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COMPOST QUALITY AND USE FROM SEWAGE SLUDGE, ORGANIC FRACTION OF MUNICIPAL SOLID WASTE AND NATURAL ZEOLITE - CLINOPTILOLITE

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ABSTRACT

Composting of sewage sludge and organic fraction of municipal solid waste can enhanced its quality and suitability for agricultural use. However the presence of the heavy metal in the raw material is one of the most serious problems in order to use its final product in agricultural. The natural zeolite has the ability by ion exchange to uptake those metals. By using 25 % of clinoptilolite during the composting process 100 % of Cd, 27 % of Cu, 13 % of Cr, 20 % of Fe, 37 % of Ni, 50 % of Pb and 55 % of Zn, can be uptaken by the zeolite. The quality of the resulting compost, showed in the plant test as growth rate increases the qualification of the compost to be used to increase soil quality. The application of compost in pepper cultivation seems to increases the final product while zeolite can retain the heavy metals and do not let them pass from the roots to the final product. The GANC test procedure showed that in the case of acid-rain the zeolite had the ability to retain the heavy metals and not let them to pass in the groundwater.

Key Words: composting, co-composting process, sewage sludge, municipal waste, pepper cultivation.

INDRODUCTION

The mineralization of biogenic substances is part of the natural recycling processes which occur at any place where organic material is synthesized by plants and degraded by animals and by microflora. This mechanism keeps upright the global balance. The wide scale use of municipal solid waste and sewage sludge compost, seems to be presently demand due to two independent reasons [1]. Firstly, it seems that there are no environmentally and economically sound alternatives beside the application of compost made from the organic biodegradable fraction of the waste, [1,2]. Sanitary land filling was found to be a potential source of pollution and is becoming very expensive. Incineration is source of air pollution and its safe running, but it is very expensive, [2,3]. Secondly, there is a wide spread demand for the structure reclamation of intensively cultivation soils, soils that are gradually losing their organic matter and that are deteriorating with time, [1,4].

The desired quality of compost, before being applied to soils, becomes more and more a local point. In the past the look of the compost ready for selling was considered under marketing aspects. In most cases, in the field of municipal waste and sewage sludge, compost has been adequately solved by technical means. The also desired inner quality of

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compost is more complicate. It depends on many factors, e.g. composition of starting materials, formation of mixtures, the choice of right C/N ratio, processing and treatment of the raw compost after being stored for a while in order to proceed its maturity, [1,5].

The disposal of huge quantities of sludge produced from wastewater treatment plant and the organic fraction of municipal waste (OFMSW), is one of the main environmental problems. This problem is especially intensified in big cities because of the high population, [6,7,8,9,10]. In the greatest Athens region with almost 4 500 000 citizens the main wastewater treatment plant operating is Psittallia. At Psittallia approximately 750 000 m^3/day of municipal wastewater and some industrial wastes are subject to primary treatment and produce about 230 tones/day de -water anaerobically stabilized primary sewage sludge, [8], while at the same time every citizen produces mainly 1.125 kg/day municipal waste (approximately 5 000 tones/day), which the 65 % of those waste are organics, [11].

The major limitation of land application of sewage sludge compost is the potential high metal content related to the metal content of the original sludge. The nature zeolite, clinoptilolite has the ability to uptake those metals. Zeolites have been world-wide for the last decades, either for their cation exchange or molecular sieving properties. Natural zeolites nowadays are mostly used in catalysis, in air enrichment, as filers in paper and rubber industry, in soil benefication, as animal feed supplements, and in water and wastewater treatment for the ammonia and heavy metal removal, [13,14,15,16].

In this work anaerobically stabilized primary sewage sludge (ASPSS) from Psitallia's wastewater treatment plant and organic fraction of municipal solid waste (OFMSW) from Ano Liosia land filled side have been collected, in order to produce a good quality compost as a soil amendment. However, the leachability of the final products have been studied in the final products. The quality of the resulting compost, showed in the plant test as growth rate increases the qualification of the compost to be used to increase soil quality.

MATERIALS AND METHODS

The anaerobically stabilized primary sewage sludge (ASPSS) samples had been collected from the Psittalia wastewater treatment plant. The samples were dried , homogenized and stored, while the organic fraction of municipal solid waste (OFMSW) had been collected from Ano Liosia land filled area. The samples were dried at room temperature and used in order to determine the following parameters: pH, conductivity, Total Organic Carbon (TOC), Organic Matter (O.M.), Total Phosphorous (TP), Total Kjendahl Nitrogen, ammonia, nitrites , nitrates, chlorites, borom, houmic substances, lignin, cellulose, C/N ratio, C/P ratio, E4/E6 ratio and heavy metals contents (Cd, Cr, Cu, Fe, Mn, Ni, Zn and Pb). The natural zeolite (clinoptilolite) was collected from Evros (region in northern Greece) and analyzed for its chemical composition and the results are given in Table 1.

