Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 4, Page 1277-1283

http://www.jmaterenvironsci.com /

Valorization of agro-industrial waste by bio-process aerobic "composting"

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Received 18 Jul 2016,
Revised 21Oct 2016,
Accepted 28 Oct 2016

Keywords

- ✓ Agro-industrial waste;
- ✓ Development;
- ✓ Composting;
- ✓ Humic substances;
- ✓ FTIR;
- ✓ Heavy metals.

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Abstract

The results of physicochemical analyzes of the compost obtained from food waste after 6 months of composting highlight:

- a value of pH (7.6) in the optimum margin for bacterial growth from 6 to 7.5 and fungi from 5.5 to 8.0.
- an enrichment of compost in organic carbon (37.70%) and in organic matter (64.99%)
- an enrichment of compost in humic substances (265.728 g / kg).
- a transformation of aliphatic structures in aromatic structures more stable and condensed.
- a very low concentration of heavy metals which are infinitely far from the most severe standard even if metallic elements were considered.

Spectroscopic characterizations were carried out and show that the obtained compost is mature and stable. The amount of nutrients (P_2O_5 + K_2O + CaO + MgO) is 10.57%. In light of these results, the obtained compost is a stable, hygienic, rich product in fertilizing elements (P_2O_5 + K_2O + CaO + MgO), in organic matter and humic substances. This finding can open the way for agricultural development.

1. Introduction

The increase of the Togolese population is followed by a significant waste production, including agro-industrial waste from oranges zests, grapefruit, lemon, cottonseed hulls and lemongrass. This agro-industrial waste contributes to the environmental pollution. Citrus juice is obtained by pressing the fruit. The remains of pulp and zest become useless and harmful to the environment [1]. These wastes, which are rich in organic matter and mineral elements, could make an interesting contribution to the soil if recovered by composting.

The direct use of these wastes poses many risks and constraints related to their control and use due to the possible presence of bacteria, viruses and protozoa such as E. coli, Salmonella, Listeria, fecal Streptococci and Sulfito-reducer. Therefore, these wastes must be conditioned chemically and biologically before any use. Experiments carried out in the USA and Europe showed that composting is a simple biological technique, which makes it possible to recover these wastes as long as the trace elements (Cd, Pb, Cu and Zn) are managed.

Composting is a biological process of degradation and humification of organic matter. The final product is very stable, free from phytotoxicity and pathogenic microbes [2]. It is an excellent soil amendment. Very rich in humic substances, it improves the physical, chemical properties and stimulates the soil biological activity [3]. Furthermore, the compost contains nutrients for plants [4]. Before using the compost for soil fertilization, itshould reach maturity. The parameters often used to evaluate the maturity and stability of a compost are chemical, physical, biological and spectroscopic [5]. The primary purpose of this work was the valorization of citrus wastes rich in organic matter, humic substance and fertilizing elements. We composted the wastes with cottonseed and lemongrass shells to obtain the physico-chemical and spectroscopic characterizations [6].

2. Materials and methods

2.1. Composting procedure

A mixture of zests of oranges, grapefruit, lemon, cotton seed husks, lemongrass characterized by a humidity of 55%, was compost in heaps for 6 months. The compost was produced in laboratory-scale tanks (1.2 mx 1.2 mx

0.5 m) under a hangar to protect the compost from heavy rain, excess sun and runoff. A slope at the bottom of each tank and glances facilitated the evacuation of watersurplus and luxiviats. The materials are deposited alternately in three series of layers (Table 1). Aeration was carried out every 8 days during the composting. The purpose of this waste mixture was to balance the C / N ratio and moisture to meet the optimal conditions for degradation and improvement of the compost nitrogen content [3, 4].

Table 1 : Homogeneous mixture of 03 waste

Types of waste	Quantity
Citrus fruits scrap	33Kg
Seed hulls of cotton	15 Kg
Waste of citronella	9 Kg
TOTAL	57 Kg

2.2. Analytical method

2.2.1. pH measurement

The pH measured is that of a compost sample suspension dissolved in distilled water (pH-water) in a ratio of 2/5 [7]. After 30 min of stirring and 2 h of pause, the measurement was made using a multifunctional pH-meter type HANNA HI 9812-5.

