Mechanism and control strategy of ammonia and nitrous oxide during composting of municipal solid wastes

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Abstract: Aerobic composting is an effective way to realize recycling of organic solid wastes. It is not only convenient for operation and management, but also can convert waste into organic fertilizer. However during the composting process, the nitrogen in the heap exists in the form of organic nitrogen, ammonium nitrogen, nitrate nitrogen and other forms and is transformed into each other. It is also a potential source of ammonia (NH_3) and nitrous oxide (N_2O), and it is closely related to the environmental problems such as haze pollution and greenhouse effect. Combining with the researches of domestic and foreign scholars, this paper summarizes the form transformation of nitrogen elements, the emission mechanism of NH_3 and N_2O , and the adjustment and control measures in the aerobic composting process of the organic solid wastes, and it prospects the research direction for aerobic composting of the organic solid wastes.

1 Introduction

In recent years, most of the organic solid wastes are randomly discarded or discharged into the environment, causing great negative impacts on the ecological environment. Municipal sludge is waste generated in the process of sewage treatment. If the sludge that has not been properly treated enters the environment directly, it will cause secondary pollution to the environment. Kitchen waste is easy to decay and deteriorate, and it is easy to breed bacteria. If placed improperly, it will have adverse effects on the social environment and human health. Aerobic composting is an effective way for minimization, hazard-free treatment and resourceful disposal of the organic solid wastes such as municipal sludge, kitchen wastes and livestock excrements. In the conditions of good ventilation and appropriate oxygen concentration, aerobic microorganisms multiply rapidly to degrade the organic solid wastes into organic fertilizers rich in humus and nutrient elements such as N, P, K [1-2].

However, the composting process is accompanied by NH_3 and N_2O emissions. NH_3 is an important precursor gas for the formation of $\text{PM}_{2.5}$, and it is easily soluble in water. When the relative humidity is high, it can react with H_2SO_4 , HNO_3 and HCl in the atmosphere to generate the secondary particles of ammonium salt, which is an important part of $\text{PM}_{2.5}$ it can cause haze pollution to reduce the quality of the atmospheric environment, but also it threatens the human health [3]. N_2O is an important greenhouse gas that affects the radiation balance of the earth. Within 100 years, its single-molecule warming potential is 296 times of CO_2 , which has a significant impact on the global greenhouse effect [4-5]. In summary, if the composting process is not properly controlled, the emitted NH_3 and N_2O will not only affect the global

climate change, but also cause harm to various organisms, including the human health. Therefore, the research on reducing NH_3 and N_2O emissions during composting attracts more and more attention from scholars at home and abroad.

2 The form transformation of nitrogen elements during composting

The composting process is divided into the heating-up period, the high temperature period and the cooling and maturing period. Among them, the nitrogen elements mainly exist in the form of organic nitrogen, ammonium nitrogen and nitrate nitrogen [6], and they are transformed by mediating of microbial communities through ammonification, nitrification, denitrification and ammonia assimilation (Fig. 1).

Fig.1 Transformation paths of nitrogen element in composting

Ammonification is a process in which organic nitrogen is decomposed by microorganisms to form NH_4^+ . It is divided into two periods: First, the organic nitrogen in the

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waste pile is decomposed into amino compounds under the catalysis of proteases. And then, the amino compounds are transformed to be NH_4^+ in the deamination process. The ammoniating reaction may occur throughout the composting cycle, and it is more intense in the heating stage, because the initial pile contains a large amount of organic nitrogen, and the temperature and pH are suitable at this time. The increase in temperature and pH will cause a large amount of NH_4^+ to volatilize in the form of NH_3 . In addition, NH_4^+ can be oxidized to NO_3^- through nitrification, or it can be utilized by microorganisms to synthesize organic nitrogen as nutrients of ammonia assimilation [7-8].