TABLE 1: Natural Clinoptilolite chemical analysis.

Components	mol/100 g	% W/W
SiO_2	1.151	69.396
Al_2O_3	0.112	11.551
Fe_2O_3	0.002	0.384
Na_2O	0.080	4.980
H_2O	0.495	8.955
K_2O	0.028	2.753
CaO	0.035	1.981
Total		100

The above analysis gives an ion-exchange capacity of 1.70 meq/g. In order to observe the effect of the zeolite and how the metal content of the final products vary, the following samples were prepared for composting as observed in Table 2.

TABLE 2: Prepared samples for composting.

So :	0 % clinoptilolite	+	100 % DASPSS	40-50 % moisture
S1 :	0 % clinoptilolite	+	100 % OFMSW	40-50 % moisture
S2 :	5 % clinoptilolite	+	95 % (90 % So + 10 % S1)	40-50 % moisture
S3 :	10 % clinoptilolite	+	90 % (80 % So + 20 % S1)	40-50 % moisture
S4 :	15 % clinoptilolite	+	85 % (70 % So + 30 % S1)	40-50 % moisture
S5 :	20 % clinoptilolite	+	80 % (60 % So + 40 % S1)	40-50 % moisture
S6 :	25 % clinoptilolite	+	75 % (50 % So + 50 % S1)	40-50 % moisture

The composting process was carried out in the Laboratory on an In-Vessel reactor of active volume of 1 m^3, [17]. The thermophilic phase lasted for 15 days in the reactor. The temperature was about 60-65 °C in the center of the reactor and the moisture was in the range of 40-50 %. After the thermophilic period in which the organic material was biodegraded, the compost was piled to an enclosed package where it remained for about 4 months to mature. For all the prepared samples the following parameters were determined: pH value, conductivity, Total Organic Carbon (TOC), Organic Matter (O.M.), Total Phosphorous (TP), Total Kjendahl Nitrogen and ammonia content, houmic substances, lignin, cellulose, C/N ratio, E4/E6 ratio, and heavy metals contents (Cd, Cr, Cu, Fe, Mn, Ni, Zn and Pb).

For the determination of pH values, conductivity, chlorites, borom, TOC, OM, TP, TKN, ammonia, nitrites and nitrate content, standard methods of analysis were used, [18,19]. For the total metal concentration, a known quantity (1g) of sample was digested with 10 ml of c. HNO_3 as discribe by Zorpas et al. [8]. After the completion of the digestion the samples were vacuum filtered and the filtrate was used for the determination of heavy metal concentration by atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer and ICP. Houmic substances were extracted according to Schintzer, while lignin and cellulose were determined by a digestion technique with 72 % of sulfuric acid as described by Zorpas et all. [8].

The GANC test procedure was used for the estimation of the leachability of metals from the sludge samples, [8]. This test is a single batch procedure that utilizes a series of sludge samples extracted with increasingly acidic leachant. A known quantity (1 g) of sludge sample is placed in a series of 100 ml polyethylene bottles. 20 ml of liquid is added to each bottle. A declining amount of distilled water is added to each bottle followed by an increasing amount of 2N acetic acid. This process produces a series of bottles containing increasing equivalents of acid per kilogram of samples but the same total liquid volume (20 ml). The mixtures were tumbled in rotating extractors for 48 hours and then were let to stand for 15 minutes. Following, in the supernatant the pH was measured and the metal concentrations were determined by AAS. Leachants strength starts out at the 0 equivalents of acetic acid and is increased until pH is below 5 for three consecutive equivalents. It is important to know that, for the characterization of all the compost samples the zeolites had been removed from the final products. The quality of the resulting compost, showed in the plant test as growth rate increases the qualification of the compost to be used to increase soil quality. For this test five different ratios (0 % , 25 %, 50 %, 75 % and 100 % of compost) with compost and soil were used in pepper cultivation.

RESULT AND DISCUSSIONS

The physico - chemical characteristic of anaerobically stabilised primary sewage sludge (ASPSS) samples and organig fraction of municipal solid waste (OFMSW) have been observed in Table 3.

Table 3. Physico - Chemical Characteristics of Raw Materials.

