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Kinetics of organic matter removal and humification progress during sewage sludge composting

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ABSTRACT

This study investigated the kinetics of organic matter (OM) removal and humification during composting of sewage sludge and lignocellulosic waste (wood chips, wheat straw, leaves) in an aerated bioreactor. Both OM degradation and humification (humic substances, HS, and humic acids, HA formation) proceeded according to 1. order kinetics. The rate constant of OM degradation was 0.196 d^{-1} , and the rate of OM degradation was 39.4 mg/g OM d . The kinetic constants of HS and HA formation were 0.044 d^{-1} and 0.045 d^{-1} , whereas the rates of HS and HA formation were 3.46 mg C/g OM d and 3.24 mg C/g OM d , respectively. The concentration profiles of HS and HA indicated that humification occurred most intensively during the first 3 months of composting. The high content of HS (182 mg C/g OM) in the final product indicated that the compost could be used in soil remediation as a source of HS for treating soils highly contaminated with heavy metals.

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1. Introduction

Municipal sewage sludge can be a source of valuable fertilizer, due to its high content of organics, nitrogen, phosphorus and trace elements. However, the presence of pathogenic organisms may pose health risks, limiting the direct application of sludge to soil fertilization. Therefore, sludge should be treated prior to application by methods such as composting.

The composting process lowers sewage sludge mass and moisture content. In addition, thermophilic conditions destroy pathogenic organisms present in waste and ensure complete hygienization of the compost. Additionally, compost contains relatively low concentrations of heavy metals and fulfills the requirements for soil amendments in most cases. For example, earlier study showed that the metal concentration in sewage sludge compost poses low ecological risk (<16) based on the potential ecological risk factor (E_r), which includes not only total metals concentration, but also their toxicity (Zhu et al., 2012; Kulikowska and Gusiatiin, 2015).

To date, as compost has been used mainly as a fertilizer, most attention has focused on transforming of OM, obtaining thermophilic conditions, transforming and conserving nitrogen (Zhu et al., 2004; Cayuela et al., 2006; Kalamdhad and Kazmi, 2009) and establishing the content of heavy metals in the mature

compost (Wong and Selvam, 2006; Manungufala et al., 2008). In recent years, compost has also been used in remediation of soils that are contaminated with heavy metals. It is known that such soil poses a potential risk of groundwater contamination, which increases when the metals are in mobile and potentially mobile fractions. Thus, one of the main goals of soil remediation should be to decrease the concentration of metals in the bioavailable and mobile fractions (stabilization) (Castaldi et al., 2005; Liu et al., 2009). Although this process does not decrease the total metal concentration in soil, decreasing metal mobility does substantially decrease environmental risk (Gusiatiin and Kulikowska, 2015). An alternative strategy for soil remediation is metals mobilization and thereafter removal from soil by soil washing (Conte et al., 2005; Tsang and Yip, 2014).

In both remediation strategies, compost plays an important role. In the former strategy (stabilization), compost acts as an organic amendment which contributes to immobilization of metals in the soil. In the second strategy (washing), compost is a source of HS, which after extraction may be used as washing agents (Kulikowska et al., 2015). However, in both cases, HS are one of the crucial factors. Thus, research on the composting of waste should also include analyses of the humification of OM. Furthermore, it is important to determine not only the concentration of HS and their fractions, i.e. HA and fulvic acids (FA), but also the kinetics of HS formation, which is extremely important in predicting the time during composting at which the humification process occurs most intensively.

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In previous study on sewage sludge composting in a two-stage system with rape straw and grass as amendments, the kinetic constants of both HS and HA were determined (Kulikowska and Klimiuk, 2011; Kulikowska, 2012): in both cases, humification proceeded according to 1. order kinetics. However, although other studies about composting have provided information about changes in HS content during composting of different wastes (Paredes et al., 2001; Domeizel et al., 2004; Goyal et al., 2005), the author of the present study is unaware of any other information on the kinetic constants of the process. So, in order to verify if the kinetic model proposed in the earlier research can be useful for calculation of the rate of both HS and HA formation for other types of waste or composting technologies, further research is needed. Therefore, the aim of this study was to analyze the transformation of OM during sewage sludge composting, including determination of both the kinetic parameters of OM removal and of HS and HA formation during sewage sludge composting in an aerated bioreactor with wheat straw and leaves as amendments.

2. Materials and methods

2.1. Bioreactor for composting

The study was conducted in an aerated bioreactor with a capacity of 1 m³. A detailed description of the bioreactor was presented in the earlier work of Kulikowska and Klimiuk (2011). The bioreactor was aerated by air pumped from the fan to the aeration box, which was built into the bioreactor floor. The intensity of the aeration was controlled by a frequency converter coupled to the fan drive. The bioreactor was equipped with PT 100 temperature sensors, coupled with LED displays, which allowed precise determination of temperature to within 0.1 °C. The sensors were mounted at two levels, i.e. at depths of 7 cm and 63 cm.

The intensity of aeration was maintained 1–1.5 L/kg d.m.min in such a way as to prevent overheating of the compost.

