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Study of the biodegradation and fertility of the co-composting produced from sewage sludge and green waste and its effects on the speciation of heavy metals

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Abstract
This study aims to determine the agronomic value of sewage sludge and green waste compost and the evolution of bioavailability of heavy metals in the course of composting. In this study (60 %) of sewage sludge and (40 %) of crushed green waste were mixed. The mixture of these organic wastes was put in a wooden cubic composter having a volume of (1.5 m^3) for a period of 90 days. The aeration of the mixture was made by manually turning the compost. The results show that electrolytic conductivity (EC) of the compost was 1.8 mS cm^{-1}, pH 7.6 and C/N ratio of 15.4. The total concentrations of Zn, Cr, Cu, Ni and Pb as mg/kg dry compost were 202.1, 98.4, 54.2, 23.2 and 5.4 respectively. They were reduced and agree with the standards of the Canadian limits indicating the maturity of the end product. It has been also observed by Fourier transform infra-red (FTIR) spectroscopic that the final compost improved the concentration of aromatic compounds with respect to the initial state of matter with a decrease of aliphatic groups and a reduction of components easily inhalated by microflors acting during the biological process.

Keywords: Sewage sludge; Composting; Duration; Heavy metals; Germination, Maturity

Introduction

The effect of sewage sludge composting from domestic wastewater treatment plants with respect to their volume on the physicochemical composition especially for heavy metals is an interesting and important research domain with respect to valorization. According to [1,2] the determination of the total concentration of heavy metals does not give sufficient information on the risks of the bioavailability , the remobilization capacity and the behavior of metals in the environment [3]. Land application of sewage sludge is the most cost-effective option of sludge disposal because of its advantages over traditional means such as land filling or incineration. However, land application of sludge represents also a potential threat to the environment because of the presence of pathogens and of toxic pollutants (i.e., heavy metals or organic pollutants). This threat is aggravated when toxic metals are accumulated or mobilized in soils [4-8].

The chemical forms of a metal or speciation allow the estimation of heavy metal bioavailability and are related to the different kinds of the metals, to their bonding strength, either in free ionic form or made complex by organic matter as well as 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 the mixture. These changes could influence the metal distribution in many ways [2,3]:

- through the release of heavy metals during organic matter mineralization,
- during the metal solubilization by the decrease of pH,
- during the metal biosorption by the microbial biomass or metal complexation with the newly formed humic substances (HS) and other factors.

Composting is a stabilization process of aerobic decomposition which has been widely used for different types of wastes. It can reduce the volume of the mixture by40–50%, effectively destroy the pathogens by the metabolic heat generated by the thermophilic phase, degrade a large number of hazardous organic pollutants and provide an end product that can be used as a soil amendment or fertilizer as indicated by [8].

The composting can act on the concentration or the dilution of heavy metals present in the sewage sludge. Verifying, confirming or infirming these results on the sewage sludge mixed with green waste, at different composting stages, is the primary objective assigned to this experimentation. The main physicochemical analyses by the method of Fourier transform infra-red (FTIR) had been carried out and a sequential extraction was applied to the compost during the different stages of composting.

The obtained results allow making decision on the possibilities of using sewage sludge which volume in Algeria is estimated about 100 000 tons /year [9].This value must be considered higher with respect to the wastewater treatment plant**.**Currently, the volume of sewage sludge is around 120 000 tons/ year a quantity that can amend annually 500 000 ha of agricultural land [10].

2. Equipments and methods

2.1Composting

The present experimental study focuses on compost elaboration for valorization of sewage sludge. The raw sewage sludge was taken from the aerobic wastewater treatment plant of the city of Sidi- Bel-Abbes located in the West of Algeria. The 60% of sewage sludge have been mixed with 30% of crushed green waste made of (10% straw of wheat, 10% of farm manure and 10% of dead leaves) and 10% resinous wood chips. The mixture of these organic wastes was put in a wooden cubic composter having a volume of (1.5m^3) for a period of 90 days. With the aim of maintaining aerobic conditions during the process, the heap was turned and mixed every 5 days to provide oxygen for the pile of manual-turned composting. Samples were collected at the end of each week of the composting process from different points of pile (bottom, side, surface and center) to ensure there presentative sampling.

Physical-chemical analysis has been carried out every 30 days (0, 30, 60, and 90 days) in order to determine the period of time that allows obtaining a compost with good physicochemical quality. Table 1 shows the experimental conditions (Sposito’s procedure). Table 2shows the physicochemical characteristics of the raw sludge and the mixture compost.

The samples of the compost used for this physicochemical analysis have been sifted to 20 mm and ground down to 1mm before each analysis. Before sampling the compost, the temperature was measured using an electronic thermometer type (VT100) equipped with a penetrating probe. The temperatures were taken every two days. The dry matter immediately after sampling and a part of each 20mm sifted compost has been dried in an isothermal chamber at 105°C during 48 hours up to a constant weight [11].