	Mean value of 20 samples					
parameters	ASPSS			OFMSW		
Moisture %	70,00	+/-	2,00	45,00	+/-	2,00
pH	7,05	+/-	0,05	8,00	+/-	0,05
Conductivity mS/cm	1,005	+/-	0,005	1,101	+/-	0,010
Organic Matter %	45,00	+/-	1,00	70,00	+/-	2,00
Ash %	27,00	+/-	1,00	40,00	+/-	2,00
TOC %	26,10	+/-	0,50	36,50	+/-	2,00
TKN %	1,90	+/-	0,20	1,80	+/-	0,20
Cl^- *	---	+/-		4,75	+/-	0,25
B^- *	---	+/-		5,25	+/-	0,25
N-NH3 10^{-1} *	9,57	+/-	0,50	19,73	+/-	0,70
N-NO3 10^{-1} *	2,53	+/-	0,20	0,45	+/-	0,05
N-NO2 10^{-6} *	258	+/-	25	2160	+/-	100
P-PO4 %	2,45	+/-	0,05	2,60	+/-	0,05
Houmic Substances %	1,80	+/-	0,05	9,50	+/-	0,50
E4/E6	1,25	+/-	0,01	1,38	+/-	0,01
Lignin %	4,50	+/-	0,50	10,50	+/-	0,50
Cellulose %	2,00	+/-	0,05	28,00	+/-	1,00
C/N	13,73	+/-	0,50	22,22	+/-	1,00
C/P	10,65	+/-	0,50	15,38	+/-	1,00

* : mg/g dry samples , --- : nod detected

As it is observed from Table 3 sewage sludge contains lower concentration of organic matter and organic carbon (45,00 % and 26,10 % respectively) than the OFMSW (70,00

% OM and 40,00 % TOC), in order to proceed for the production of a good soil conditioner. The pH values of ASPSS samples were about 7 and about 8 for the OFMSW. The total phosphorous content was found in high levels due to the fact that the main load of the treated wastes were municipal. The total humics were found in lower levels (1,80 %) than the OFMSW (9,50 %). The E4/E6 ratio shows the characterization of humic materials. As the E4/E6 ratio is bellow 5, the samples are characterized as Humic Acid (whereas if the ratio is above 5 the sample is characterized as Fulvic Acid), [8]. The ASPSS contain high amounts of organic constituents. However, if the sludge is used for the production of compost, the organic amount is considered to be low. The ASPSS solid wastes are amenable for composting treatment due to the low C/N ratio. It's necessary to proceed for co-composting with the OFMSW which contain higher amount of organic matter, houmic substances, C/N ratio, lignin and cellulose than the ASPSS.

Table 4 shows the characterization of the final product after from 150 days of maturity.

Table 4: Compost characteristics.

	So	S1	S2	S3	S4	S5	S6
Moisture %	27,20	30,00	32,00	29,50	28,75	29,65	31,50
pH	7,01	7,16	7,48	7,16	7,56	7,09	7,25
Conductivity mS/cm	1,001	1,250	1,128	1,002	1,258	1,345	1,450
OM %	32,81	42,00	36,23	35,34	36,14	35,29	38,23
TOC %	19,03	23,05	21,01	20,49	20,96	20,46	22,17
TKN %	1,65	1,75	1,61	1,85	1,66	1,62	1,89
P-PO4 %	2,45	2,50	2,48	2,54	2,35	2,50	2,35
N-NH4 *	0,735	0,563	0,011	0,107	0,180	0,090	0,080
C/N	11,53	13,17	13,04	11,07	12,93	12,62	11,73

* : mg/g dry samples

Table 5 shows the concentration of the houmic substances after of 150 days of maturity. The sewage sludge contained low concentration of houmic. That requires the addition of ligno-cellulose product. The OFMSW as it is observed from Table 3 contains higher concentration of houmics, lignin and cellulose than the sewage sludge. At that point it is important to know that the most of the paper was removed during the initial selection of the biodegradeble matter from the municipal refuse. However the co-composting of the ASPSS and OFMSW increase the total amount of the houmics substances in the final product.

Table 5: Houmic substances in the final product.

	So	S1	S2	S3	S4	S5	S6
Total Humics	3,50	18,50	4,25	5,82	6,02	7,49	9,50
E4/E5	1,81	1,92	1,75	1,80	1,81	1,79	1,85
Lignin %	3,69	7,50	4,00	4,25	4,58	5,00	5,56
Cellulose %	---	9,25	1,05	1,55	2,06	3,74	4,24
Houmofication factor	0,248	0,445	0,117	0,165	0,166	0,212	0,248

--- : not detected

The houmofication factor according to Zucconi F. and Bertoldi M., may provide information on stabilization. The H.I is the ratio between total houmics and organic matter, [20].

