

## INFLUENCE OF OZONE AERATION ON TOXIC METAL CONTENT AND OXYGEN ACTIVITY IN GREEN WASTE COMPOST

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### ABSTRACT

This paper presents the results of work on the reduction of toxic metal content while decreasing its oxygen activity. During the study the effects of different doses of ozone in the air used for aeration of the stabilized compost in the first post-thermophilic phase were analyzed. The results showed the possibility of reducing the concentrations of toxic metals and decrease the activity of oxygen by up to 30%, compared to traditional stabilized compost aeration system without using ozone.

**Keywords:** compost, ozone, toxic metals

## INTRODUCTION

The intensive socio-economic development that we observe in Poland causes an increase in the fraction of biodegradable waste. In accordance with applicable Polish law and EU guidelines called circular economy, a lot of efforts should be made to make the best use of raw materials which may be subject to the processes of recovery and recycling of waste. In Poland, material recovery is governed by the provisions of the Waste Act of December 2012 and the guidelines of the Department of Waste Management in the Ministry of Environment of December 2008. By analyzing the above documents, it was found that the main process of recovering biodegradable raw materials is composting [Grzesik and Malinowski 2016, Guidelines ... 2008, Dz. U. 2013 poz. 21, Ghiselliniet al. 2016, Morales et al. 2016].

In moderate climate conditions composting process is divided into two stages, with a total length of about 60 days. The duration of the process depends on the choice of the composting method (active system with aeration of material or passive without aeration) and the material to

be processed. Based on the literature analysis of the subject, it was stated that the first stage of the composting process should take up to 14 days.

Then the material is subjected to stabilization, which lasts about 6 weeks. At present, the works on optimization of the composting process kinetics in the first phase and elimination of accompanying odor emissions in the whole process are carried out in the world. [Lebrero et al. 2011, Gutierrez et al. 2015, Yuan et al. 2015, Fernández et al. 2016, Jinyiet al. 2016, Sileset al. 2016, Yongjian et al. 2016].

Optimization of the stabilization phase of the obtained compost relates to the possibility of using various substances neutralizing additional impurities (e.g. toxic metals, petroleum products, etc.). The literature on the subject also describes the experience that refers to the hygienisation of stabilized compost and the possibility of using gases produced during the process. [Benl-boukhet et al. 2016, Junya et al. 2016, Lian et al. 2016, Mukesh et al. 2016, Vandecasteele et al. 2016, Yuquan et al. 2016].

From a review of the subject literature, it appears that the major problem limiting the use of

compost as a fertilizer is high concentration of pollutants – mainly toxic metals. Previous studies on the use of ozone in the composting process centered around the disposal of effluents [Ciesielczuk and Kusza 2009, Mokhtarani et al. 2014, Amin et al. 2014].

In Poland, the possibility of using compost as a fertilizer is regulated by the Act on fertilizers and fertilization [Dz. U. 2007 No. 147, item. 1033], which classifies compost as an organic fertilizer. According to the guidelines of the Regulation of the Minister of Agriculture and Rural Development of 18 June 2008 on the implementation of certain provisions of the Act on fertilizers and fertilization, compost must meet strict quality requirements [Dz. U. 2009 No. 224, item. 1804].

Due to the lack of research and literature data, it was decided to investigate whether it was possible to use ozone as a substance that could reduce the toxic metal content and decrease the aerobic activity of the compost.

## MATERIALS AND METHODS

The composting process was conducted in an isothermal bioreactor adapted for studies

of biodegradable waste degradation processes (Figure 1). Based on laboratory research described in the literature [Kasiński and Wojnowska-Baryła 2013; Hurka and Malinowski 2015; Grzesik and Malinowski 2016] it was found that the course of the decomposition of organic matter in the bioreactor corresponds to composting processes on a technical scale. The study used a mixture of biodegradable waste consisting of grass (50%), sawdust (25%) and food waste (25%) with a total fresh weight of 30 kg.

The composition of the mixture was based on the literature data, to ensure obtaining the structural properties of the compost and providing a sufficient flow of air in the bioreactor, the biomass moisture content during the process (54–68%) and C:N ratio in excess of 20 units. For the correct composting process the air flow in the bioreactor was set at  $0.035 \text{ m}^3 \cdot \text{h}^{-1} \cdot \text{kg}_{\text{dw}}^{-1}$  (calculated as the composted mass of waste is  $0.4 \text{ m}^3 \cdot \text{h}^{-1}$ ).

After the completion of the thermophilic phase of the composting process (reaching a material temperature of  $45^\circ\text{C}$ ), 3 representative samples of 1500 g material were collected from the bioreactor, stabilized with air at ozone levels of 0, 10 and  $20 \text{ mgO}_3 \cdot \text{dm}^{-3}$ . Each representative sample was divided into 3 equal parts of



Fig. 1. Composting stand (photo: Rotameter, 2012)

500 g each, resulting in a total of 3 sets of ozone aeration samples. The ozone generator O3PRO DRP-30,7VW from Prozonex (Poland) was used to produce ozone-containing air. The aeration process was carried out in 500 ml round bottom flasks equipped with an air diffuser located at the bottom. During the aeration, the flask was shaken in a LP-Shaker360 laboratory shaker. The sample aeration process lasted 1 day.