The pH is measured for 10 gr of compost in 100ml volume of bi-distilled water. The pH measure was made after 10 minutes of homogenization at ambient temperature using a Metrohm pH meter 744.

The electrical conductivity for the same conditions, proportion and volume as for the pH has also been determined. The total electrical conductivity is measured on a sample of 1/25(mass compost/ volume of solution) at 25°C by means of two platinum electrodes [11].

The proportioning of the total organic carbon referred to as TOC has been made using Anne’s method [12].The organic matter is oxidized by a mixture of bi-chromate of potassium and sulfuric acid. The excess of bi-chromate is dosed by the Mohr’s salt. The proportioning of nitrogen was made using Kjeldahl’s method.

The proportioning of ammonium ions NH_4^+ has been obtained by distillation in alkali environment and the nitrate NO_3^- was obtained by reduction using Devarda’s alloy technique [13]. Ash content was determined after calcinations at 550°C. Decomposition (Dec) was calculated according to the following formula [11]:

$$\text{Dec}\ \% = 100 \times [(A_f - A_i)/A_f \times (100 - A_i)] \times 100, \quad (1)$$

where: A_f is final ash and A_i is initial ash.

2.2 Extraction and assay of humic substances

The humic acids (HA) and fulvic acids (FA) are extracted by shaking a rotating evaporator during two hours from 10 gr of compost added to 100 ml of NaOH 0.1 M in 250 ml Erlenmeyer bowls. This soluble fraction in alkaline environment (HA+ FA) is recovered by centrifugation at 2500 rpm during 25 min. The solution is acidified at pH 1 by adding chloride acid HCl 6M after one night at a temperature of +4 °C. The soluble fraction in fulvic acid (FA) environment is separated from the insoluble fraction in humic acid (HA) environment by centrifugation at 10000 rpm during 10 min. The two fractions are dried in the oven at 105 °C during 48 hours [14].

2.3 Extraction of lignin

The fractioning made is adapted to the method of [8].The lignin and the hemicelluloses are extracted from the dissolution in a mixture of acetic acid- formic acid –water (50-30-20 v/v). The ratio solid/liquid is 1/12 or 60 ml for 5 gr of compost. The first step consists of impregnation during 30 min at 50 °C in the reactive environment then during 1 hour at 107 °C (azeotropic boiling point of the mixture acid/water). The soluble fraction is then recovered by filtration (Whatman glass fiber filter). The acids used are separated by distillation from the residual made of lignin and hemicelluloses. The addition of water to this residual leads to the precipitation of the lignin whereas the hemicelluloses stay in solution. A centrifugation of 30 min at 10000 rpm has allowed the separation of the two bio-polymers. The lignin is then washed with bi-distilled water up to a neutral pH then dried at 105 °C during 48 hours.

According to the French association of normalizations [15], to obtain the total Zn, Cu, Pb and Ni content; 1 g of each sample was mineralized for 4 h at 550 °C, and then dissolved in 5 ml of hydrofluoric acid. The obtained solution was evaporated to dryness, the residue was then dissolved with concentrated HNO_3/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 [16,17,18].This method is used due to the availability of instruments necessary for the experiment.

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 (1/5) (Table 1). However, as the final reagent (4 M HNO_3) still did not extract all of the residual metal, standard test [15] was applied on as hed residue obtained from the last step of the extraction. The amount dosed represent ''residual fraction''. All filtered supernatants were directly analyzed by Plasma-Atomic Emission Spectrometry (ICP).

Table 1: Extractants and experimental conditions used to determine various extractable heavy metal forms (Sposito's procedure).

Extractant		**Duration of shaking**	**Heavy metal form**
(1)	KNO_3 (0.5 M)	16 hours	Exchangeable "mobile"
(2)	H_2O	2 hours, three times	Soluble "(mobile)"
(3)	NaOH (0.5 M)	16 hours	Organically bound "mobilizable"
(4)	EDTA (0.5 M)	6 hours	Organically complexed
			or carbonates "mobilizable"
(5)	HNO_3 (4 M)	16 hours in 80°C	Sulfides "mobilizable"

2.4 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 the compost substrate extractas described in detail in. Two gram 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 a 0.45 µm Millipore filter. Two mL of the 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 ^{o}C for 4 days [19].

2.5 Fourier transform infrared spectroscopy

KBr pellets of each sample to be analyzed were prepared by compression under vacuum of a mixture of 2mg dry sample (105°C, 24 h) with 400 mg KBr. Spectra were obtained with a (FTIR) Perkin Elmer 1600 spectrophotometer by subjecting the pellet to a frequency of 4000-400 cm^{-1} at 16 nm s^{-1}.

