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Research Article

Carbon Mineralization of Sewage Sludge and Fly Ash

Kanalizasyon Çamuru ve Uçucu Külün Karbon Mineralizasyonu

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Abstract

In this study, it was aimed to determine stabilization degrees of important wastes those both used as amendment and disposed as waste. Because, the stabilization degree of the wastes are important for the prediction of the degradation pattern of the organics, the adequate supplement of essential nutrients to the plants, the nutrient release pattern and the organic matter application time. For this aim, sewage sludge and fly ash were selected and their carbon mineralization rates were determined. The wastes were added to the soil at various amounts (Reactor 1 with soil and sewage sludge, Reactor 2 with soil, sewage sludge and 5% fly ash, Reactor 3 with soil, sewage sludge and 10% fly ash and Reactor 4 with soil and fly ash), and incubated at 22 ^{o}C. The carbon mineralization followed two steps with a rapid and slower step. The degradation patterns were similar to each other during the incubation period, especially at the second step. It was seen that the ash added could avert the degradation of the organics in the sewage sludge and the outflow of CO_2-C. During the incubation period, the lowest CO_2-C outflow was mostly seen in the reactor that the ash was added as a percentage of 10. During step two, the maximum CO_2-C outflows were seen in the reactor with ash alone. It could be said that ash with sewage sludge results in less CO_2-C outflow than being alone in the soil. Analysis of variance (ANOVA) was used to determine if significant differences existed among the reactors used. The model used confirmed that significant differences existed between reactors used ($F=14.68$, $P<0.05$).

Keywords: Sewage sludge, Fly ash, Carbon mineralization, Waste, Soil, Stabilization

1. Introduction

Combustion of coal to generate electricity produces large volumes of coal combustion residues particularly fly ash (Singh 2005). Coal is a major source of energy in Turkey and its combustion is predicted to increase in the future in order to meet the continuous demand for electric power generation (Baba and Kaya 2004). In Turkey, power plants were generated 25.62 million tons of waste in year 2008. 79%, 16% and 3% of these wastes were disposed to ash mountain/ash dam, penetrated or stored in mining areas and sold or given to the firms for recycling, in that order.

Mineral wastes (ash, slag, fly ash and gypsum) have the maximum percentage (99.4%) in these wastes (TSI, 2010; Topal et al., 2011). Fly ash is the finely divided mineral that results from the combustion of pulverized coal produced during the steam generation process in the power plant (Pando et al., 2006). The fly ash dominated coal combustion residues accumulates in on-site piles and ash ponds leading to serious environmental problems, particularly contamination of ground and surface waters due to leaching of trace elements (Singh, 2005). Also lands may adversely affected by power plants because of the fly ashes those suffuse to soil. On the other hand, fly ash is used as back fill material for reclamation of mined out areas as investigated by Singh (2005).

Sludge is produced from wastewater treatment plants. Its treatment and disposal is perhaps one of the most complex environmental problems facing the engineer, and the disposal cost is greater than 50% of the total operation cost (FREC 1987, Chiang et al. 2003). Sludge from a wastewater treatment plant can contain proteins, carbonhydrates, fats and oils, and some metals, which diffuse into sludge from industrial processes, households, ground surface activities, corrosion, and erosion of pipes (Chiang et al. 2003). Urban wastes, such as sewage sludge, are increasingly used to amend soils, especially those with a low organic matter content, to improve their fertility (Garcia et al. 1994, Moreno et al. 2002). In many industrialized countries the application of sewage sludge to agricultural land is a major route for disposal (Wild et al. 1990). Land application of raw or treated sewage sludge can reduce significantly the sludge disposal cost component of sewage treatment as well as providing a

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large part of the nitrogen and phosphorus requirements of many crops (FAO, internet). Considerable research has shown the benefits of using composts and other amendments to improve soil physical (water holding capacity, porosity, and bulk density), chemical (pH, electrical conductivity, and nutrient content), and biological properties such as soil microbial populations and plant growth (Mamo et al. 1999, Stoffella and Kahn 2001, Wolkowski 2003, Flavel and Murphy 2006).

