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Sorption of ammonia and carbon dioxide evolved during composting of winery and tobacco waste in reactor system

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ABSTRACT

Two major gaseous byproducts of microbial transformation during aerobic biodegradation of solid waste are carbon dioxide (CO_2) and ammonia (NH_3). As is well known that CO_2 is the greenhouse gas and NH_3 is a noxious, toxic gas. It is important to find ways to efficiently control and remove these gases from waste gaseous streams.

The purpose of this work was to investigate sorption of ammonia and carbon dioxide on zeolite during composting of winery and tobacco waste mixture. Composting experiments were carried out with forced aeration in thermally insulated packed bed reactor (10 dm^3 of working volume) during 16 days. During the process, temperature changes in the reactor were continuously monitored and evolved CO_2 and NH_3 in the gaseous stream, pH value, C/N ratio, volatile solids content and mesophilic and thermophilic microorganisms in the composting mass were determined periodically.

At the end of the composting process 54% of volatile solids were degraded and zeolite showed good efficiency in sorption of ammonia as well as of carbon dioxide.

Keywords: composting, grape and tobacco waste, adiabatic reactor, ammonia and carbon dioxide emission, sorption, zeolite

INTRODUCTION

Composting is a biochemical process converting various components in organic wastes into stable humus suitable for use as a soil amendment or organic fertilizer and can provide sufficient sanitation effect [1, 2]. Tobacco and grape waste are classified as agro-industrial waste and as such can be decomposed by composting [3]. Composting is used widely, especially in developing countries because of its inexpensive costs and simply technique. But composting also has a negative influence on environment due to the emission of polluting gases [2].

Two major polluting gases during composting of tobacco and grape waste are carbon dioxide (CO_2) and ammonia (NH_3) [3]. CO_2 is a greenhouse gas and is a main gas generated during organic matter degradation [4]. Ammonia (NH_3) is a colorless air pollutant with a strong, repellent odor and it is an environmental hazard. It is commonly emitted by composting plants, livestock farms, meat-processing plants and sewage treatment plants [5]. During composting of organic waste which contains materials such as proteins, amino acids and urea results in considerable release of free ammonium (NH_4^+/NH_3) in surrounding atmosphere. Several factors such as C/N ratio, pH value, temperature aeration rate can influence the volatilization of ammonia during composting [2].

Some solid media such as potting soil, peat, zeolite, basalts, and activated carbon have been used for adsorption of ammonia which is evolved during composting [1, 6, 7]. Zeolite is mineral with a unique structure and with high adsorption capacity [8]. Also, it can adsorb carbon dioxide because CO_2 has a great quadrupole moment and might interact strongly with electric field of zeolites [9].

The aim of this study was to remove gases from exhaust air, carbon dioxide and ammonia, which are evolving during composting of winery and tobacco waste in an adiabatic reactor by adsorption onto natural zeolite in a laboratory-scale adsorption column.

MATERIALS AND METHODS

Materials

For the composting experiments, mixture of winery and tobacco solid waste was used as a composting substrate. Winery waste (WW) mostly consisted of grape marcs were 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, winery waste was kept in a freezer at -18 ºC until it was used for the experiments. Tobacco waste (TW) was generated during tobacco production in tobacco factory TDR, Rovinj, Croatia. The tobacco waste product consisted from very fine, powdery residues to 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.

Adsorbent used for sorption of NH_3 and CO_2 was natural zeolite, clinoptilolite originated from natural source nearby Krapina in western region of Croatia. 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 investigation zeolite was air dried in oven at 200 °C for 12 hours [10].

Experimental run and physical-chemical monitoring and analyses

Composting was conducted in specially designed thermally insulated, forcefully aerated reactor with 10 dm^3 of working volume. The composting substrate was prepared by mixing of grape marcs and tobacco waste in the ratio of WW: TW = 55: 45 (dry weight). The moisture content (MC) of the substrate was set to about 60 % by adding the water and the 4.0 kg of substrate was put into reactor from the top. During composting continuous upward aeration was provided by an air compressor and airflow was set to 0.56 $dm^3\ min^{-1}\ kg^{-1}_{init.volat.matter}$. To ensure permanent air humidity at the reactors inlet, prior to entering the reactor air was saturated with moist by passing through Drechsel bottle. After leaving the reactor, the hot spent air cooled down naturally and the condensate collected into the graduated cylinder (Fig. 1a). Reactor was placed on the scale in order to periodically determine total mass inside the reactor. During composting samples were collected daily and the most relevant physical-chemical parameters were analyzed (pH, MC and dry matter, volatile matter (VM) 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 [11]. Content of the NH_4^+-N in the composting mass was determined spectrophotometrically according to standard methods [12]. During 16 day of composting temperature was continuously monitored by RTD probes placed at the reactors inlet and in the middle of the reactor.