3. Results and Discussion

3.1 Progression of composting

Seven analyses made on 20 parameters were carried out every 30 days from 0to 90 days ($t_{0,}$ t_{30}, t_{60}, and t_{90}) show an evolution of different parameters and allow identifying the best composting duration for obtaining better and interesting characteristics.

The recorded temperature during the process (Fig1) shows a good evolution of the composting process by succession of two phases in microbiologic activity [20,21].The initial stabilization phase is characterized by an increase in temperature which reaches 69°C after a period of four days corresponding to the degradation of simple organic compounds. Then, during the maturation phase, the temperature decreases progressively until ambient temperature of 27°C corresponding to the degradation of lignin-cellulolytics molecules. In other works, some authors suggested that the temperature could be considered as a good indicator at the end of the bio-oxidation phase, which is in good agreement with the observations of [22, 23].

According to [24], the measure of the temperature is an indirect measure of the degradation intensities. During the humification process, the pH slightly increased from 7.4 to 7.6. The disappearance of fat acids can explain the increase in pH during the composting process. [25] also observed a similar increase in pH (from 7 to 9) during the composting of industrial waste of olives. The olives waste contains an important part of lipids and free organic acids [25]. [26] suggested the freed ammonia ions NH_4^+during the process contribute to the increase in pH.The conductivity of the compost is highly dependent on its contained nutriments. However, it is noticed a decrease in conductivity from 2.2 to 1.8 mS.cm^{-1} after a period of 90 days. It is observed that the final compost does not overrun the salinity limit value of 3 mS.cm^{-1}to be used in good fertilizers [27]. The conductivity is very variable according to the compost even it has a natural tendency to diminish with the progression of maturity [28].

Table 2: Physico-chemical properties of raw sludge (S) and sludge mixture at different times of composting (results expressed in dry basis).

Properties	S	0 days	30 days	60 days	90 days
Moisture %	55.7± 0.2	53.8 ± 0.3	62.2 ± 0.2	69.4 ± 0.1	66.7 ± 0.1
pH	7.1± 0.1	7.4 ± 0.05	7.3 ± 0.1	7.1 ± 0.1	7.6 ± 0.1
E.C (mS cm^{-1})	2.1± 0.07	2.2 ± 0.1	1.8 ± 0.1	1.8 ± 0.05	1.8 ± 0.05
TOC %	17.5± 0.1	35.5 ± 0.6	36.6 ± 0.1	42 ± 1.09	29.3± 1
TKN %	1.1± 0.01	1.3 ± 0.1	1.4 ± 0.2	1.9 ± 0.05	1.9 ± 0.1
Ash (g kg^{-1})	62.8± 1.3	62.8 ± 0.2	64.3 ± 1.02	66.3 ± 2.2	62.4 ±0.5
C/N	15.9	27.3	26.1	22.1	15.4
Dec %	/	/	6.5	34.3	66.3
N-NH$^+_4$ (mg g^{-1})	/	2.5 ± 0.1	2.3 ± 0.1	2.6 ± 0.1	1.9 ± 0.1
N-NO$^-_3$ (mg g^{-1})	/	2.7 ± 0.1	2 ± 0.05	0.5 ± 0.1	0.06± 0.3
Mg total (g kg^{-1})	2.1± 0.2	2.5 ± 0.1	2.6 ± 0.05	2.8 ± 0.1	2.8 ± 0.3
K total (g kg^{-1})	6.4± 0.15	13.6 ± 0.1	9.9 ± 0.1	8.7 ± 0.2	8.7 ± 0.2
P total (g kg^{-1})	3.6± 0.2	2.3 ± 0.1	2.2 ± 0.05	2.5 ± 0.1	1.9 ±0.05
Mn total (mg kg^{-1})	59.5± 0.3	48.6 ± 0.05	50.6 ± 0.5	50.6 ± 0.5	78.8 ±0.6
Fe total (mg kg^{-1})	3650± 0.01	4875 ± 3.6	4777 ± 2.6	3058 ± 1.5	3703 ±1.5
Humic acids (g kg^{-1}dry matter)	/	29.5 ± 1.3	30.6 ± 0.5	36.5 ± 0.6	39.1 ± 0.6
Fulvic acids (g kg^{-1}dry matter)	/	32.1 ± 1	23.2 ± 1.4	23.8 ± 2.05	10.9±1.02
Lignin (g kg^{-1})	/	305.8 ± 1	287.4 ± 4.5	298.7 ± 0.3	275.6±3.7
Cellulose (g kg^{-1})	/	74.5 ± 1.3	68 ± 1	52.4 ± 0.6	54 ± 2
Hemicellulose (g kg^{-1})	/	132.1 ± 1.9	131.3 ± 0.3	120.2 ± 1.2	66.1± 1.7

where: E.C: Electrical conductivity, TOC: total organic carbon, TKN: total kjelahl nitrogen, Dec %: degree of decomposition.

