

Sorption of exhaust gases, CO₂ and NH₃, during biodegradation of solid waste in reactor system

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ABSTRACT

Composting is a biological treatment in which aerobic mesophilic and thermophilic microorganisms transform the biodegradable organic matter into CO₂ and H₂O, as well as into more stable organic matter. Two major byproducts of microbial transformation during biodegradation of solid waste are carbon dioxide (CO₂) and ammonia (NH₃). Carbon dioxide is a greenhouse gas, while ammonia is a noxious, toxic gas that can cause serious damage to human health and to the environment. Therefore, it is important that studies be carried out to find ways to efficiently control the emission of these gases.

The purpose of this work was to investigate sorption of gases, ammonia and carbon dioxide, on different sorbents during composting of mixture of tobacco waste and grape marcs. Composting process was carried out with forced aeration (0.645 dm³ min⁻¹ kg_{vs}⁻¹) in column reactor (10 dm³) under adiabatic conditions during 21 days. During the process, temperature changes in the reactor, pH value, COD of condensate, C/N ratio were closely monitored while evolved CO₂ and NH₃ were analyzed periodically. Ammonia was measured both in the condensate and in 4 % boric acid trap (which was placed after adsorbent), while CO₂ was trapped in 1 M NaOH.

The results showed that zeolite and potting soil are good adsorbents for sorption of ammonia gas. The concentration of ammonia in exhaust gas increased after 12 days of composting process, when the pH-value in composting mass increased to 9. It can be concluded that ammonia emission mainly depended on increase of pH-value of composting mass. The amount of ammonia in condensate was higher than in exhaust gases. The emission of carbon dioxide is in correlation with the temperature in the reactor and it was found that the highest CO₂ concentrations were measured in thermophilic stage during high activity of microorganisms.

Keywords: Composting of winery and tobacco waste, sorption of exhaust gases, zeolite, potting soil, adiabatic reactor.

INTRODUCTION

Composting is an environmentally friendly process for stabilization of biodegradable organic solid wastes and is considered as one of the most suitable ways of disposing such wastes [1, 2]. Environmental pollution from agricultural wastes, including tobacco and grape wastes, and inflation of fertilizers prices, composting has acquired widespread usage as biodepositional method in developing countries [3, 4]. Tobacco waste is generated during different processes of the tobacco and cigarette production cycles and grape waste is a primary waste of wine production [5, 6]. Except many benefits of composting, emission of polluting gases is one disadvantage of this process [4].

Most of the engineering research on composting process aims to find a way to remove gases which are evolved during composting. Ammonia (NH₃) and carbon dioxide (CO₂) are two major gases which appear in exhaust air. Ammonia is a colorless air pollutant and it is an environmental hazard [7]. Emission of ammonia contributes to bad odors around composting plants, takes part to the eutrophication of ecosystem and to acid rains. Also, losses in nitrogen reduce the fertilizer value of the compost [8]. The pH value, temperature, C/N ratio and aeration rate enhance volatilization of ammonia during composting [9]. Carbon dioxide is a greenhouse gas with the largest impact on climate changes [5].

The exhaust gases, ammonia and carbon dioxide, which are evolving during composting of tobacco and grape waste can be efficiently removed by adsorption on different solid media like potting soil, peat, zeolite and activated carbon [10, 11]. Zeolites are minerals with a unique structure which allows them to entrap or release various cations as a consequence of cation exchange reactions and adsorption [12]. Zeolites have a high adsorption capacity for ammonium ions and also can adsorb carbon dioxide because carbon dioxide has a great quadrupole moment and might interact strongly with electric field of zeolites [13]. Potting soil is an organic material with high adsorption capacity for ammonium ions and because of its high availability and low cost often is used as an adsorbent (biofilter) for ammonia [11].

The aim of this study was to remove gases (NH₃ and CO₂) from exhaust air evolved during composting of tobacco and grape waste in an adiabatic reactor by adsorption on zeolite and potting soil in a laboratory-scale adsorption column.