Soil organic matter is a heterogeneous mixture that comprises an accumulation of partially disintegrated and decomposed plant and animal residues addition to other organic compounds synthesized by soil microbes as decay occurs (Baldock and Nelson 2000; Bol et al., 2003; Zhang et al., 2009) and it has far-reaching effects on soil physical, chemical, and biological properties (Doran and Parkins 1994; Campbell et al. 1999; Zhang et al., 2009). Increasing the soil organic carbon content also enhances soil quality, reduces soil erosion, improves water quality, increases biomass and agronomic productivity, and improves environmental quality by adsorbing pollutants from natural waters and reducing atmospheric carbon dioxide (CO_2) concentration (Lal and Kimble 1999, Pedra et al. 2007). It proposed that the decomposition of soil organic matter is regulated by three groups of variables, physical rate determinants (primarily temperature and moisture), the chemical composition of the resource (quality), and the organisms (invertebrates and microorganisms) (Swift et al., 1979; Bol et al., 2003). Also, other abiotic constraints as (i) physicochemical soil characteristics and (ii) the role of organic-inorganic complexes in the formation of soil aggregates and protection of the organic compounds from biological degradation were important (Tisdall and Oades 1982, Coûteaux et al. 1995, Mclnerney and Bolger 2000a, b, Bol et al. 2003).

Mineralization of soil organic carbon plays a key role in supplying nutrient elements essential to plant growth, in providing long-term carbon sequestration and the nutrients required for ecosystem productivity (Zhang et al. 2009) and is a key indicator of soil functional capacity (Mutuo et al., 2006). Carbon mineralization is generally determined by monitoring CO_2 fluxes from field-moist samples that are wetted to roughly 50% of field capacity and subsequently incubated in the laboratory for various periods of time (Haney et al., 2004). CO_2 evolution resulting from the degradation of organic materials is a good indicator to measure the organic compound decomposition rate and also is a good index to determine the nutrient release pattern and the optimum time for organic matter application (Naher et al. 2004, Ahmad et al. 2007). Also, predicting carbon mineralization of residues returned to soils is important for forecasting carbon dioxide (CO_2) emissions into the atmosphere (Li et al. 2013).

Knowledge about the stability of materials is important in terms of effects of disposal of them to the soil and usage of them as amendment in the soil. Determination of the degree of stabilization of wastes can be used to predict the degradation pattern of the organics, the adequate supplement of essential nutrients to the plants, the nutrient release pattern and the organic matter application time. In this study, carbon mineralization rate was investigated to determine the stability of materials those either mostly thrown away from various sources (sewage treatment plants and thermal power plants) to soil without precautions or given to the soil for various aims (e.g. amendment, reclamation and etc.). Also, to our knowledge, the wastes chosen in this study were not used by the other researchers at the same time in another study.

2. Materials and Methods

2.1. Materials

Soil samples were obtained from Elazığ city, Turkey. They were obtained from five random points from 10 cm soil depth and mixed together. Stones and plant roots were removed from samples. The characteristics of the soil used in this study were given in Table 1.

Two wastes commonly used as amendment or thrown away were selected as materials. The sewage sludge which is given to the farmers as amendment by the wastewater treatment plant managers was selected as

Table 1. The characteristics of the soil

Parameter	Value
Sand (%)	26.33
Clay (%)	50.59
Dust (%)	23.08
Dust+clay (%)	73.67
pH	8.09
Salt (mmhos/cm)	0.167
Lime, total (%)	28.35
Lime, activated (%)	10.85
Organic matter (%)	1.656
Nitrogen (%)	0.082
P_2O_5 (ppm)	30.03
K_2O (ppm)	448.42
Na (ppm)	10.42

one of these wastes. It was obtained from the municipal wastewater treatment plant located in Malatya city, Turkey. Characteristics of the sewage sludge were given in Table 2. The other waste selected, fly-ash, was collected from Kangal thermal power plant located in Sivas city, Turkey and its characteristics were given in Table 3.

Soil mixture proportions were as following:

Reactor 1. 10 g soil + 0.2 g sewage sludge

Reactor 2. 9.5 g soil + 5 % ash + 0.2 g sewage sludge

Reactor 3. 9.0 g soil + 10 % ash + 0.2 g sewage sludge

Reactor 4. 10 g soil + 0.2 g ash

2.2. Methods

The moistures of the soil mixtures were adjusted to 60% of their water-holding capacity by adding distilled water. Soil mixtures were placed in 1 L incubation jars for the carbon mineralization. The aerobic incubation procedure as described by Bernal et al. (1998) was used to measure the carbon mineralization. The experimental setup used to evaluate carbon mineralization was illustrated in Figure 1A and the photograph of the three replicates of one of the reactor was given in Figure 1B.