2.2.2. Organic matter

The organic matter content is determined by two methods: material calcinations at 550 ° C. for 4 h in a Nabertherm electric controller type P 320 [8, 9, 10] and by the Walky and Black method described by Aziablé and Al., 2014 [7].

2.2.3. Humic substances

Humic substances extractionwas carried out by 0.1 N NaOH with 2 h stirring and the experiment was repeated several times until a clear extract was obtained. A pre-treatment with water is carried out under the same conditions to eliminate certain soluble molecules like sugars, amino acids, etc. The separation of the humic and fulvic acids was carried out by precipitation in a strongly acidic medium of pH = 2; At 4 ° C for 24 h. Different humic fractions determination was carried out after carbon oxidation by $KMnO_4$ in an alkaline medium [11,12].

2.2.4. Metal trace elements content and chemical composition

Trace elements total content as well as the chemical composition were determined using ICP (Inductively Coupled Plasma) after mineralization by hot acid etching of the samples with aqua regia (1/3 HNO_3, 2/3 HCl).

2.2.5. Infrared spectroscopic analysis (FTIR)

This method is based on electromagnetic radiations which allow to assign the infrared absorption bands to the functional groups. The infrared spectroscopy technique was used on compost samples primarily dried at 105 ° C and then mixed with potassium bromide (KBr). The mixture wasat that point pressed into pellets. The analyzes were carried out using a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and OPUS 6.5 software (128 scans at a resolution of 2 cm^{-1}). The spectral data are obtained as absorbance values over a frequency range of 4000-400 cm^{-1}.

2.2.6. Thermogravimetric and Differential Thermal Analysis

Differential thermo-gravimetric and thermal curves of the compost were carried out on a Labsys apparatus of the type TG DTA DSC 1600 ° C. Analyzes were carried out in platinum crucibles in air (combustion) in a temperature range from ambient to 1000 ° C with a ramp of 5 ° $C.mn^{-1}$

2.2.7 Germination test

Phytotoxicity is a peculiarity of composts which makes it possible to evaluate their maturity. It was in that perspective that the composts effect on the germination of maize seeds (Zea mays) was measured by the percentage of germination defined by GR, germination rate.

To do so, we used sand / compost mixtures as follows:

- 100% compost
- 1/2 (v / v) of compost and 1/2 (v / v) of sand

- 1/3 (v / v) compost and 2/3 (v / v) sand
- 1/4 (v / v) compost and 3/4 (v / v) sand
- 100% sand

(v / v): part by volume

In each pot we sow 10 corn seeds (*Zea mays*), considered as staple crops in Togo and a control pot made up of 100% sand.

The number of germinated seeds was counted. The germination rate, as a percentage, is calculated according to this Formula:

$$GR\ (\%) = 100 \times NGG / NGS\ [13]$$

NGG = Number of sprouted grains;
NGS = Number of grains sown.

Table 7 shows the results of this test, expressed as the number of seeds which germinated after six days of growing.

3. Results and Discussion

3.1. Physico-chemical parameters

Table 2 shows the physico-chemical parameters of the compost used.

Table 2: Physico-chemical parameters of the compost used

	Ph	CO (%)	MOw (%)	MOp (%)	TH (%)
Compost	7.6	37.70	64.99	67.92	68.77

CO: Organic carbon; MOw: Organic matter determined by the method of Walky and Black; MOp: Organic matter determined by the method of loss on fire; TH: Water content.

The pH value of the compost was 7.6. Mature composts have a pH close to neutrality or higher (between 7 and 9) [14]. The pH value was within the optimal margin for the development of bacteria 6-7.5 and fungi 5.5-8.0 [15, 11]. The TOC content of the compost was 37.70%, this value showed the richness of the carbon raw material, indicating a significant presence of organic matter. This important organic matter content of this compost would improve soil properties if used as an organic input.