MATERIALS AND METHODS

Materials

For the composting experiments, mixture of grape and tobacco solid waste was used as a composting substrate. Grape waste was generated in the wine production on Plesivica hill in western part of Croatia. The pH-value and moisture content of the waste product were 4.3 and 60 %, respectively. In order to avoid any kind of degradation, fresh winery waste was kept in a freezer at -18 °C until it was used for the experiments. Tobacco waste (TW) was generated during tobacco production in tobacco factory TDR d.d., Rovinj, Croatia. The tobacco waste product was composed of very fine powdery residues, leaf stalks and wet leaf parts with average moisture content of about 75%. Freshly collected tobacco waste was dried in the laboratory with natural convection and stored in dry place, until it was used for the experiments.

Adsorbents used for sorption of NH₃ and CO₂ were natural zeolite, clinoptilolite, and potting soil. Zeolite originated from natural source nearby Krapina in western region of Croatia and potting soil originated from Zrinjevac, Zagreb. Zeolite was crushed in laboratory jaws crusher (Matest, A092 TE, Italy) and sieved to particle size from 1.0 to 2.0 mm. For the adsorption experiments sieved zeolite was air dried in oven at 200 °C for 12 hours [14].

Potting soil was sterilized in autoclave at 121°C for 30 minutes. The relative humidity of potting soil was 60%.

Composting Experiments

The composting experiments of tobacco and grape waste were conducted in a closed thermally insulated column reactor with effective volume of 10 dm³. Two sets of experiments were conducted, one with zeolite and second with potting soil as an adsorbent with the same initial parameters. The composting mixture was prepared by mixing of grape marcs (GM) and tobacco waste (TW) in the ratio of GM: TW = 55: 45 (dry weight). The moisture content of the substrate was set to about 60 % by adding the water and the 4.0 kg of mixture was put into reactor from the top. The reactor was operated at an airflow rate of 0.645 dm³ min⁻¹ kg⁻¹ volatile solids(VS) and temperature was monitored by thermocouples placed at the reactor's inlet and in the middle of the reactor connected to the data logger during the 21 days of composting. Condensate was collected into the graduated cylinder. During composting, samples were periodically taken and the most relevant physical-chemical parameters were analyzed (pH, moisture content (MC), dry matter (DM), volatile solids (VS), Kjeldahl-N content). All analyses were carried out in duplicate and according to the Austrian standard methods for analysis of compost, which are widely used in Europe [15]. Content of the NH₄⁺-N in the composting mass was determined spectrophotometrically according to standard methods [16].

The stream of spent air from composting process was split proportionally in two streams by two airflow meters with regulation valves. In order to determine concentration of evolved NH₃ and CO₂, the one stream was passing through 4% H₃BO₃ and after that in 1M NaOH solution, respectively. The adsorption efficiency of zeolite and potting soil was examined by passing the second stream through the adsorption column and then through 4% H₃BO₃ and 1M NaOH. Adsorption column was made of PVC with inner diameter of 35 mm. 170 g of pre-dried zeolite and 55 g of potting soil with 60% of moisture content were placed in the column and the height of the zeolite and potting soil bed were 200 mm. During composting, samples of potting soil were periodically taken and concentration of ammonium ions were determined [16]. CO₂ was analyzed daily by titration of the excess of 1M NaOH with 1M HCl. Ammonia was determined according to literature [16].

RESULTS AND DISCUSSION

Generation of ammonia and carbon dioxide and sorption on natural zeolite and potting soil

During composting of organic wastes, i.e. tobacco and grape waste, the mineralization of some organic nitrogen (ammonification) present in materials such as proteins, amino acids and urea release considerable free ammonium (NH₄⁺/NH₃) which run out into the atmosphere with the exhaust air [17]. These emissions cause environmental problems, so it is important to find efficient process for removing ammonia from exhaust air. The pH value, temperature, C/N ratio are the main factors which have influence on ammonia emission [4].