Table 2. The characteristics of the sewage sludge

Parameter	Value
pH	6.5
Organic matter	65%
P	0.7 %
N	5 %
K	0.6 %
C/N	7
Silica	18.168 %
Al_20_3	1.093 %
Fe_2O_3	3.632 %
CaO	20.796 %
MgO	1.424 %

Table 3. The characteristics of the fly-ash

Parameter	Value
Silica	21.276
Al_20_3	8.20
Fe_2O_3	4.39
CaO	28.03
MgO	2.63
Loss of ignition	7.48
Total	72.02

The small vials containing 10 mL of 0.1 M NaOH were placed on top of the soil mixtures in the incubation jars to trap the evolved CO_2 and replaced with a freshly prepared NaOH at days 1, 3, 4, 5, 7, 9, 11, 13, 15, 17, 20, 24 and 30. The control soil without any amendment was also run. Additionally, the empty jars without soil and amendment were considered as blanks. The incubation jars were closed with air-tight seals and incubated in temperature-controlled incubator at 22 ^{o}C. The jars were opened and soil mixtures were aerated for several minutes every day to maintain aerobic conditions during incubation period. The amount of the evolved CO_2 was measured by using titrimetric determination method. The evolved CO_2 was trapped in NaOH, and the alkali trap solution was titrated with 0.1M hydrochloric acid (HCl) to pH 8.3 following precipitation of carbonates with saturated barium chloride ($BaCl_2$) solution. All the experiments were done triplicate. All reagents used in this study were in the analytical reagent grade.

2.3. Statistical analysis

Analysis of variance (ANOVA) was used to determine if significant differences existed among the reactors used and significant F-value was obtained. The differences between the reactors were compared at the level of 5%.

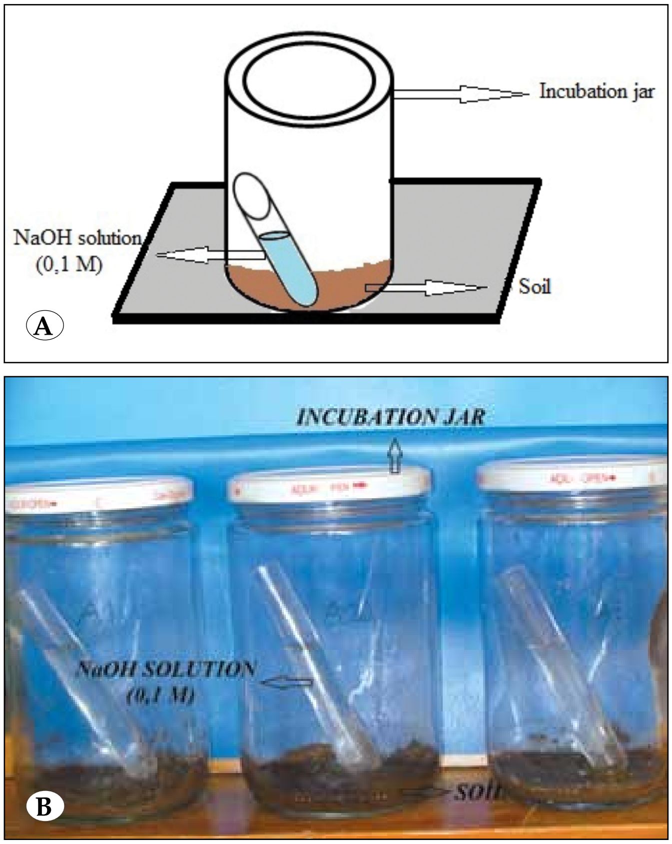

Figure 1: A) The experimental setup used to measure the CO_2-C evolution rates. **B)** Three replicates of one of the reactor.

3. Results and Discussion

The carbon mineralization patterns in Reactor 1, 2, 3 and 4 during the incubation period were given in Figure 2a,b,c and d, in that order.