The stream of spent air from composting process was split proportionally in two streams by two air flowmeters with regulation valves (Fig.1b.). In order to determine concentration of evolved NH_3 and CO_2, the stream b1 was passing through 4% H_3BO_3 and 1M NaOH solutions, respectively. Zeolite adsorption efficiency was examined by passing the stream b2 through the adsorbtion column and then through 4% H_3BO_3 and 1M NaOH. Adsorption column was made of PVC with inner diameter of 35 mm. 170 g of pre-dried zeolite was placed in the column and the height of the zeolite bed was about 200 mm. Carbon dioxide was analyzed daily by titration of the excess of 1M NaOH with 1M HCl. Ammonia was determined according to literature [12].

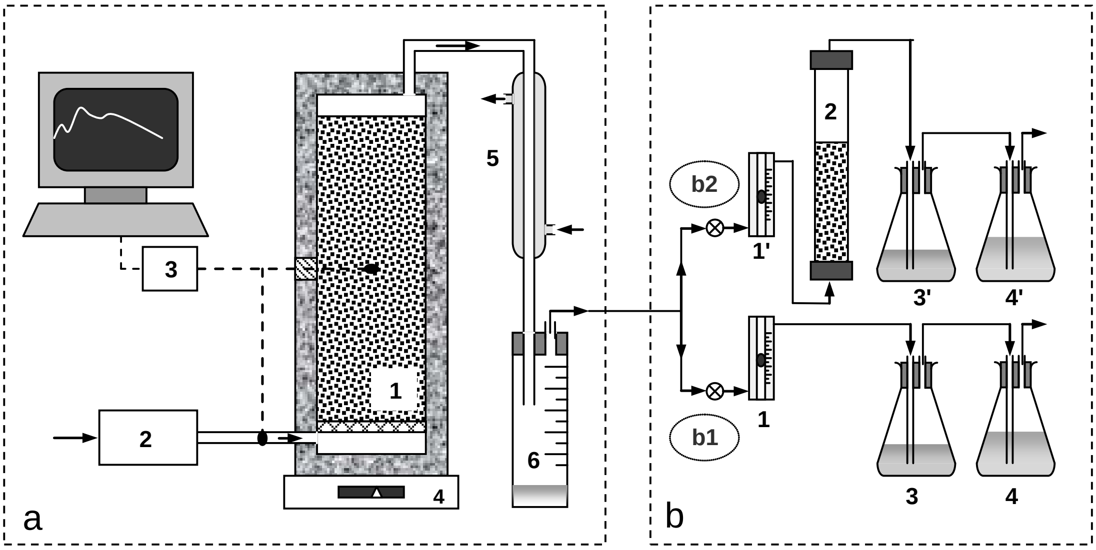

Fig. 1. Schematic diagram of composting process **(a) - 1**-composting reactor, **2**-compressor and airflow regulation, **3**-temperature data acquisition, **4**-scale, **5**-condenser, **6**-graduated cylinder; and gas sorption and analysis **(b) - 1,1'**-flowmeter, **2**-adsorption column, **3,3'**-H_3BO_3, 4%, **4,4'**-NaOH, 1M.

RESULTS AND DISCUSSION

Temperature

Temperature is one of the most important parameters for maintaining the efficiency of composting process. It is directly correlated to the biochemical activity in the composting mass, because the heat of reaction involved in the cellular anabolism and catabolism processes causes a temperature increment in the composting mass [3]. During composting of winery and tobacco waste organic matter is decomposed at various speeds at several temperature stages at which specific microorganisms play a dominant role. Composting process is known to go through tree stages: mesophilic, thermophilic and cooling. Stentiford suggested that temperatures higher than 55^{o}C maximized sanitation, those between 45 and 55^{o}C maximized the biodegradation rates, and between 35 and 40^{o}C maximized microbial diversity in the composting process [8].