Figure 1 shows the concentration of ammonia in exhaust air and ammonia adsorbed on zeolite and potting soil during composting. It can be seen that concentration of ammonia increased at day 12, when the pH of composting mass became 8.7, and at the end of process started to decrease. The optimum pH-value for composting is between 5.5 and 8.0. At the start of process the pH-value of composting mass was 5.3 and during another three days it dropped to acidic range because of production of organic acids. Afterward, the pH of substrate became more and more alkaline. As a concentration of ammonia in exhaust air increased the concentration of ammonium ions in substrate started to decrease because the air flow stripped off the ammonium from composting mass (Figure 2). Since the ammonification process in composting mixture is generally higher than that of immobilization, it causes an accumulation of $\text{NH}_4^+/\text{NH}_3$ which is then stripped with aeration flow [17]. From Figure 1 also it can be seen that zeolite adsorbed whole concentration of ammonia which is evolved during composting of tobacco and grape waste which was not the case with potting soil. At day 15 the concentration of ammonia in exhaust air started to increase at the exit of column with potting soil (Figure 1). Potting soil and zeolite have a high adsorption capacity for ammonium ions. To obtain the same height of adsorbent in column the mass of zeolite was larger than the mass of potting soil (170 g and 55 g, respectively). Further, the samples of potting soil were periodically taken to measure adsorbed ammonia which was not the case with zeolite. At the end of the process the concentration of ammonia in exhaust air was equal with the concentration of ammonia in exhaust air after adsorption on potting soil. Potting soil was saturated and reached plateau which indicates that there was no more available sites for adsorption of ammonia (Figures 1 and 2).

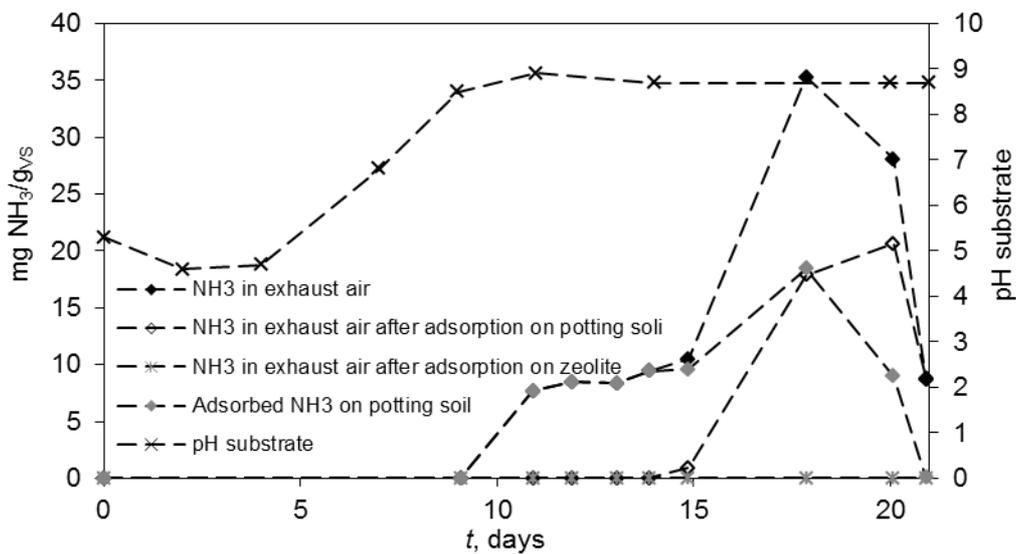


Figure 1 Evolved ammonia in exhaust air and sorption on zeolite and potting soil during composting.

