation of Zn from exchangeable to stable organic forms.

For Cu, there were good correlation between the decrease of Cu-H<sub>2</sub>O and the increase in humic substances ( $R=0.92^{**}$ ), and the decrease of pH ( $R=0.99^{***}$ ), this is consistent with the known affinity of Cu to organic acids which contribute to the formation of humic substances [49]. Cu-EDTA also shows a good correlation with humic substances ( $R=0.93^{**}$ ). This supports the high affinity of Cu for functional groups OH or COO<sup>-</sup> of humic substances [50,51]. The exchangeable Cu-KNO<sub>3</sub> and humic substances present a good correlation coefficient ( $R=0.93^{***}$ ).

In case of Pb and Cd, mainly the fraction HNO<sub>3</sub> presented a good correlation with the increase of humic substances, which

**Table 8**

Evaluation of Chinese cabbage and lettuce germination index in the aqueous extract of tannery sludge composted for different intervals.

Time/day	Germination index (%)	
	Chinese cabbage	Lettuce
$T_0$	11.1 ± 0.1	7.1 ± 0.1
$T_{10}$	17.0 ± 0.9	13.0 ± 0.4
$T_{20}$	30.3 ± 3.0	22.6 ± 3.0
$T_{30}$	45.5 ± 1.2	40.2 ± 1.2
$T_{40}$	60.4 ± 3.2	55.4 ± 3.0
$T_{50}$	70.6 ± 4.4	63.6 ± 3.4
$T_{60}$	97.5 ± 2.3	97.5 ± 0.3

All values are reported as mean ± standard deviation between three replicates.

confirms the high affinity of Pb and Cd to  $\text{HNO}_3$  form, although in the presence of humic substances [11]. Indeed, Bodog et al. [52] found that Pb and Cd were mainly present in the most resistant fractions such as residual and sulfide fractions of the soil. Unlike Pb and Cd, total Zn and Cu present a significant degree of correlation during composting with organic matter. The decrease of Cu  $\text{HNO}_3$  presents a good relationship with the decrease of Pb, Cd–NaOH ( $R=0.96^{***}$ ,  $0.95^{***}$ , respectively) and with Pb, Cd–EDTA ( $R=0.91^{***}$ ,  $0.90^{***}$ , respectively). For Zn, significant correlations were found between the increase of Zn–NaOH and Pb, Cd– $\text{HNO}_3$  ( $R=0.99^{***}$ ,  $0.98^{***}$ , respectively) or between the decrease of Zn– $\text{HNO}_3$  and Pb, Cd–NaOH ( $R=0.95^{***}$ ,  $0.94^{***}$ , respectively). Thus, the observed affinities of heavy metals to the various fractions after treatment by composting could be ranked as follows:  $\text{KNO}_3 + \text{H}_2\text{O}$ ;  $\text{Cu} = \text{Zn} > \text{Cr}$ ;  $\text{NaOH}$ ,  $\text{Cu} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Cd}$ ;  $\text{EDTA}$ ,  $\text{Cu} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Cd}$ ;  $\text{HNO}_3$ ,  $\text{Pb} = \text{Cd} > \text{Cu} > \text{Zn} > \text{Cr}$ .

**Table 9**

Linear correlation coefficients of heavy metal fractions and total content with humic substance (HS), organic materials (OM), ash, and pH of tannery sludge during composting treatment.

Heavy metals fraction	Humic Substances	Organic materials	Ash	pH
Cr– $\text{KNO}_3$	0.08ns	0.90**	–0.89	0.50ns
Cr– $\text{H}_2\text{O}$	0.94**	0.76*	0.78*	0.99**
Cr–NaOH	0.85**	–0.69*	0.45	0.75*
Cr–EDTA	0.93**	–0.66	0.70	0.87**
Cr– $\text{HNO}_3$	0.90**	0.40ns	–0.09	–0.48ns
Cr-total	–0.09ns	0.95**	–0.09	–0.53ns
Zn– $\text{KNO}_3$	0.07ns	0.89**	–0.88**	0.49ns
Zn– $\text{H}_2\text{O}$	0.75*	0.24ns	–0.28	–0.25ns
Zn–NaOH	0.96**	0.32 ns	0.33	–0.72*
Zn–EDTA	0.93**	–0.08ns	0.07	–0.59
Zn– $\text{HNO}_3$	0.69	0.38ns	–0.40	–0.16ns
Zn-Total	–0.09ns	0.92**	–0.92**	–0.65
Cu– $\text{KNO}_3$	0.93**	–0.14ns	0.07	–0.57ns
Cu– $\text{H}_2\text{O}$	0.92**	0.73*	0.76*	0.99***
Cu–NaOH	0.75*	–0.64*	0.43	–0.51ns
Cu–EDTA	0.93**	–0.65	0.60	–0.84**
Cu– $\text{HNO}_3$	0.88**	0.05ns	–0.07	–0.46ns
Cu-total	0.08ns	0.80*	–0.83*	0.40ns
Pb–NaOH	0.83*	0.15ns	–0.12	–0.44ns
Pb–EDTA	0.80*	0.13ns	–0.08	–0.47ns
Pb– $\text{HNO}_3$	0.97**	–0.15ns	0.18	–0.67
Pb-total	0.53ns	0.57ns	0.55	0.03ns
Cd–NaOH	0.82*	0.16ns	–0.11	–0.43ns
Cd–EDTA	0.81*	0.14ns	–0.09	–0.43ns
Cd– $\text{HNO}_3$	0.96**	–0.16ns	0.17	–0.65
Cd-total	0.54ns	0.55ns	0.52	0.02ns

\*, \*\*, \*\*\* statistically significant at the probability level 0.05, 0.01 and 0.001, respectively. ns: non-significant at same level.

## 4. Conclusions

The study concludes that throughout the 60 days of tannery sludge composting, physicochemical analysis and 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 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 physicochemical 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 consequently considered unavailable for plant uptake.

The amount of potentially bioavailable metals was less than 2%. The germination index for both Chinese cabbage and lettuce was 97% after 60 days of composting, showing that the final compost was not phytotoxic.

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