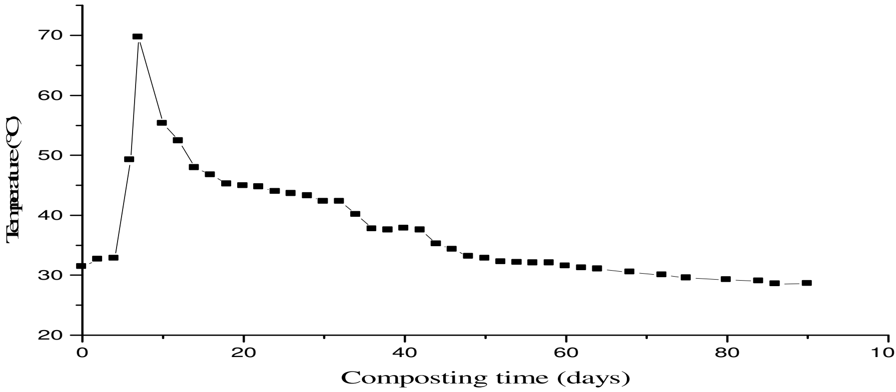

Figure 1: Variation of temperature during composting of sewage sludge and green waste.

After a period of 90 days, the change in C/N ratio goes from 27.3 to 15.4 and the quantity of ash from62.8 to 62.4 g/kg^{-1}which reflects the microbial decomposition of the organic matter and the stabilization during the composting. The first phase of the decrease of organic matter can be attributed to an important degradation and a mineralization of organic matter for a period between 0 and 50 days. The second phase is characterized by the stabilization of the two parameters indicating a retardation of the mineralization and the beginning of the maturation phase. The organic nitrogen presents an increase for a period from 0 to 90 days respectively proportions of 1.3 and 1.9 of dry matter as given in Table 2. This effect is due to its concentration generated by the high degradation of carbonized compounds reducing then the total mass of the compost [29].

The nitrogen N with respect to the dry mass of the initial mixture decreases during the composting. For this concentration of nitrogen and the mineralization of carbon, the C/N ratio decreases during the composting for values between 27.3 and 15.4. As indicated in many investigations [30,31].This decrease is related to the degree of maturity which is a preponderant factor. A great part of the organic matters in the initial mixture are mineralized during the composting process. The residual organic matters are transformed in other organic matters with respect to humic substances produced by the humification process [32]. After a period of 90 days, the decomposition of the mixture has reached a proportion of C/N ratio of 15.4. A slight acidification of the mixture during the first 10 days is the combined result of bio-acid production during composting and the carbon dioxide CO_2 during the aerobic decomposition of the organic matter [33].

The observed decrease of nitrates is related to the nitrification process during the composting as indicated in Table 2 which reflects the maturity of the compost[34].The inorganic nitrogen $N\text{-}NH^{+}_{4}$ and $N\text{-}NO^{-}_{3}$ are in general affected by the action of proteolytic bacteria which a part is incorporated in the stable organic forms such as amid heterocyclic nitrogen. The organic matter is decomposed then, transformed to stable humic compounds [35]. The humic substances (HS) had the capability of interacting with metallic ions to stamp the pH and to act as a potential source of nutritive substances for plants. The decrease of C/N ratio is varying from 27.3 to 15.4 and put into evidence the supported decomposition of organic matter. The rest of the process is distinguished by a phase of stabilization showing a retardation of the mineralization and indicates the beginning of the maturation phase according to [30,31]. This diminution is related to the degree of maturity. [36] reported that the modifications of the C/N ratio reflect the decomposition and stability of organic matters as mentioned in Table 2.

After 90 days, a biodegradation is reached respectively for the cellulosis, hemicellolusis and lignin. The micro-organisms making rapid call to the glucid oligomers freed during the degradation of the cellulosis as an energy source which is diminished during the composting of values in the range of 74.5 to 54g/kg^{-1}. The chemical fractioning of the lignin has slightly decreased from 305.8 to 275.6 g/kg^{-1} which confirms the resistance of the compound to the biodegradation by undergoing a partial bio-transformation [37,38].This decrease has been correlated to the increase of humic acid [39]. The hemicellulose is the component that has undergone the most important degradation. The value is higher at the beginning of the composting cycle going from 132.1to 66.1g/kg^{-1}. This compound and others such as the xylans are easily degraded with respect to the cellulosis and lignin. According to these results the low ratio of the decomposition of the cellulosis and hemicelluloses at the beginning of the composting process is due to the inhibition of the micro-organisms activity during high temperatures. The total P, K, Mg, Fe and Mn were more important to use this material as mineral fertilizers [27].This material will increase the stable organic N and humic carbon and improve mineral elements necessary for the humification process results show the process during the stabilization of organic matters and composting. This corresponds partially to the transformation of lignin into humic acids. On one hand, the concentration of humic acids increases from 29.5 to 39.1 mg/g; on the other hand, the concentration of the fulvic acids varies from 32.1and 10.9 mg/g between the period from 0 to 90 days of composting a great increase of the ration HA/FA. Several studies revealed that the increase of HA is an indicator of the degree of humification of organic matters and of the degree of maturity of composts [40, 36]. It has also been explained that the humification of organic matters takes place mainly through the HA fraction and less through FA fraction [36]. Thus, the ratio HA/FA is then an indicator of humification processes than a maturity index.