3.2. Humic substances of the compost

The humic solution extracted from the compost corresponds to 265.728 g / kg of compost material. Chemical fractionation of the compost material made it possible to differentiate the different humic fractions. The organic matter mass contents of the various fractions of the compost are presented in Table 3. These results indicated that the biodegradation of the organic matter is accompanied by enrichment of the compost in humic acids. Likewise, a higher polymerization of the humic acid was noted and the AH / AF ratio of 2.94 was a confirmation. These results followed those of EL Herradi et al., 2014 [16]. This high ratio (AH / AF) could be explained by the formation of complex molecules (humic acids) and polymerization of simple molecules (fulvic acids). The relative AF / SH fraction of 0.25 was low, indicating the intermediate nature of AF (fulvic acids) to the formation of large molecules of HA (humic acids).

Table 3*:* Composition in humic substances of the compost

	SH g/Kg	AH g/Kg	AF g/Kg	AH/AF	AF/ SH
Compost	265.728	198.258	67.47	2.94	0.25

3.3 Thermal analysis of compost

Thermal analyzes of the compost were carried out under oxidizing atmospheres (air) corresponding to a combustion.

The ATD of the compost made in air (FIG. 1) showed that between 33 and 185 ° C, an endothermic phenomenon occurs due to the dehydration of the compost. Alike, the mass loss associated with this phenomenon confirmed the large domain covered by the width of the peaks relative to OH functions observed by IR. However, the decomposition of organic matter between 200-550 ° C was carried out in two stages. The first exothermic phenomenon between 200-366 ° C is often related to the decomposition of carbohydrates [17, 18]. The second phenomenon between 367-550 ° C is generally related to the degradation of aromatic compound. These results were similar to those of Dell'Abate et al., 2000 [19]. The latter showed that during the

ATD analysis of a compost two exothermic peaks (295-307 ° C. and 436-469 ° C.) are observed and correspond respectively to aliphatic and aromatic compounds.

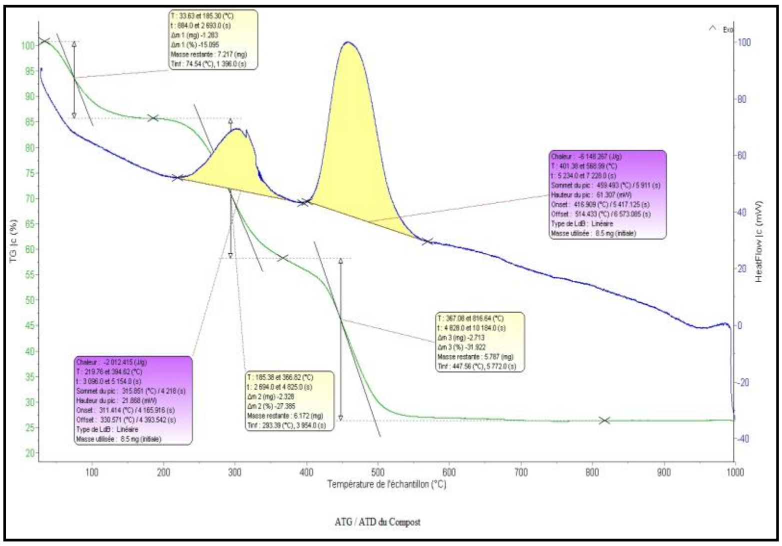

Figure 1: ATD-ATG of the compost carried out under air (oxidizing atmosphere).

3.4. Major components composition of the compost

Table 4 summarizes the results of analysis in major elements present in the compost expressed as oxides. It resulted that the compost studied was poor in aluminum and rich in carbonates, potassium and especially very rich in silica. These values are higher than those of [1]. The sum of the nutrient contents (P2O5 + K2O + CaO + MgO) in the final compost was 10.57%. The mineral composition showed that the compost can be used to improve soil fertility [4]. The percentages of metal oxides (Table 5) of elements such as Copper; Cadmium; Lead and Zinc were very low and under the recommended limits. The loss on fire was high and equal to 67.92%, indicating a significant presence of organic matter.