The temperature of composting mass at beginning of process was 22^{o}C and after 4 days rapidly increased to 55^{o}C. After eight days of composting the composting mass started to cool until the compost and ambient temperature leveled (Fig. 2.). During the composting process it was observed a change in number of mesophilic (20-45^{o}C) and thermophilic (45-70^{o}C) microorganisms (bacteria and fungi) (Fig. 2.). The microbial species involved in the degradation of the substrate and their number has been changing with the change of the temperature in reactor. The rise of temperature in composting mass enabled the growth of thermophilic microorganism and their activity. In thermophilic stage the metabolic heat started to decrease as a result of biodegradation of macromolecules that uses a large amount of energy, and temperature started to drop. At the beginning of composting the number of mesophilic bacteria were $8.5x10^{7}$ and after 7 days increased to $1.2x10^{9}$ and remained at this level till the end of process. The exponential growth ($1.7x10^{6}$ to $3.0x10^{7}$) of thermophilic bacteria started after third day when the temperature increased. Bacteria are mostly responsible for starting the composting process because they consume available soluble nutrients, which produces metabolic heat. The mesophilic and termophilic fungi at the beginning of process increased ($1.8x10^{8}$-$2.8x10^{9}$), ($9.7x10^{3}$-$3.5x10^{4}$) and after 7 days of composting decreased ($2.8x10^{9}$-$1.7x10^{7}$), ($3.5x10^{4}$-$2.8x10^{3}$).

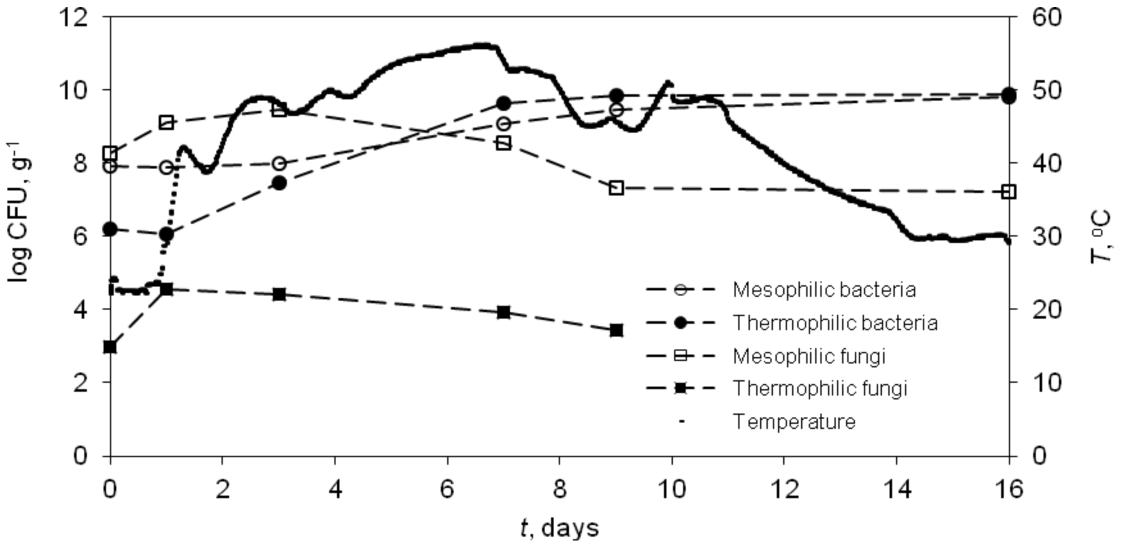

Fig. 2. Temperature changes in composting mass and growth of microorganisms during 16 days of composting.

Evolution of ammonia and carbon dioxide and sorption on natural zeolite

During composting of winery and tobacco waste the emission of ammonia and carbon dioxide were monitored. Ammonia is generated from decomposition of organonitrogen materials and depending on the condition of the mixture being composted [13]. The pH value, temperature, C/N ratio are the main factors which have influence on ammonia emission [3].