According to [41] the increase in HA/FA ratio comes from the formation of HA by polymerization of the FA or by the degradation of non-humic substances of the FA fraction followed by the formation of AH poly - condensed humic structures. In fact, the infrared spectra of the compost at the different phases of treatment (06, 30,60 and 90days show the locations of similar peaks but the relative intensities of the absorbance are seen to change during the composting process (Figure 2). The interpretation of the recordings is based on the data of numerous studies [42,31,43] and are summarized in Table 3.

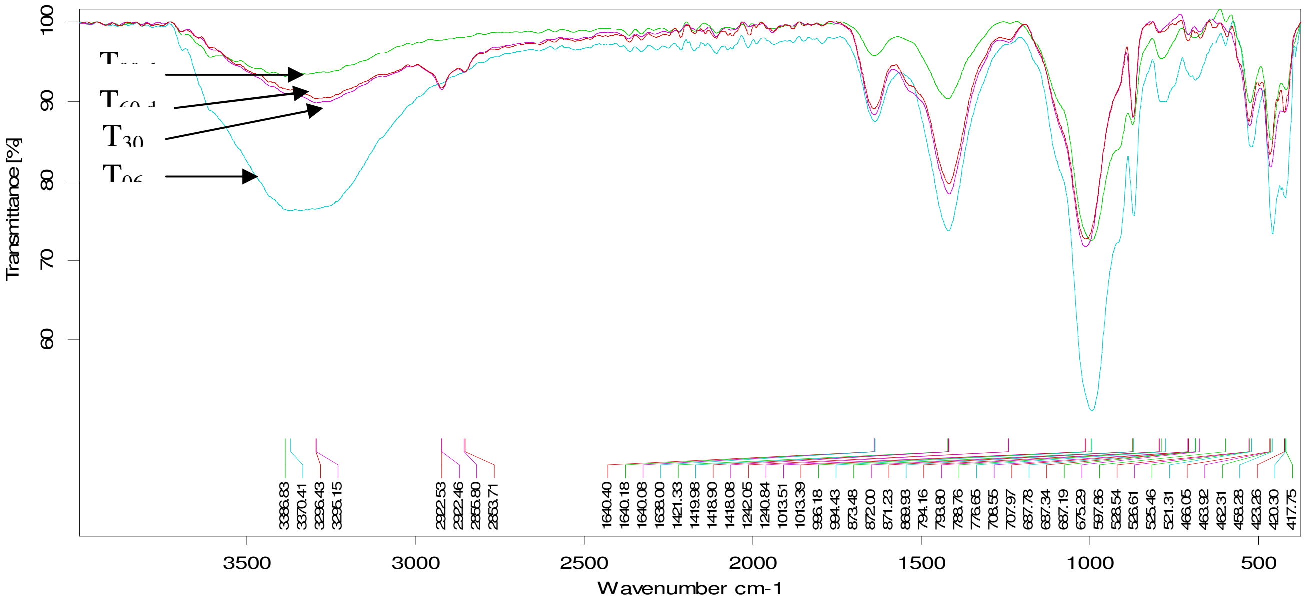

Figure 2: Infrared spectra showing the evolution of a sewage sludge and green waste during composting.

Table 3: Attribution of absorbance bands for infrared spectra.

Wave-number (cm^{-1})	Assignment
3400	- O–H stretching in alcohols and carboxyl functions; - bonded OH groups of phenols; - N–H stretching in amides and amines second.
2922	- Symmetric C–H stretching of aliphatic chains (fatty acids, waxes and aliphatic components).
2855	- C–H stretching of aliphatic methylene.
1640	- Aromatic C=C, C=O stretching of amide groups; - C=O of quinone and/or H-bonded conjugated ketones in acids and primary amides.
1421	- C–H deformation in lignin and carbohydrates; - phenolic OH; - COO– asymmetric stretching and stretching of O–distributed aromatic rings.
1013	- C–O–C stretching of polysaccharides; - Si–O stretching.

The evolution of FTIR spectra exhibit the same absorbance area at different stages of composting, but they differ in the intensity of some peaks. It noticed a remarkable decrease of aliphatic structures and lipids (3400, 2855 cm^{-1}) that probably corresponds to the fatty acids and lipid compounds contained in the sludge and carbohydrates (1421-1013 cm^{-1}). In parallel the decrease of intensity of aromatic structures occurred with phenolic OH and carboxylates extrimity $–COO^-$ around (1421 cm^{-1}).