Table 4: Chemical composition by ICP of the compost (results expressed in % of dry mass (MS)).

Elements	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**MnO**	**P_2O_5**	Loss on fire
Composition (%)	16.99	1.45	2.35	4.21	1.54	4.47	0.02	0.35	67.92
*****	-	-	-	2.82	1.05	2.89	-	2.05	-

* Compost of the citrus fruits scrap and the manure Tchéguéni et al., 2010 [1].

Table 5: Chemical composition out of metallic oxides by ICP of the compost (results expressed in % of dry mass (MS)).

Eléments	**CdO**	**CuO**	**PbO**	**ZnO**
Composition (%)	0.00034	0.00964	0.00538	0.01556
*****	-	-	-	-

* Compost of the citrus fruits scrap and the manure Tchéguéni et al., 2010 [1].

3.5. Infrared Spectroscopy

FTIR spectrum (Figure 2) is characteristic of compost. The indexing of these FTIR spectra was difficult because of the presence in the same zones of bands relative to the minerals. It was difficult in this case to precisely assign all absorption bands of the FTIR spectrum to the 3500-3280 Cm^{-1} and 1200-1000 Cm^{-1} regions [20, 21]. The profile and position of the bands observed in these regions of the FTIR spectrum vary from one author to another and various assignments of the bands have been proposed:

- Large and intense dissymmetrical bands appearing in 3500-3280 Cm-1 were attributed to the elongation vibrations of the hydrogen-bonded OH groups and NH groups of AH extracted from the soil or sewage sludge [22, 23, 24].
- The bands appearing in the region 1200-1000 Cm-1 were the subject of several assignments. Either the elongation vibrations of aromatic ethers or Si-O [24], the C-O-C elongation vibrations of the carbohydrates; or aromatic ethers and polysaccharides [25, 26, 27, 28]; and even to OH elongation vibrations [27]. These

bibliographic references illustrate that the bands appearing in the aforementioned regions of the FTIR spectrum characterize both the mineral phase and the organic phase.

In the FTIR spectrum (FIG. 03), the band at 3420 Cm-1 may be attributed to elongation vibrations of the O-H hydroxyl groups. Its broad profile and the value of the wave numbers lower than that of the free OH suggest that the hydroxyls are interacting via the hydrogen bond. For example, in olive-pomacesludges and soils rich in organic matter, this band was attributed respectively to phenols and hydroxyls of carboxylic acids [30]; Phenol hydroxyls and N-H elongations [27]. Our FTIR spectrum is consistent with these assumptions. The dissymmetry of the band makes it possible to point two components located at 3420 Cm-1 and at 3280 Cm-1 which we attribute respectively to OH and NH groups. The bands in the 2925-2850 Cm-1 region are characteristic of vibrations of aliphatic chains (methyl and methylene) not consumed by microorganisms.

The distribution of FTIR spectrum bands located in the 1800-1600 Cm-1 region is delicate and due to overlapping vibration bands associated with mud and green waste. For example, in the compost samples, the bands observed around 1750-1600 Cm-1 provide information not only on the nature but also on the quantity of C = O functions contained in the organic matter [21]. A deep analysis of bibliographic references revealed that in the region 1750-1600 Cm-1, the number of waves and the position of the vibration band attributed to the C = O group vary from tens of Cm-1 from one author to another. Its attribution to a specific functional group (aldehyde, ketone, ester, acid etc.) should be done with much caution. The difference in the observed frequencies would probably be due to the vibration movement of the oscillator C = O and depends very sensitively on the environment of a carbon carrying other groups, in this case the electronegativity of the other atoms which provide the carbon atom with its tetra valence as well as the mesomeric effect of the other adjacent bonds.