The pH value is one of the important characteristics of the composting process and optimum pH value for composting is between 5.5 and 8.0 [14]. The pH value of the composting mass was at the beginning of process 5.3 and dropped to acidic range (pH=4.6) because of production of organic acids. Afterward pH value increased to alkaline range (pH=8.6) due to the production of ammonia [14]. The increase of concentration of ammonia in exhaust air is caused by microbial decomposition (Fig. 3.). Also, the pH level affects the ammonium sorption on zeolites. At low pH value, the ammonium ions had to compete with hydrogen ions among the exchange sites [6]. For practical applications, the best pH value is between 4 and 8. Fig. 3. shows the evolved ammonia in exhaust gases during composting and concentration of ammonia after adsorption on zeolite. It can be seen that zeolite adsorbed the whole evolved ammonia from composting process. Also, the concentration of ammonia in exhaust gas increased as temperature decreased.

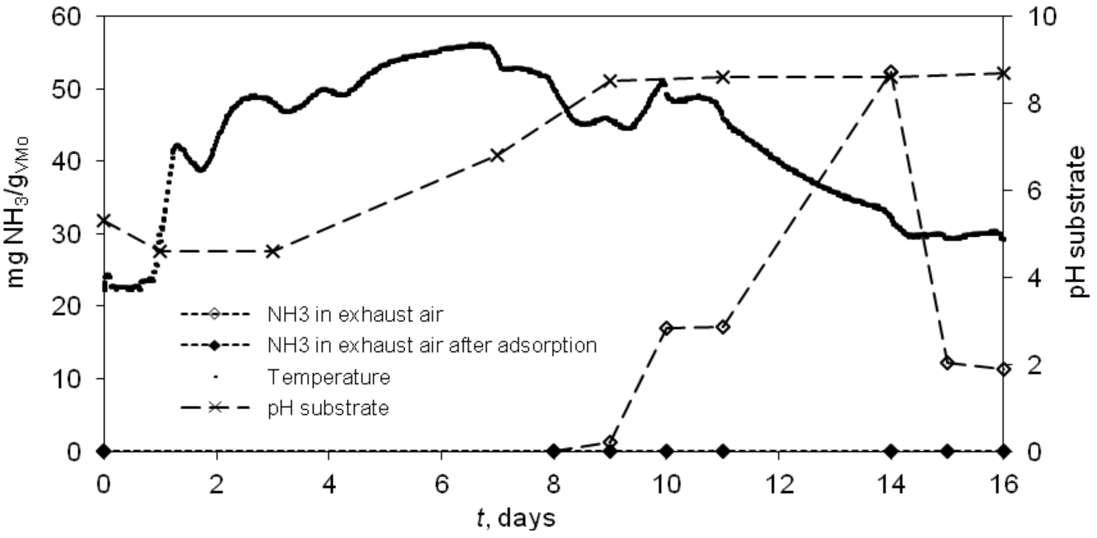

Fig. 3. Evolved ammonia in exhaust air versus temperature and sorption on zeolite during composting.

Fig. 4. shows that concentration of ammonium ions in substrate started to increase after 4 days and reached a maximum after 10 days. Then, due to the NH_3 emission, the concentration of ammonium ions in substrate began to decrease.