These changes indicate themicro-organisms used in the structures and the peptide carbohydrates such as polysaccharides, cellulose and hemicelluloses in their energy needs, following the disappearance of the elements more easily degraded. Accordingly, all of these physico-chemical changes and spectroscopic characteristics are similar to the results of other studies and could reflect the stability and maturity of the end product [44, 30, 42].

3.2. Heavy metal speciation during composting

Composting can concentrate or dilute heavy metals present in sewage sludge [1, 2].Lowering the amounts of those metals depends on metal loss through leaching. The increase of metal level is due to weight loss during the composting process following organic matter decomposition, release of carbon dioxide and water and mineralization processes [45, 46, 47].

Figure 3 illustrates the total concentration of metals (Zn, Cr, Cu, Ni, Pb) during composting. The order of total metal content in the composted sludge was Zn >Cr >Cu > Ni >Pb. During composting, all total metal amounts decreased except for Ni.

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, by a change of moisture and change of other oxide and anionic conditions in the area increasing so the solubility of metals[47, 48, 27].

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, the metal total concentration is steady indicating that leach ability is stopped; this demonstrates the interest in mature compost for land application.

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 According to French association of normalizations [15] . Therefore, even 4 M HNO_3 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.

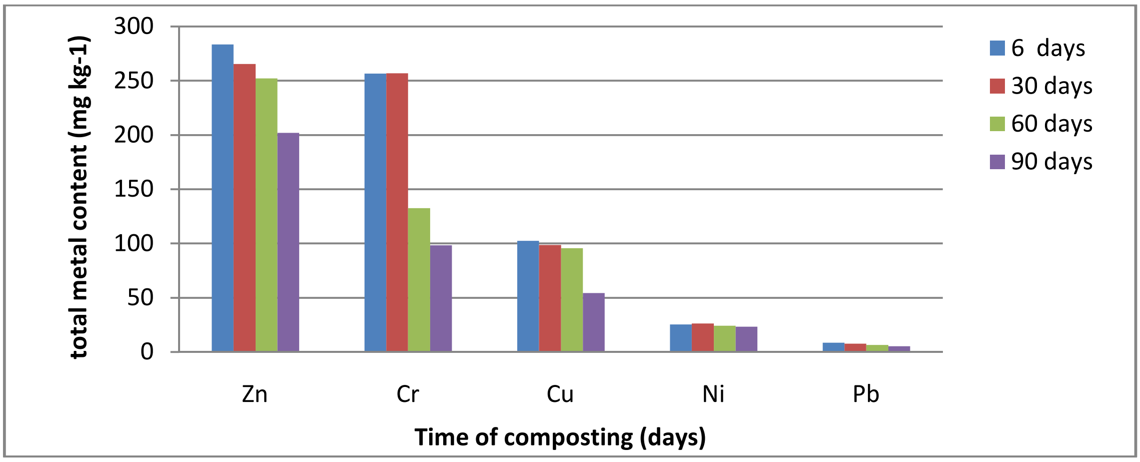

Figure 3: Total amounts of Heavy Metals during Composting of Sewage Sludge and Green Waste.

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 Canadian Council of Ministers of the Environment Standards (Table 4) [49] as available recommendation for sludge compost. This is confirmed by the values obtained from other research for different sludge composts [2,50]. 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– HNO3 (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_3 + H_2O). Similar results have been reported by [2, 27].

Table 4 : Heavy metal contents in the final compost (90 days) and limit values for Class A of composts ‘‘which have no restrictions in use’’ and Class B of compost ‘‘which can be used on forest lands and road sides and for other landscaping purposes’’, according to Canadian normalization [49].

Heavy metal	Final compost content (mg kg^{-1} dry wt)	Allowable limit (mg kg^{-1} dry wt) Class A	Allowable limit (mg kg^{-1} dry wt) Class B
Zn	202	500	1850
Cu	54.2	100	757
Pb	98.4	150	500
Ni	23.2	62	180
Cd	nd*	3	20

* nd : non- dectectable.
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).

A good correlation coefficient (R = 0.96) was found at each stage of composting between metal total amount and total amount 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 the percentage (%) of total extractable amounts.

$$\% \text{ of total extractible metal} = (\text{X-fraction} / \text{total extractible metal}) \times 100 \quad (2)$$

Where:
(X-fraction = amount of metal in form KNO_3 or X-H_2O, or X-NaOH or X-EDTA or X-HNO_3),
(Total extractible metal = X-KNO_3+ X-H_2O+ X-NaOH+ X-EDTA + X-HNO_3).
We observe, the mobile fractions X–KNO_3 and X–H_2O of Cr, Zn, and Cu tended to decrease (Fig 4). The element Pb was not detected in the easily mobile class at any time of composting; indeed, Pb is known to be almost insoluble in water [49].