In order to use the final products in agricultural with no problems in case of leachate of the heavy metals , natural zeolite has been used to uptake those metals. Table 6 presents the metal content in ASPSS, in OFMSW, and in the final product. (At that point it is important to know that the amount of zeolite has been removed from the compost in order to determine the concentration of heavy metals.)

Table 6: Metals concentration in the raw materials and in the final products.

	ASPSS	OFMSW	So	S1	S2	S3	S4	S5	S6
Cd	0,002	---	0,002	---	---	---	---	---	---
Cu	0,258	0,130	0,205	0,128	0,238	0,225	0,212	0,199	0,186
Cr	0,552	0,118	0,578	0,120	0,616	0,520	0,507	0,494	0,481
Fe	5,098	4,201	4,118	4,001	5,741	5,547	5,201	5,001	4,099
Mn	0,150	0,106	0,168	0,110	0,161	0,151	0,137	0,128	0,115
Ni	0,041	0,012	0,045	0,012	0,035	0,035	0,031	0,027	0,026
Pb	0,326	0,113	0,335	0,114	0,218	0,206	0,193	0,179	0,166
Zn	1,739	0,263	1,801	0,264	1,005	0,979	0,952	0,926	0,784
Na	0,723	0,604	0,772	0,680	0,723	0,733	0,775	0,805	0,884
K	0,724	0,587	0,796	0,655	0,721	0,809	0,815	0,915	0,989

Al metals in mg/g dry samples.

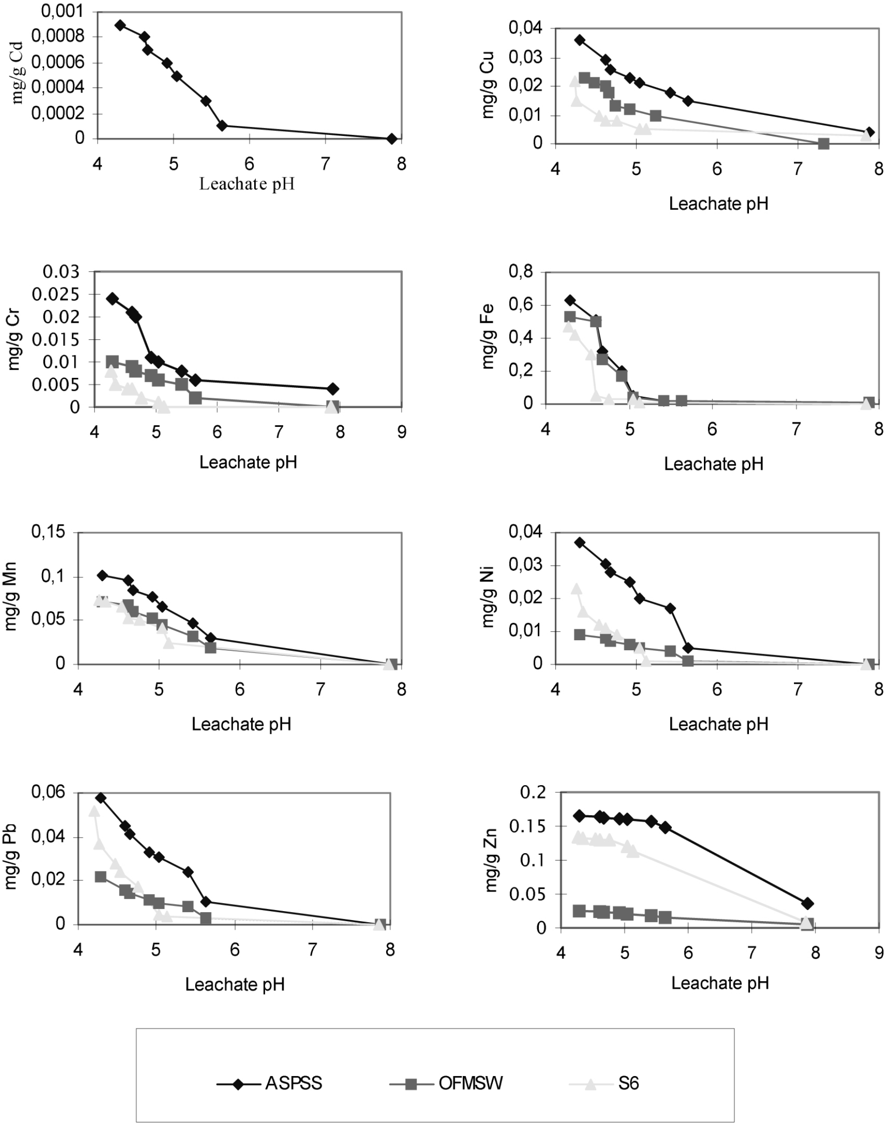
When comparing the metal content of the first sample (So), sewage sludge compost with no zeolite and ASPSS sample, it can be observed that the concentration of chromium, nickel, manganese, lead and zinc appeared increase while that of copper and iron decrease. Composting can concentrate or dilute heavy metals present in sewage sludge. This change in metal concentration depends on the metal loss through leaching and on the overall concentration of metals due to organic matter destruction.