As seen from the figures, the carbon mineralization followed two steps. First step (from beginning to day 15) was rapid decomposition step that results from the degradation of easily degradable components. The following step (after day 15) was slower than the first step. The following step resulted from the hardly degradable components. Similar result was reported by Nourbakhsh et al. (2006). In their study, a rapid increase during the initial stages of incubation followed by a slower.

As seen from the figures generally, the degradation patterns in the reactors were similar to each other during the incubation period, especially at the second step. CO_2-C increased at day 2 in control and Reactor 1 those do not have ash (Figure 2A). Contrary, it decreased in the other reactors. During the incubation period, the lowest CO_2-C outflow was mostly seen in Reactor 3 that the ash was added as a percentage of 10 (Figure 2C). Reactor 2 that the ash was added as a percentage of 5 intimately followed Reactor 3 (Figure 2B). The control reactor, Reactor 1 (with sewage sludge alone) and Reactor 4 (with ash alone) followed these reactors. At step two, the maximum CO_2-C outflows were seen in Reactor 4 (Figure 2D). It could be said that ash alone began to degrade rapidly after some time. It could be also said that ash with sewage sludge (Figure B and C) gives rise to less CO_2-C outflow than being alone (Figure D) in the soil. It was seen that the ash added could avert the degradation of the organics in the sewage sludge and the outflow of CO_2-C. Fly ash was probably caused the decreased decomposition of organics as a result of decreased oxygen for microorganisms by preventing