We attribute the band located towards 1642 cm-1 to the C = O bonds of the characteristic groups of the acid, ester functions. The band towards 1384 cm-1 is attributed to the presence of nitrogen. The presence of this strip in this compost showed that our compost wasat a very good maturity. This result was in agreement with the work of [31], which showed that the presence of this band (around 1384 cm -1) is observed only in composts of good maturity. Moreover, the band located towards 1255 cm-1 is characteristic of C-O bond or of OH deformation. In the 1040-1030 cm-1 region, the band at 1035 cm -1 was characteristic of silica. This attribution was made in previous studies by several authors [12, 32, 24]. These results are in agreement with the results of the composition obtained by ICP which showed the existence of a mineral phase having a silicate character.

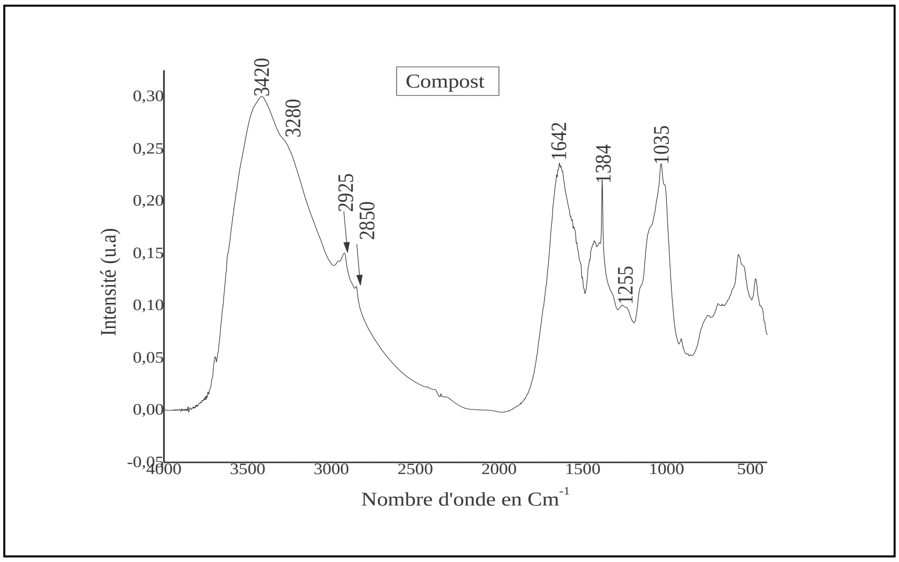

Figure 2: Spectrum FTIR of the compost used

3.6. Metallic trace elements content of the compost used

In this work, we chose to measure four metallic elements: cadmium, lead, copper and zinc. The metal concentrations of the compost in the final phase are presented in this section. In Table 6, we present the results of the heavy metals contents of the compost.

Table 6: Contents (ppm) of heavy metals of the compost used.

Compost	Pb	Cd	Cu	Zn
	Nd	Nd	0,24	10,64

Nd = Not determined

Table 7: Comparison of the contents of heavy metals of the compost used with those of the Standards German and French.

Compost	Cd	Pb	Ni	Cu	Zn
	(in ppm)				
Standards German	1	100	50	75	300
Standards French	8	800	200	-	-
Compost utilisé	ND	ND	11.34	12.96	10.64

A comparison of these grades with the most stringent European standard (Blue Angel standard) and the French standard (see Table 8) showed that heavy metal contents of the compost used was very far from the most severe limits. Additionally, our compost did not present any potential pollution hazard. It can be used in agriculture as a soil amendment without risk of contamination of the system soil-plant.

Tableau 8*:* Comparison of the contents of heavy metals of the compost used with those of the German Standards `' Blue Angel" and Frenchwoman.