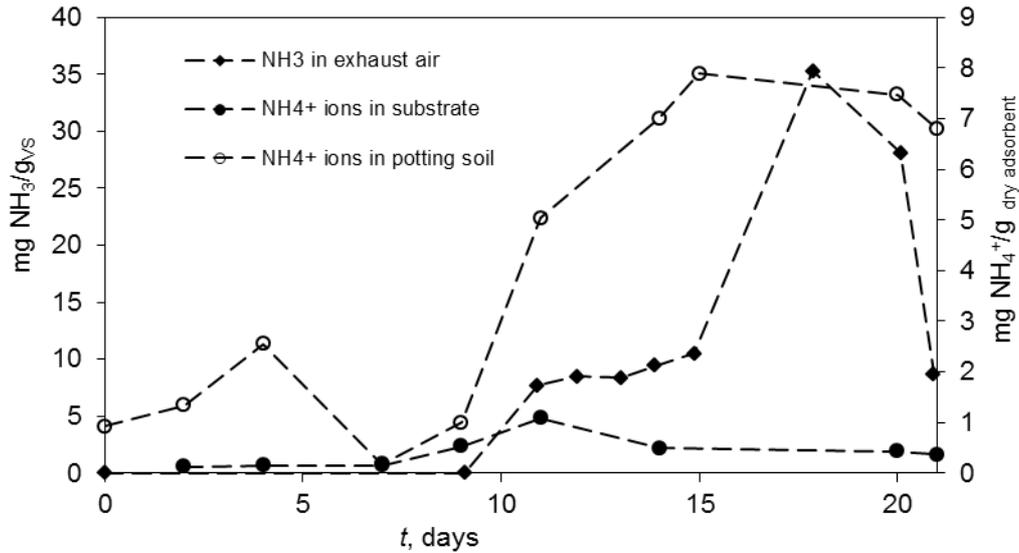


Figure 2 Concentration of ammonium ions in substrate and potting soil during 21 days of composting.

The dynamics of CO₂ release in the compost reactor is highly influenced by the temperature regime. Equation (1) and (2) describe production of CO₂, and equation (3) the absorption of CO₂ in the hydroxide solution [18]:



Figures 3 and 4 show concentration of carbon dioxide in exhaust air and concentration of carbon dioxide after adsorption on zeolite and potting soil. Adsorption processes for gas separation via selective adsorption on solid media are well-known. These adsorbents can operate via weak physisorption processes or strong chemisorption interactions [14]. It can be seen that zeolite adsorbed carbon dioxide but not the whole evolved CO₂, only 31%. It is known that zeolites have a high potential for CO₂ capture, but CO₂ adsorption is influenced by different parameters like size of zeolites, number of exchangeable cations in their cavities, polarity, and presence of water, gas phase pressure and temperature [13]. From Figure 4 it can be seen that potting soil has not removed carbon dioxide from exhaust air. The relative humidity of potting soil was 60% and presence of water inhibited the adsorption of CO₂. The formation of bicarbonates is a result of reaction of water and carbon dioxide which can take the place on the specific area of potting soil.

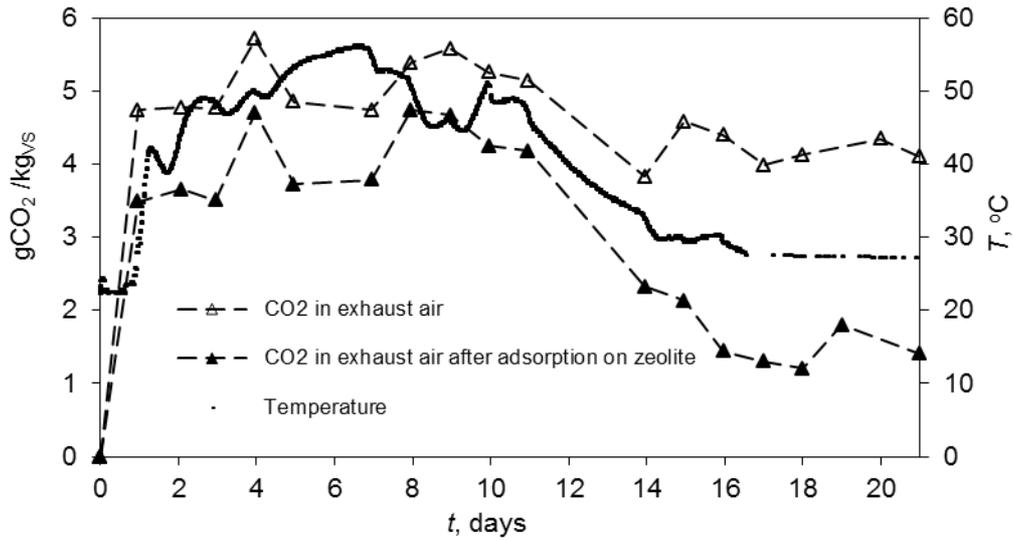


Figure 3 Generation of carbon dioxide versus temperature and sorption on zeolite during composting.