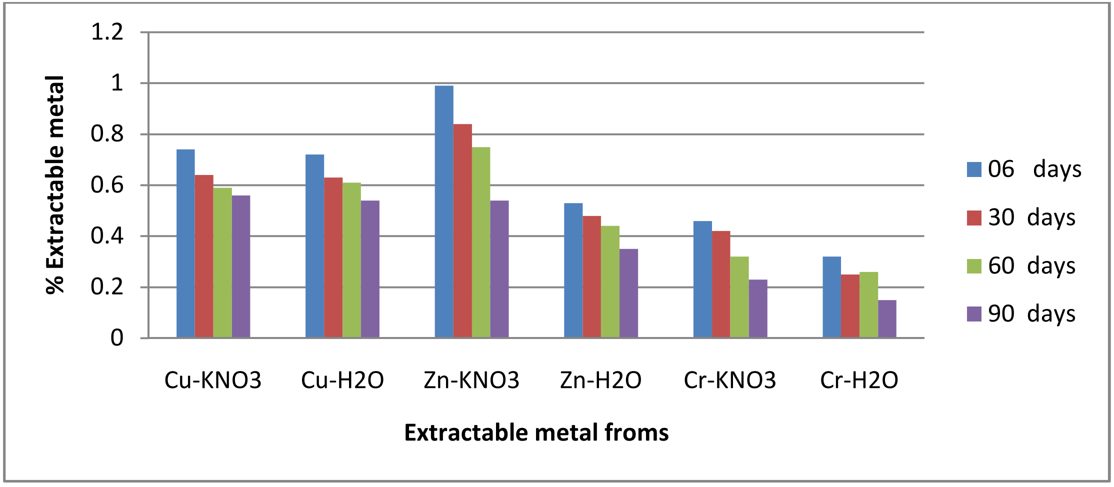

Figure 4: Percentage of Extractable Metal Forms Change [(X-KNO_3 (Exchangeable) and X-H_2O (Soluble)] During Composting Sewage Sludge and Green waste.

For mobilizable fractions (Figure 5, a-e), the distribution of Extractable Total Metal (ETM) showed some changes in the composting which depends on the metal in question and the physicochemical properties of the area. For mobilizable fractions (Figure 5, a-b) of Cu and Zn during composting there was a decrease of the X-HNO_3fraction with an increase of X-EDTA and X-NaOH froms. In contrast, Pb showed a slight increase of X-HNO_3 with a decrease of NaOH and EDTA soluble forms. For Cr, it presents a significant decrease of X-HNO_3 fraction and an increase under the form of EDTA and NaOH (Figure 5, c- d).
During composting process, in the thermophilic phase, intense microbial decomposition of organic matter was achieved and could involving the release of Ni from organic sites (Figure 5, e).The results of selective extractions applied to these composts put into evidence greater heavy metals concentrations in the most resistive fractions: non extractible > HNO_3> EDTA > NaOH with negligible quantities in the labile fraction: exchangeable + soluble. This allows to suggest a great immobilization of metals by the resistive fractions, thus a high reduction of their bioavailability for the plant.

Conclusion

The results of the present study show that the two classical phases of composting resulting from microbiologic activity were identified as the biodegradation followed by the stability and maturity of the final product. The C/N ratio reached the optimal level (15.4) of stable compost. Inorganic nitrogen is transformed in stable organic forms. The compost can give all the micro and macro nutriments required for plant growth. The lower total concentration of Zn(202.1), Cr(98.4),Cu (54.2), Ni(23.2) and Pb(5.4) makes the final compost acceptable for use in agriculture. The follow of heavy metals characterization during composting shows that the mobility and bioavailability of metals depend on other physicochemical properties such as the decomposition of the organic matter, humic substance content, pH as well as the affinity of metals to various chemical forms. The largest proportion of metal concentrations was found in the residual fraction and fractions more resistant to extraction indicating that metals were in more stable forms and consequently considered unavailable for plant uptake. The amount of potentially bioavailable metals was less than 2%.The spectroscopic analysis FTIR reveals the biodegradation of components which can be easily inhaled by microorganisms such as aliphatic and peptidic structures as well as carbon hydrates especially celluloses and hemicelluloses.

This investigation revealed that the total concentrations of heavy metals agree quiet well with some typical soil sampling standards considered for purpose of comparison. The results of the principal physical and chemical properties and FTIR spectroscopic characterization of the sludge compost show the stability and maturity of the end product and thus make it suitable for agricultural use utilization.