After completion of the stabilization process, lasting 16 days, the resulting compost was sieved through a sieve with a mesh of 2 mm. The resulting material was mineralized in Milestone MLS1200 microwave oven. For the mineralization process, 3 sample weights of 0.25 g were prepared from each aerated compost sample. The samples were mineralized wet with 5 cm<sup>3</sup> of a solution of aqua regia. The samples were digested using a microwave mineralizer according to the recommended mineralization program. The samples after mineralization were quantitatively transferred to 25 cm<sup>3</sup> volumetric flasks using 1% HCl solution. The content of selected toxic metals (Pb, Cd, Ni, Zn, Cr, Cu) was determined by the atomic absorption spectrometer in a laboratory accredited to EN 13657: 2006.

From the obtained stabilization samples, 40 g of a sample was collected in 2 replicates to determine the aerobic activity of the material (AT<sub>4</sub>) according to the Richtlinie für die mechanisch-biologische Behandlung von Abfällen. Analogous material samples were subjected to the moisture analysis according to PN-EN 15169: 2007.

## RESULTS AND DISCUSSION

The content of selected toxic metals in the tested compost is shown in Table 1. The determined metal concentrations in the atmospheric air-borne ozone-free sample do not differ from

the literature values for green waste compost obtained in household appliances [Lima et al. 2004, Madrid et al. 2007, Puglisi et al. 2007, Ciesielczuk and Kusza 2009]. The use of the additive of 10 mg·dm<sup>-3</sup> of ozone in the air at the beginning of the compost stabilization phase resulted in a 10% reduction in the content of Pb and Cd, 6% drop in the concentration of Ni and Cr, and loss of Cu and Zn at 4 and 2.5% in relation to the compost aerated without ozone additive.

The addition of ozone at the level of 20 mg·dm<sup>-3</sup> to the air during stabilization of the compost caused an increase in levels of the reduction of toxic metal concentrations in the samples. The greatest reduction was noted for zinc, which 3.5 times exceeded the removal of Zn for a dose of 10 mg·dm<sup>-3</sup> of ozone. The lowest reduction of toxic metal content in the compost, with the application of 20 mg·dm<sup>-3</sup> ozone, is characterized by chromium and lead. The reduction of these metals in relation to the halftime of the ozone dose is 1.6 times. In other cases (Cd, Ni, Cu) twice the increase in ozone in the air caused a double increase in the removal of toxic metals. Comparing the results of the reduction of toxic metals concentrations in air-borne samples with the addition of 20 mgO<sub>3</sub>·dm<sup>-3</sup> with ozone-free aerobic results, the concentration of metals was reduced from 8% (for Zn and Cu) to 27% (for Cd).

Compost produced from biodegradable waste is characterized by small concentrations of toxic metals – especially cadmium and chromium (Table 1). Compared to the compost obtained in professional municipal waste installations, concentrations of toxic metals were reduced by 5÷10 times [Lima et al. 2004, Madrid et al. 2007, Puglisi et al. 2007, Ciesielczuk and Kusza 2009].

By analyzing the data presented in Table 2, the positive effects of the use of ozone on the stabilization process of compost can be shown. The addition of ozone to the air during stabilization

**Table 1.** The average content of heavy metals in the examined compost along with a standard deviation [mg·kg<sub>dw</sub><sup>-1</sup>]

Toxic metal	Ozone content in the air [mg·dm <sup>-3</sup> ]			Acceptable content of toxic metals for organic fertilizers acc. Dz. U. 2009 No. 224, item. 1804
	0	10	20	
Pb	26.19±0.17	23.57±0.33	22.04±0.29	140
Cd	1.06±0.02	0.93±0.07	0.77±0.08	5
Ni	9.81±0.11	9.23±0.09	8.45±0.15	60
Zn	190.74±6.38	185.98±9.21	174.08±7.03	-
Cr	3.49±0.71	3.26±0.4	3.1±0.59	100
Cu	60.8±2.93	58.27±6.09	55.69±4.62	-

**Table 2.** Average value of AT4 and humidity in the tested compost.

Parameter	Ozone content in the air [mg·dm <sup>-3</sup> ]		
	0	10	20
Humidity [%]	28.62±2.53	22.49±2.18	18.03±1.94
AT4 [mgO <sub>2</sub> ·g <sub>dw</sub> <sup>-1</sup> ]	12.06±1.13	9.53±0.88	8.72±0.92

had a positive effect on the moisture content of the stabilizer in the range 22–37%. Blank test (0 mgO<sub>3</sub>·dm<sup>-3</sup>) does not meet the regulatory requirements for mature composts (AT4 indicator above 10 mgO<sub>2</sub>·g<sub>dw</sub><sup>-1</sup>). The use of ozone at the start of the stabilization phase resulted in a reduction in aerobic activity of compost from 21 to 28%.

## CONCLUSIONS

Experimental experience has shown a positive effect of ozone on the reduction of toxic metals – Pb, Cd, Ni, Zn, Cr, Cu – in the obtained stabilized compost to 30% of the base value. The research has shown the significant effect of ozone on the quality parameters of the resulting compost. In both anaerobic analyzes (10 mgO<sub>3</sub>·dm<sup>-3</sup> and 20 mgO<sub>3</sub>·dm<sup>-3</sup>), a decrease in the stabilized compost humidity up to 40% and an oxygen activity up to 30% in relation to the aerobic sample without ozone.

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