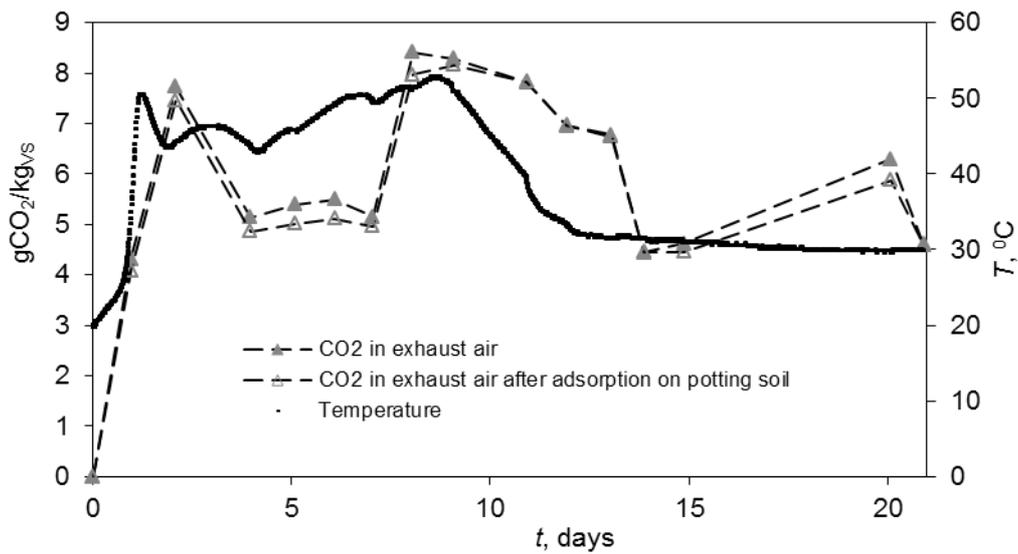


Figure 4 Generation of carbon dioxide versus temperature and sorption on potting soil during composting.

Emission of carbon dioxide is proportional with temperature. The higher production of CO₂ occurred at the beginning of the process, characterized by high temperatures and intense biodegradation of organic fraction of tobacco and grape waste (Figs. 3 and 4). After 10 days, the concentration of carbon dioxide started to decrease until the end of process.

During composting of tobacco and grape waste the evolved condensate was collected and chemical oxygen demand (COD) was daily determined spectrophotometrically [16]. From Figure 5 it can be seen that in the first several days of process the COD of condensate was high (10000 mgO₂/dm³) because of intensive biodegradation and formation of volatile

organic compounds. This result suggests that volatile organic compounds were also blown out with moisture and appeared in exhaust air and after cooling in condensate as well. In the later stage of composting the biodegradation became slower and the concentration of volatile compounds decreased, and accordingly the COD value in condensate decreased. The COD of condensate at the end of composting process was 100 mg O₂/dm³.

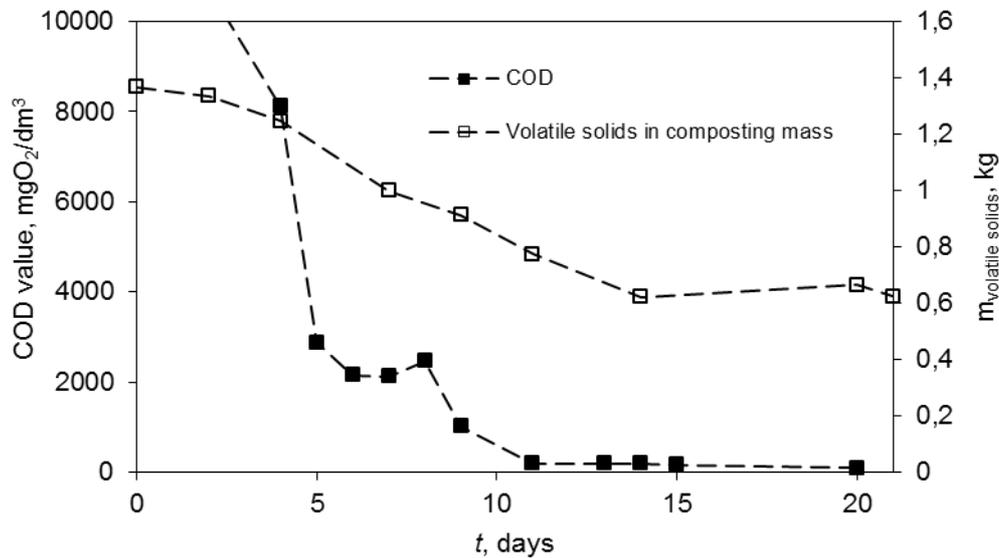


Figure 5 Changes of volatile solids mass in substrate and organic load of condensate expressed as COD during composting process