As it is observed in Table 6 natural zeolite (Clinoptilolite) has the ability to exchange sodium and potassium. It is also clearly seen that with increasing amount of zeolite the concentration of all heavy metals content in the compost samples decreases, while the concentration of sodium and potassium increases. It is seen that in sample S6, containing 25 % of clinoptilolite maximum metal uptaken occur and specifically 100 % of Cd, 27 % of Cu, 13 % of Cr, 20 % of Fe, 23 % of Mn, 37 % of Ni, 50 % of Pb and 55 % of Zn.

The GANC test and the sequential extraction procedure was applied in the ASPSS, in the OFMSW and in the final product S6 where maximum metal was uptaken after 150 days.

The GANC test results, Figure 1, show that by increasing the leachate pH, a decrease to the heavy metal concentration was caused. It is obvious that the compost produced from the OFMSW has a low extraction of metals due to the fact that the metals concentrations are in low levels, especially for lead and zing. However the co-composting product S6 (containing 25 % of zeolite and 75 % of ASPSS and OFMSW) has the ability to uptake a high amount of each metal and not to let them pass to the groundwater's.

FIGURE 1: GANC metals release to leachates from primary sludge samples (Psittalia) as a function of pH of leachate.



Using the final product So, S1 and S6 in pepper cultivation found that the S6 compost containing 25 % of natural zeolite and 75 % (50 % ASPSS + 50 % OFMSW) of ASPSS and OFMSW increased the production to 20 %.

Although zeolite bounds the heavy metals and donut let them to pass through the routs to the final product. It is observed from Table 7 almost all of the metal concentration in S6 seem not to transfer into cultivation while in So and S1 compost does.

TABLE 7: Metal distribution in Roots, loom and leaves for pepper cultivation.

	mg/g *	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
	Roots	---	0,092	0,086	3,442	0,105	0,001	0,025	0,108
So	loom	---	0,045	0,004	0,408	0,008	0,003	0,018	0,014
	leaves	---	0,010	---	0,012	0,003	---	0,002	0,002
	Roots	---	0,040	0,031	2,935	0,086	0,004	0,014	0,089
S1	loom	---	0,026	0,001	0,301	0,003	0,001	0,011	0,010
	leaves	---	0,007	---	0,011	---	---	0,001	0,001
	Roots	---	0,025	0,022	1,114	0,014	0,002	0,009	0,047
S6	loom	---	---	---	0,256	0,002	---	0,008	0,007
	leaves	---	---	---	0,006	---	---	---	---

* : dry samples

CONCLUTIONS

Concluding, it can be stated that while the amount of natural zeolite (clinoptilolite) increases the concentration of heavy metals in the final compost decreases. It was found that by using 25 % of clinoptilolite during the composting process 100 % of Cd, 27 % of Cu, 13 % of Cr, 20 % of Fe, 23 % of Mn, 37 % of Ni, 50 % of Pb and 55 % of Zn, can be uptaken by the zeolite. Using the Generalized Acid Neutralization Capacity (GANC) procedure was found that increasing the leachate pH, the heavy metal concentration was decreased. The GANC test procedure showed that in the case of oxic rain the zeolite had the ability to retain the heavy metals and not let them to pass in the groundwater.

The application of compost in pepper cultivation seems to increases the final product while zeolite can retain the heavy metals and do not let them pass from the roots to the final product.

The sewage sludge contained low concentration of houmic. The OFMSW as it is observed contains higher concentration of houmics, lignin and cellulose than the sewage sludge and the co-composting of the ASPSS and OFMSW increase the total amount of the houmics substances in the final product.

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