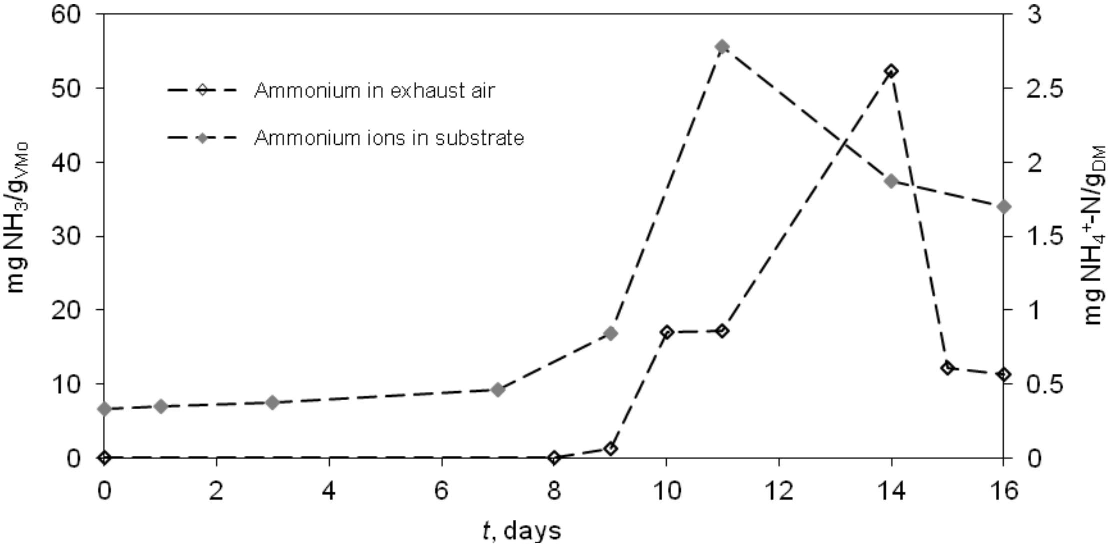

Fig. 4. Comparison of ammonium ion in substrate and evolved ammonia in exhaust air during 16 days of composting.

The dynamics of CO_2 release in the compost reactor is highly influenced by the temperature regime. Equation (1) and (2) describe the production of CO_2, and equation (3) the absorption of CO_2 in the hydroxide solution [15]:

$$C_5H_{19}O_3N + 12.5O_2 \rightarrow 10CO_2 + NH_3 + 8H_2O \quad (1)$$
$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \quad (2)$$
$$NaOH + CO_2 \rightarrow NaHCO_3 \quad (3)$$

Fig. 5. shows emission of carbon dioxide and concentration of CO_2 after sorption on zeolite. Adsorption processes for gas separation via selective adsorption on solid media are well-known. These adsorbents can operate via week physisorption processes or strong chemisorption interactions [10]. It can be seen that zeolite adsorbed carbon dioxide but not whole evolved CO_2, only 31%. It is known that zeolites have a high potential for CO_2 capture, but CO_2 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 [9]. Regeneration of zeolite is also very important. Zeolites have good regeneration properties without significant degradation even after numerous cycles of adsorption and desorption [9].

Emission of carbon dioxide is proportional with temperature. CO_2 production has been used as a respirometric index to measure microbial activity. The higher CO_2 production occurred at the beginning of the process characterized by high temperatures and intense biodegradation of organic fraction of tobacco and grape waste (Figs.2. and 5.). After 10 days, the concentration of carbon dioxide started to decrease until the end of process.

The C/N ratio is one of the vital aspects of composting. Values between 25:1 and 35:1 are considered to be optimal. If the C/N ratio exceeds 35:1 the composting process is slowed down, while ratio less than 20:1 results in a loss of nitrogen which occurs mainly as NH_3 emissions [8].

The initial C/N ratio of tobacco and grape waste was 35:1. The organic matter which is biologically degradable is converted into volatile CO_2 and H_2O and is removed from compost and the total N content increases which results in a C/N decrease toward the end of composting (Fig. 6.). The highest nitrogen losses during composting were caused by gaseous emissions in the form of NH_3 (Fig. 4.). The most intense biodegradation is evident in the first 9 days, i.e. in the first half of the composting process. The conversion of substrate at the end of composting was 54% and C/N ratio was 17.