C/N ratio and conversion of substrate during composting of tobacco and grape waste

The initial C/N ratio is one of the most important factors affecting the composting process and the compost quality. Haug [19] proposed an optimum C/N ratio of composting mass to be within 15-30. The initial C/N ratio of tobacco and grape waste was 35 and it was gradually decreasing with increasing of conversion of volatile solids, expressed as degradation of organic matter in a waste solid (Fig. 6). The highest nitrogen losses during composting were caused by gaseous emissions in the form of NH₃ (Fig. 2). The most intense degradation is evident in the first 9 days. The conversion of substrate at the end of composting process was 54% and C/N ratio was 17.

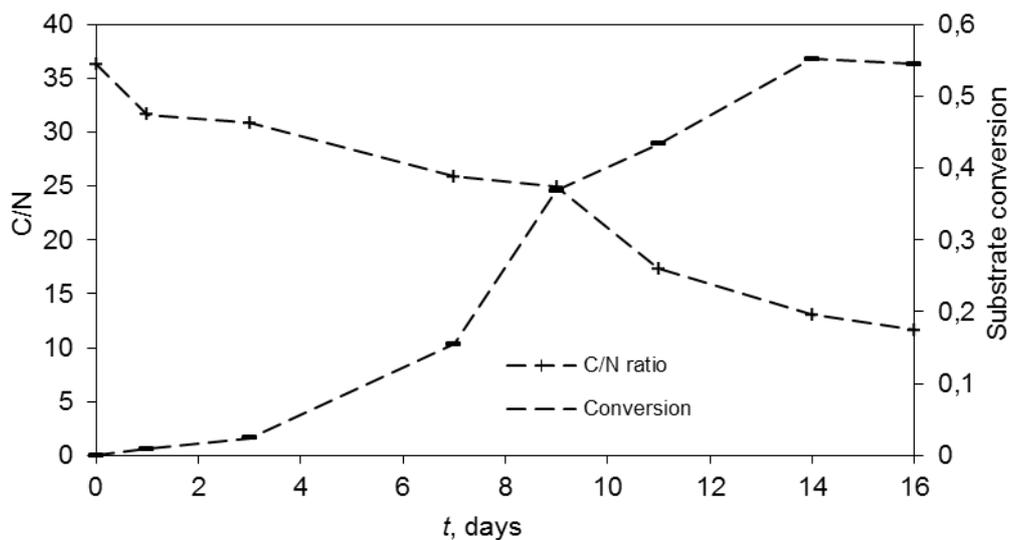


Figure 6 C/N ratio versus conversion of mixture of grape and tobacco waste during 21 days of composting.

CONCLUSIONS

During 21 days of composting process of tobacco and grape waste in a closed reactor the following parameters were determined. Initial pH value of substrate was 5.3, initial C/N ratio was 35 and till the end of process the values were 8.7 and 17, respectively.

The C/N ratio, pH value and temperature had a great influence on ammonia emissions. The concentration of ammonia in exhaust air increased with increase of pH value of substrate. During 21 days of composting in exhaust air evolved 116.54 mg NH₃/g_{VS} of ammonia and in the experiment with zeolite, a whole amount of ammonia was adsorbed from exhaust air. In second experiment with potting soil this amount was not completely adsorbed. The remaining mass of ammonia in exhaust air after adsorption was 48.03 mg NH₃/g_{VS}.

The most of carbon dioxide evolved in the first 10 days of process during the elevated temperature in composting mass. The cumulative evolved mass of carbon dioxide in exhaust air in the experiments with zeolite and potting soil was 84.34 g CO₂/kg_{VS} and 91.42 g CO₂/kg_{VS}, respectively. After adsorption on zeolite and potting soil the cumulative remaining carbon dioxide in exhaust air was 53.78 g CO₂/kg_{VS} and 88.56 g CO₂/kg_{VS}, respectively.

The value of chemical oxygen demand in the condensate at the beginning of composting process was 10730 mgO₂/dm³ and as the biodegradation process stopped at the end of process COD was 95 mgO₂/dm³.

Acknowledgement

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