2.2. Characterization of sewage sludge and feedstock preparation

Dewatered sewage sludge from a municipal wastewater treatment plant (operated as an SBR system) was mixed with lignocellulosic materials in the following proportions (w/w): sewage sludge 65%, wood chips 15%, wheat straw 10%, and leaves 10%. The sewage sludge did not contain bacteria of *Salmonella* spp. or parasite eggs of *Ascarsis*, *Trichuris* or *Toxocara* spp.

The characteristics of the composted waste and feedstock are shown in Table 1. Sewage sludge was characterized by the highest moisture and nitrogen content, wheat straw and wood chips had high OM content, and wheat straw had the lowest moisture content. Lignocellulosic materials were added to increase the C/N ratio, lower moisture content and improve the structure of the composted feedstock.

2.3. Analytical methods

Samples of composted waste were collected in accordance with the guidelines contained in the Polish standard PN-Z-15011-1.

Table 1
Characteristic of the components used for composting and composted feedstock.

Characteristic	Components				Feedstock
	Sewage sludge	Wood chips	Wheat straw	Leaves	
Moisture (%)	87.0 ± 3.2	34.0 ± 1.5	14.0 ± 0.8	58.0 ± 2.1	70.4 ± 1.4
Organic matter (%)	73.2 ± 2.6	97.2 ± 2.3	97.8 ± 1.4	63.0 ± 4.1	72.4 ± 1.7
TOC (% d.m.)	38.6 ± 1.8	48.1 ± 2.2	51.3 ± 2.4	19.04 ± 1.1	38.4 ± 0.8
N (% d.m.)	5.34 ± 0.6	0.88 ± 0.03	0.97 ± 0.03	0.42 ± 0.02	3.32 ± 0.08

The number of samples was adjusted to the volume of the bioreactor. Primary samples (3 samples, about 1 kg each, taken from the top, middle and bottom of the bioreactor) were piled up on a paved surface, and then thoroughly mixed to create a representative sample. In order to reduce volume, the representative sample was piled up in the shape of a truncated pyramid with a square base and a height not exceeding 30 cm. It was then divided with diagonals into 4 parts. Two of the opposing parts were discarded and the remaining two parts were mixed. The procedure was repeated in the same manner until a representative laboratory sample with a mass of 0.5 kg was obtained. The samples were mixed, dried at 105 °C and ground to a diameter of 0.5 mm using a Retsch SM 100 mill.

OM was determined by ignition of the samples at 550 °C (PN-Z-15011-3:2001); TOC in compost, HS and HA was determined using a Shimadzu Liquid TOC-VCSN analyzer; total N by the Kjeldahl method (PN-Z-15011-3:2001).

The dewatered sewage sludge was tested for *Salmonella* spp., and eggs of *Ascarsis*, *Trichuris* and *Toxocara* spp. in a specialized Laboratory of Microbiology and Parasitology which meets the requirements of the Polish standard PN-EN ISO/IEC 17025:2005.

2.3.1. Humic substances (HS) extraction

Before extraction of the HS, samples of compost were washed three times with distilled water to eliminate soluble non-humic substances (e.g. sugars and proteins). 50 ml of water were added to 2.5 g of compost, and the resulting mixture was shaken for approximately 1 h at 150 rpm. Then, the sample was centrifuged for 10 min at 9000 rpm. Next, the supernatant was discarded, and the above procedure was repeated three times.

In the second step, the samples were defatted with a chloroform:methanol (2:1) mixture (Jouraiphy et al., 2005) in a MarsX-press microwave oven. 1.5 g of the compost was transferred to a Teflon vessel and 20 ml of chloroform were added, as well as 10 ml of methanol. The extractions were carried out at 60 °C for 10 min. After extraction, the supernatant was discarded and a chloroform:methanol (2:1) mixture was again added to the sample. The extraction was repeated until a colorless supernatant was obtained. After that, the defatted samples were evaporated to eliminate the solvents.

The study used a two-stage extraction process (Boratyński and Wilk, 1965), which allows two kinds of HA to be obtained, i.e. labile humic acids (L-HA) (extraction with 0.1 M Na₄P₂O₇ at pH 7) and stable humic acids (S-HA) (extraction with 0.1 M NaOH at pH 12, after separation of L-HA). Sequential extraction with Na₄P₂O₇ and then NaOH enables the contents of L-HA and S-HA to be determined separately, and thus their contribution to total HA content can also be determined.

0.3 g of compost were shaken with 6 ml of 0.1 M Na₄P₂O₇ for 1 h, and then the mixture was centrifuged at 15000 rpm for 15 min. After the supernatant was transferred to a 50 ml volumetric flask, the procedure was repeated until a colorless supernatant was obtained. The extract in the 50 ml flask was filtered through a 0.45 µm filter, and then 0.1 M Na₄P₂O₇ was added for a final volume of 50 ml.

Next, this extract was acidified to pH 1 with H₂SO₄, after which the precipitated L-HA were left to coagulate at 4 °C for 24 h. After

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