Heavy metals	Contents of the compost used	French Values	Normalizes
	Ppm		
Cd	Nd	3.5	2 – 5
Cu	12.96	71.7	100
Hg	Nd	0.2	2
Pb	Nd	106.0	150
Zn	10.64	375	400

3.7. Maturity of compost: germination test

Maturity is an essential criterion for assessing the agronomic quality of compost; thephytotoxicity being caused by non-mature compost. To assess the phytotoxicity of the compost produced, we applied the germination test. For this test, the results obtained are showed in Table 9, expressed as the number of seeds which germinated after six days of culture. These results are an indicator of the toxicity of compost. The compost produced is non-toxic since all mixtures made in this study showed a germination rate greater than 50%. Chikae et al., 2006, recognized a germination rate higher than 50% as compost with no phytotoxic effect [33]. The germination index has high levels, therefore a very low content of toxic substances such as acetic acid. The latter can prevent the germination of cress seeds from a concentration of 300mg / Kg (De Vleesschauwer et al., 1981 cited by Kolédzi 2011) [34]. The reduction of germination of cress and maize seeds by acetic acid has been reported by Keeling et al., 1994, cited by Kolédzi 2011 [34]. The germination index for maize in this study exceeded 50% indicativeofthe compost maturity. This mature compost can lead to a reduced mineralization of the carbon brought in parallel to a regular release of the associated organic nitrogen. An unripe compost would lead to a decrease in the level of oxygen and the oxidoreductive potential of the soil which would cause the creation of an anaerobic and reducing medium. These conditions would favor the mobilization of trace metal elements or lead to inhibitory or phytotoxic reactions [35], linked to the production of ammonia, ethylene oxide or organic acids.

Table 9 : Index of germination

Substrat Composition (v /v)	Sand	Compost			
	100%	100%	½	1/3	¼
Index of germination in %	90	40	60	70	70

Conclusion

Waste treatment, zests of oranges, grapefruit, lemon, cotton seed husks, lemongrass, through composting process resulted in stable and mature compost after 6 months of composting. The phytotoxicity test applied in this study had a germination index exceeding 50%. This rate has been recognized by several authors as being that of a mature compost. Thus, the spectroscopic characterizations carried out showed that the compost obtained is ripe and stable. Moreover, the IR absorption band observed at 1384 cm -1 and attributed to the presence of nitrogen confirmed this result since the presence of this band is only recorded in compostsof very good maturity.

In our experimental conditions, the compost showed a very low total concentration of heavy metals, lower than the currently legislation limits in agricultural for composts and a fertilizing capacity (nitrogen, phosphorus, humic substances ...) valuation.

Thanks-Our thanks go to Dr. Mongo AHARH- KPESSOU, the Secretary of State SP-PRPF; the Center of Analysis and Characterization (CAC) of the University, Faculty of Science Semlalia Cadi Ayyad, Marrakech, Morocco and the University Agency of the Francophonie (West Africa Bureau).