Nitrification is a process in which NH_4^+ is successively oxidized to NO_3^- by nitrifying bacteria. Ammonia oxidation is the first step of nitrification, which is divided into two periods: One is that NH_3 is oxidized to NH_2OH under the action of ammonia monooxygenase; the other is that NH_2OH is oxidized to NO_2^- under the action of hydroxylamine oxidoreductase; and as an intermediate product of ammonification, NH_2OH can further react with NO_2^- to form N_2O . The NO_3^- generated by nitrification can be absorbed and utilized by plants to synthesize nitrogen-containing organic matters, or it can be transformed to N_2 through denitrification in anaerobic conditions [9-10].

Denitrification is the process in which NO_3^- , NO_2^- , NO and N_2O are successively reduced to N_2 by denitrifying bacteria. The accumulation or compaction of the compost materials will prevent oxygen from entering the inside of the waste pile to form a local anaerobic environment and promote denitrification. *Pseudomonas* and *paracoccus* are typical aerobic denitrifying microorganisms, and their abundance is relatively less during the heating-up period of composting, and it will be gradually increased until the high temperature period and the cooling and maturing period [11-12].

Ammonia assimilation is a process in which α -ketoglutarate, an intermediate product of NH_4^+ and carbon source metabolism, is catalyzed to synthesize glutamate and finally transformed to organic nitrogen. The synthesis of glutamate by NH_4^+ can be achieved in two ways, one is that glutamate dehydrogenase catalyzes NH_4^+ to directly react with α -ketoglutarate; the other is that glutamine synthetase acts together with glutamate synthetase, and it catalyzes NH_4^+ to react with α -ketoglutarate and glutamine [13-14].

3 The emission mechanism of NH_3 and N_2O during composting

The organic nitrogen in the waste pile undergoes ammoniating to form NH_4^+ . As the temperature and the pH increase, NH_4^+ is quickly transformed to NH_3 , which accelerates the emission of NH_3 . Therefore, the high temperature period is the main period of NH_3 volatilization during the composting process. When the temperature of the waste pile is reduced to the air temperature, the composting enters the maturing period. At this time, the content of NH_4^+ decreases and the volatilization rate of NH_3 also decreases due to the nitrification and the ammonia assimilation of NH_4^+ as well

as the continuous volatilization of NH_3 [15-16].

In the composting process, both the nitrification of NH_4^+ and the denitrification of NO_3^- will cause emission of N_2O . Maeda et al. [17] use the priority point value (SP) to study the N_2O emission mechanism of the cattle manure composting process. The results show that the SP value of N_2O emission in the initial stage of composting is 0 to 12, and the N_2O emission reaches the peak after the turning over the pile, the corresponding SP value is 0 to 5, while the SP value of N_2O emitted by nitrification is about 33, and the SP value of N_2O emitted by denitrification is about 0, which indicates that N_2O can come from both nitrification and denitrification, and denitrification is the main way to produce N_2O during the composting process. The researches of Ge et al. [11] show that, during the compost heating-up period and the high temperature period, N_2O is mainly emitted through the nitrification process led by ammonia oxidizing bacteria; when entering the cooling and maturing period, N_2O is mainly emitted through the denitrification process of ammonia oxidizing bacteria and denitrifying bacteria.

4 The reduction measures of NH_3 and N_2O during composting

The initial characteristics of compost material such as temperature, pH, and moisture content significantly affect the carbon and nitrogen metabolism, and then affect the production and emission of NH_3 and N_2O during the composting process. The biochemical reactions in aerobic composting are generally manifested by temperature changes. pH is not only related to the life activities of microorganisms, but also closely related to the existence of ammonium nitrogen [18]. The moisture content of the compost material is generally 50% to 70%, which mainly affects the diffusion of O_2 in the waste pile, thereby indirectly affects the emission of NH_3 and N_2O during the composting process [19]. Too high water content is not conducive to the diffusion of O_2 in the waste pile, which weakens the mineralization of organic nitrogen thus reducing the emission of NH_3 [20]. When the moisture content of the material reaches more than 60%, N_2 is formed mainly by denitrification of nitrogen elements, so that the emission of N_2O is reduced [21]. Therefore, it is possible to reduce the emission of NH_3 and N_2O during the composting process by adjusting and controlling the moisture content of material. For raw materials with low moisture content, it can be adjusted by adding water. When the raw material has a high moisture content, auxiliary materials such as straw and sawdust can be added.