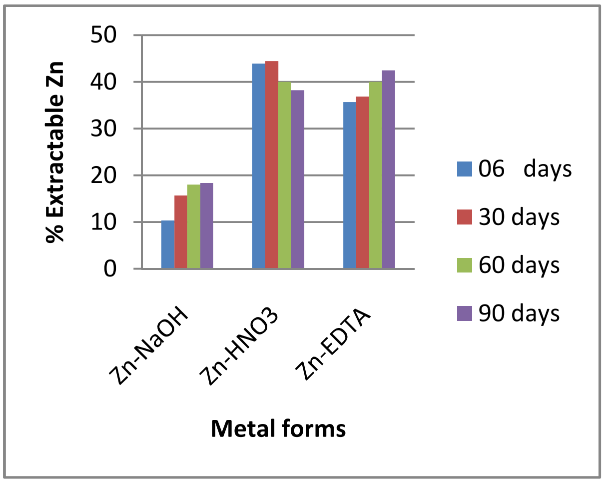

Figure 5 (a)

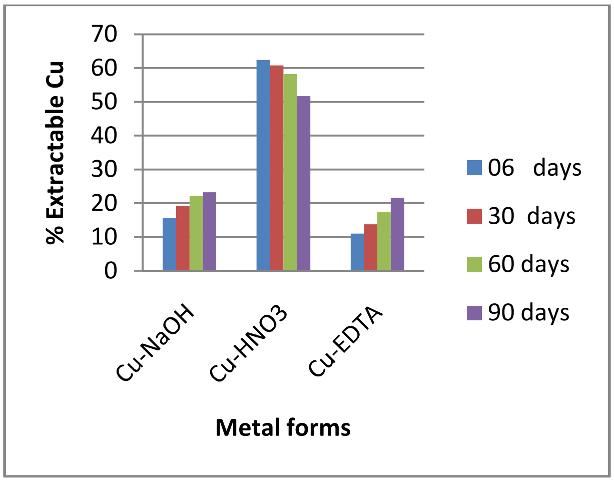

Figure 5 (b)

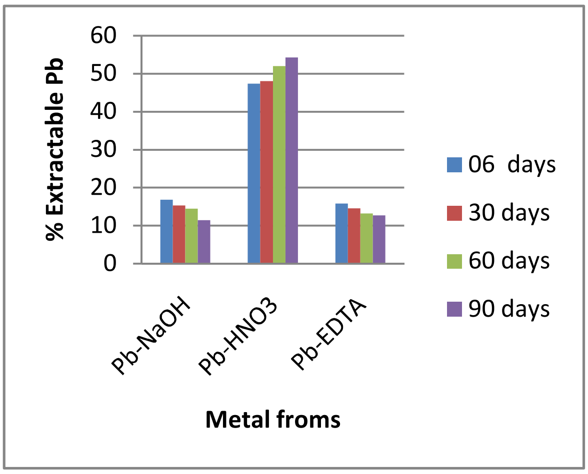

Figure 5 (c)

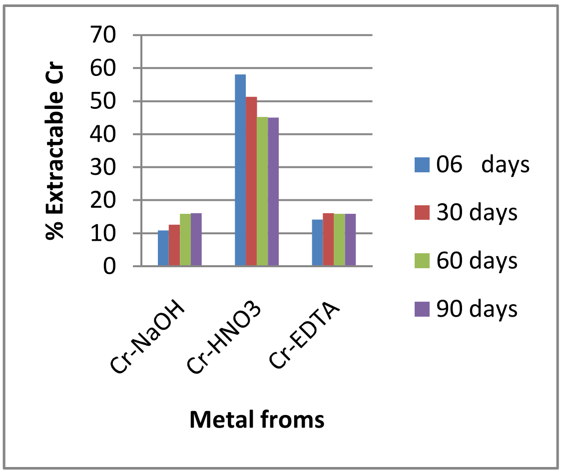

Figure 5 (d)

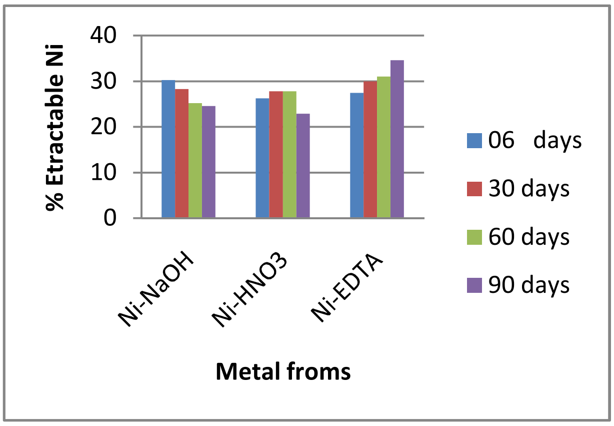

Figure 5 (e)

Figure 5 (a- e): Percentage of Variation of Extractable Metal Forms during composting Sewage sludge and Green waste.

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