References

1. Tchéguéni S., Kili A.K., Bodjona B.M., Tchangbédji G., Baba G., Hafidi M., *Bull. Info. Soachim.* 007 (2010) 61 – 69.
2. Bernal M. P., Alburquerque J. A. and Moral R., *Bioresour. Technol.* 100 (2009) 5444–5453.
3. Mustin M., *Le compost : gestion de la matière organique* Paris (1987).
4. Inkel M., De P. Smet, Tersmette T. and Veldkamp T., *Fabrication et Utilisation du compost, Wageningen, Pays-Bas* (1990), p. 37
5. Bernal M. P., Paredes C., Sanchez M. A. and Cegarra J., *Bioresour.Technol. 63* (1998) 91–99
6. Sellami F., Hachicha S., Chtourou M., Medhioub K. and Ammar E., *Bioresour.Technol. 99*(2008) 6900-6907
7. Aziablé E., Tchéguéni S., Sabi K., Bodjona B.M., Djahini K., Kili A.K., Tchangbédji G., *E.S.J* 10 (6) (2014) 156-167.
8. Bodjona B.M., Kili A.K, Tchéguéni S., Kennou B., Tchangbédji G., El Meray M., *Int.J.Chem.Sci.* (2012) 6(3) 1368-1380.
9. Charnay F., *Thèse de Doctorat, Université de Limoges*. (2005) p. 34.
10. Aloueimine S.O., *Thèse de Doctorat, Université de Limoges.* (2006) p.119.
11. Amir, S., Hafidi, M., 2001. *Journal: Ann. Chim. Sci. Mat*. 26 (2001) S409-S414.
12. El Fels L., Zamama M., El asli A., Hafidi M., *Int. Biodeter. Biodegr*. 87 (2014a) 128-137.
13. Toundou O., *Thèse de doctorat, Universités de Lomé et de Limoges*. (2016).p.59.
14. Avnimelech Y., Bruner M., Ezrony I., Sela R & Kochba M., *Comp.Sci.Util*. 4 (2) (1996) 13-40.
15. Zorpas, A.A., Arapoglou, D., Panagiotis K., *Waste Manage*. 23 (2003) 27-35.
16. EL Herradi E. H., Soudi B., Naman F., *J. Mater. Environ. Sci.* (5) (5) (2014) 1382-1389
17. Otero, M., Calvo, L. F., Estrada, B., García, A. I., et Morán, A., *Thermochem. Acta*. 389 (2002) 121-132.
18. Som M.P., *Thèse de doctorat, Université de Poitiers, France* (2006).
19. Dell'Abate, M. T., Benedetti, A. et Sequi, P., *J.Therm. Anal. Calorim*. 61 (2000) 389-396.
20. Haberhauer G., Rafferty B., Strebl F., Gerzabek M.H. *Geoderma*. 83 (3-4) (1998) 331-342.
21. Kaiser M., Ellerbrock R.H. *Geoderma*. 127 (2005) 196-206.
22. Senesi N., D'Orazio V., Ricca G. *Geoderma*, 116 (2003) 325-344.
23. González-Pérez M., Martin-Neto L., Saab S.C., Novotny E.H., Milori D.M.B.P., Bagnato V.S., Colnago L.A., Melo W.J., Knicker H. *Geoderma*, 118 (2004) 181-190.
24. Polak J., Bartoszek M., Su1kowski W.W., *J. Mol. Struct*. 924-926 (2009) 309-312.
25. Niemeyer J., Chen Y., Bollag J.M., *Soil Sci. Soc. Am. J.* 56 (1992) 135–140.
26. Laguirtati A., Ait Baddi G., El Mousadik A., Gilard A., Revel J.C., Hafidi M., *Int. Biodeter. Biodegr*. 56 (2005) 8–16.
27. Madari B.E., Reeves III J.B., Machado P.L.O.A., Guimarães C.M., Torres E., McCarty G.W., *Geoderma*. 136 (2006) 245-259.
28. Sawalha M.F., Peralta-Videa J.R., Saupe G.B., Dokken K.M., Gardea-Torresdey J.L. *Chemosphere*. 66(2007) 1424–1430.
29. Laurent J., Pierra M., Casellas M., Dagot C. *Chemosphere*, 77 (2009) 771-777.
30. Ait Baddi G., Alburquerque J.A., Gonzálvez J., Cegarra J., Hafidi M. *Int. Biodeter. Biodegr*. 54 (1) (2004) 39-44.
31. Grube M., Lin T, J.G., Lee P.H., Kokorevicha S. *Geoderma* 130 (2006) 324–333
32. Fernandez J.M., Sensi N., Plaza C., Brunetti G., Polo A. *Pedosphere*.19 (2009) 281–291.
33. Chikae M., Ikeda R., Kerman K., Morita Y., Tamiya E. *Bioresour. Technol*. 97 (2006) 1979 – 1985.
34. Kolédzi K.E., 2011. *Thèse de Doctorat Universités de Lomé et de Limoges*, p. 163.
35. Bustamante M.A., Paredes C., Marhuenda-Egea F.C., Perez-Espinosa A., Bernal M.P., Moral R., *Chemosphere*, 72 (2008) 551-557.

(2017) ; http://www.jmaterenvironsci.com