Ventilation conditions have an important impact on the emissions of NH_3 and N_2O during composting. Turning the pile will increase the O_2 concentration in the pile, thereby promoting the mineralization of organic nitrogen and increasing the volatilization of NH_3 [22]. It is generally believed that the amount of ammonia volatilization is positively correlated with the frequency of dumping [23]. Turn over the pile to homogenize the material, and the NO_x^- inside the pile body undergoes denitrification to generate N_2O , thereby increasing N_2O

emissions[24]. Zhao et al. [25] investigate the effect of turning frequency on greenhouse gas and ammonia emissions during the composting process of pig manure strips, and the results show that the increasing of turnover frequency has increased greenhouse gas and ammonia emissions. The intermittent ventilation method has a good emission reduction effect on NH_3 and N_2O generated during the composting process. Zhang et al. [26] adopt three intermittent ventilation methods to carry out the composting experiment, and the results show that, the emission of NH_3 is the least after a 20-minute stop for every 40 minutes of ventilation. Ma et al. [27] find that, the intermittent ventilation method of a 10-minute stop for every 10 minutes of ventilation can reduce the emission of N_2O by 47.10%.

Adding conditioners is an effective strategy to reduce NH_3 and N_2O emissions during composting. Physical additives have abundant pore structures and negative charge adsorption sites, which can adsorb NH_3 and NH_4^+ , and it can reduce the abundance of genes related to N_2O production and increase the abundance of genes related to N_2O reduction, so that N_2O emissions such as biochar, medical stone, bentonite, etc. are reduced [18]. Biochar reduces NH_3 emissions by 28.30~74.32% and N_2O emissions by 79.51~81.10% [28]; while medical stone reduces NH_3 emissions by 38.20~78.50% and N_2O emissions by 46.60~82.40% [29]. Chemical additives can reduce NH_3 emissions by lowering the pH of the material, fixing NH_4^+ or reacting with NH_4^+ [30]. When Lei et al. [31] add phosphogypsum, the NH_3 emissions are reduced by 59.74%, while the N_2O emissions are increased by 8.15%. This may be the reason that the chemical additives reduce the pH of the material and inhibit activity of the N_2O reductase. In addition, the promotion of nitrification or assimilation of NH_4^+ through biological additives can reduce the NH_3 emissions by 10.20% to 42.80% [30]. Jiang et al. [32] find that, when the addition amount of dicyandiamide was higher than 2.5%, the nitrification is inhibited, and the N_2O emissions is reduced by 77%.

5 Conclusions

The reduction measures of NH_3 and N_2O emission during the composting process include the conditioning of material properties, the optimization of process conditions, the addition of conditioners, etc. At present, the emission reduction mechanism of NH_3 and N_2O in the composting process still needs to be explored. This is because the adjustment and control measures will affect multiple factors at the same time, and the trade-off phenomenon may even occur. Therefore, in the future, it is necessary to increase research on the influencing factors of composting effect, and further narrow the scope of the most suitable conditions for operation. In addition, on the basis of adjusting the material properties and optimizing the process conditions, the use of additives shall be combined to realize the coordinated emission reduction of NH_3 and N_2O during the composting process. Aerobic composting can not only reduce environmental pressure, but also make organic solid waste resources. With the continuous deepening of research, the improvement of composting

technology will make aerobic composting more environmentally friendly, more efficient, and more suitable for large-scale composting.

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