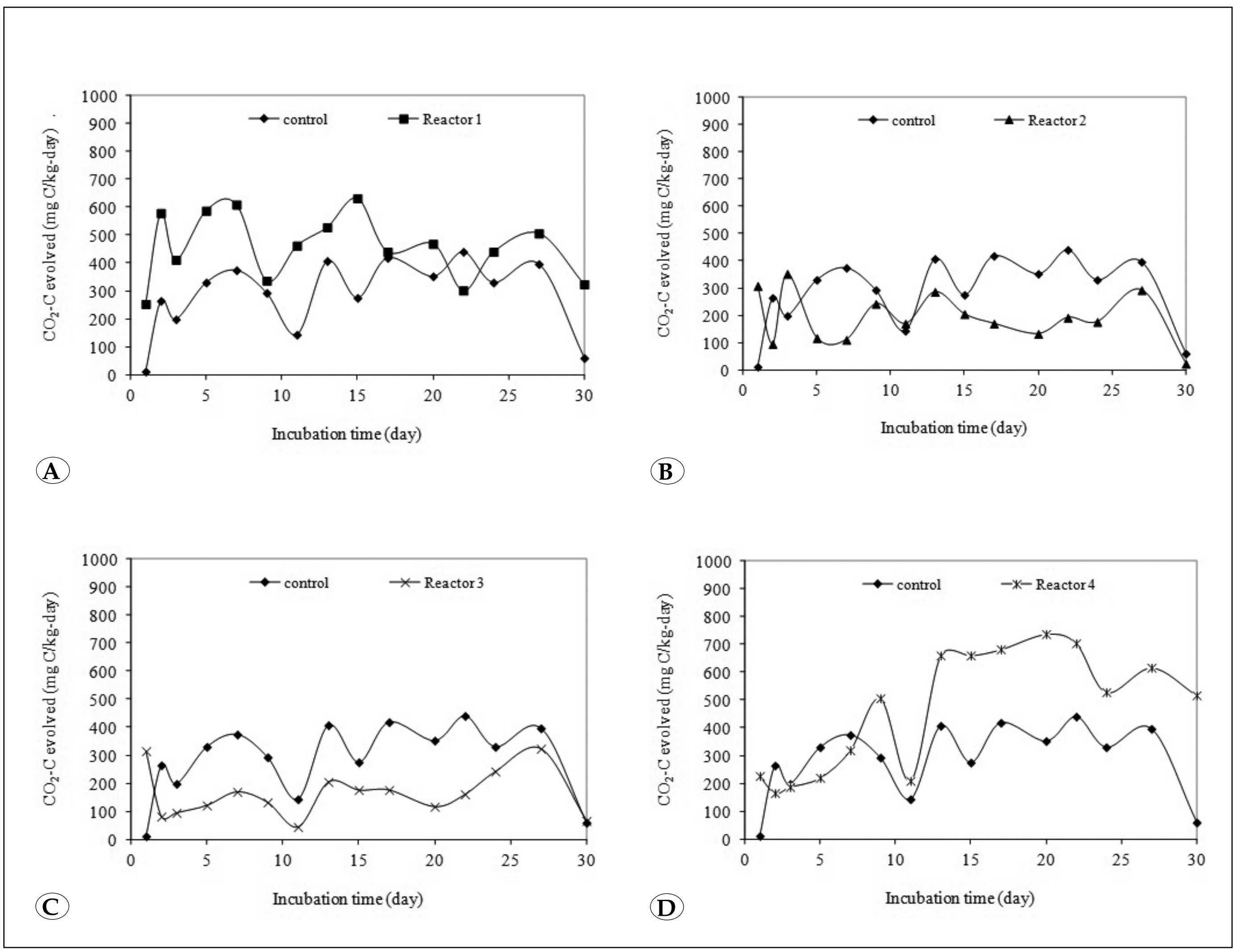

Figure 2: A) CO_2-C evolved in Reactor 1 during incubation. **B)** CO_2-C evolved in Reactor 2 during incubation. **C)** CO_2-C evolved in Reactor 3 during incubation. **D)** CO_2-C evolved in Reactor 4 during incubation.

oxygen diffusion. Similarly, in the study of Naher et al. (2004) which determined the CO_2–C evolution rate for cowdung and poultry manure alone and with rice straw and lime under covered condition, rice straw addition to the cowdung and poultry manure treatment the CO_2–C evolution rate was delayed and took more time.

The model used confirmed that significant differences existed between reactors used ($F=14.68$, $P<0.05$).

Similar to our results, some authors were reported that the various amendments resulted in different rates of CO_2–C evolution. In the study of Flavel and Murphy (2006), soil CO_2–C evolution rates varied significantly among treatments. The control remained low (<2 mg CO_2–C kg^{-1} d^{-1}) for the duration of the incubation. Treatment compressed poultry manure pellets was initially much higher than the other amendments at > 85 mg CO_2–C kg^{-1} d^{-1}, then showed a rapid decline in mg CO_2–C evolution rates over time. The CO_2–C evolution values indicate straw based compost and vermi-cast amendment were the most stable amendments tested. The values reported by Flavel and Murphy (2006) are lower than the ones in our study. Similarly, in the study of Nourbakhsh and Sheikh-Hosseini (2006), the different initial composition of residues applied to the soil resulted in different rates of CO_2 evolution. The total amount of CO_2–C released from alfalfa residue treated soils under non-saline condition was about 6, 1.9 and 1.4 times that of control, corn residue and wheat residue treated soils, in that order. Also, under salinized condition the total amount of CO_2–C released from alfalfa residue treated soils was about 4.8, 1.6 and 1.2 times that of control, corn residue and wheat residue treated soils, in that order. The greater amounts of CO_2 produced in alfalfa residue treated soils can be attributed to the higher biodegradability of these residues. In the earlier study of us (Arslan et al. 2009), the compost types effected C mineralization, similar to the results of current study. Vegetable waste compost had the highest evolution rates while grass clippings compost had the lowest rates during the incubation period. Li et al. (2013) were investigated carbon mineralization of residues of soybean (*Glycine max*), maize (*Zea mays*), and their mixture. The residue type significantly affected carbon mineralization. The soybean residue had a higher decomposition rate than the maize residue.

Significantly lower results than ours were reported by Yang et al. (2008). They were obtained that soil respiration rates ranged between 22.1 and 36.2 mg CO_2–C kg^{-1} soil d^{-1}, with the highest value for forest and lowest value for cropland soil.

4. Conclusions

CO_2–C evolution rates effected from different treatments. Reactor 4 which did not have treatment sludge had the highest evolution rates during the second incubation period. Reactor 3 that the ash was added as a percentage of 10 had the low evolution rates during the incubation period. Therefore, it could be said that the low CO_2–C evolution rates seen in Reactor 3 was not as a result of stability, it was a result of the negative effect of the fly ash on sewage sludge by affecting the decomposition of the organics in the sludge.

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