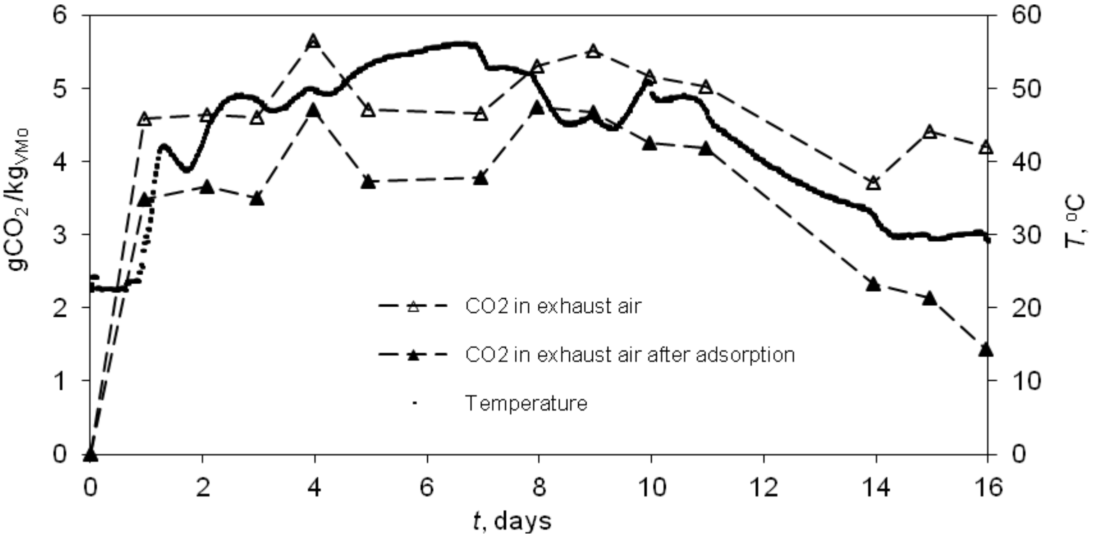

Fig. 5. The evolution of carbon dioxide versus temperature and sorption on zeolite during composting.

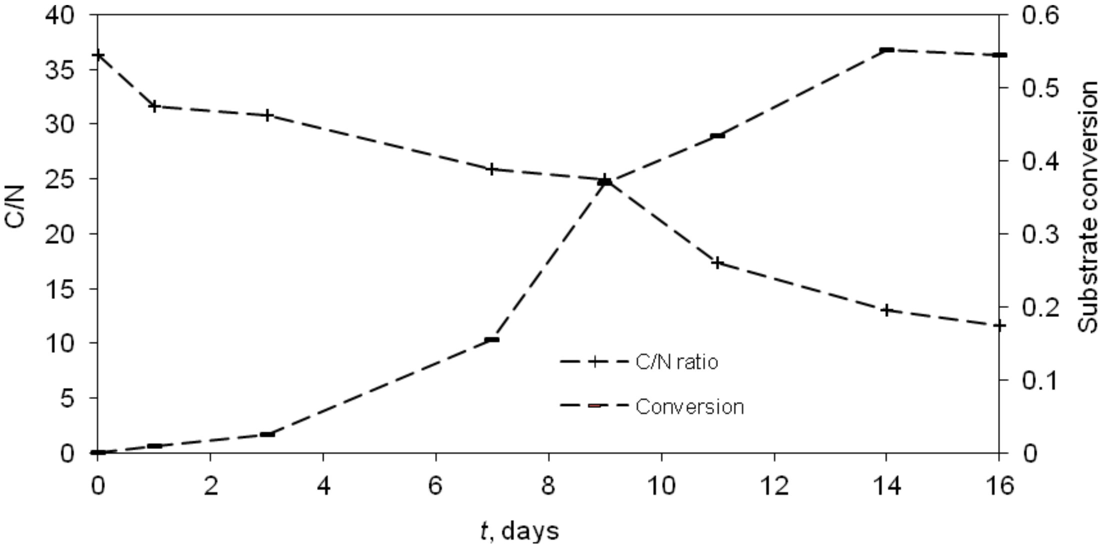

Fig. 6. C/N ratio versus conversion of mixture of winery and tobacco waste during 16 days of composting.

CONCLUSIONS

During 16 days of composting of winery and tobacco 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 8.6 and 17, respectively.

As a temperature started to increase (T= 55°C) in composting mass, the concentration of carbon dioxide in spent air also increased. The cumulative evolved carbon dioxide without sorption on zeolite was 65.57 g CO_2/kg_{VM0}, while adsorbed on zeolite 18.96 g CO_2/kg_{VM0}. Zeolite adsorbed approximately 30% of carbon dioxide from exhaust air.

The pH value, C/N ratio and temperature influenced on ammonia emission. The concentration of ammonia in spent air increased with increase of pH value of composting mass (day 9) and with the decrease of concentration of ammonium ions of substrate. The total concentration of ammonia in exhaust air without zeolite was 111.32 mg NH_3/g_{VM0}. In experiment with zeolite, a whole amount of ammonia was adsorbed from exhaust gas.

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