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Denitrification removal of nitric oxide in a rotating drum biofilter

Jiade Wang, Chengqiang Wu, Jianmeng Chen *, Haijie Zhang

College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, China

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Abstract

A rotating drum biofilter (RDB) was applied and evaluated for nitric oxide (NO) removal by denitrification from a synthesized waste gas using glucose as carbon source. The effects of drum-rotating speed and empty bed residence time (EBRT) on NO removal were investigated under anaerobic conditions. With the increase of drum-rotating speed higher than 0.5 rpm and the decrease of EBRT at a certain feed loading rate, there existed a lower NO removal efficiency influenced by mass transfer. At an EBRT of 65 s and a drum-rotating speed of 0.5 rpm, NO removal efficiency was over 97.9% with inlet NO concentration of 524 ppm. When oxygen existed, NO was removed as the function of denitrification of the main role and chemical oxidation. With the increase of inlet oxygen concentration, denitrification decreased and chemical oxidation increased and the optimal inlet oxygen concentration of about 5.2% was obtained.

Keywords: Rotating drum biofilter; Nitric oxide; Mass transfer; Denitrification; Chemical oxidation

1. Introduction

Emissions from fossil fuel combustion and biomass burning degrade local air quality and affect global tropospheric chemistry. Nitrogen oxides (NO_x) are emitted from all combustion processes and play a key part in the photochemically induced catalytic production of ozone and also result in nitric acid deposition. Nitric oxide (NO) is the major NO_x component [1]. The pollution from NO_x is a global environmental problem. Richter et al. [2] reported that NO_x keep increasing during recent years in some areas such as East Central China and Hong Kong, and NO_x concentration still remains high in North America and Japan.

Although NO_x production can be significantly reduced by combustion control methods, post-combustion treatment is required to achieve current regulatory air standards. Methods to control and reduce NO_x were commonly studied, in which an ammonia-based selective catalytic process was focused on NO_x reduction [3]. Although this is an effective technique, the catalysts are easily poisoned and pose a hazardous waste disposal problem.

In recent years, research on the accessibility and transferability of best available control technologies, specifically environmentally sound technologies, has expanded rapidly. Biofiltration is regarded as a viable and potentially cost-effective alternative to conventional technologies for the treatment of low-concentration polluted gas [4,5]. It has been used successfully to control odors as well as volatile organic compounds (VOCs) and more than 7500 biological waste gas treatment systems were installed [6–8]. A biotrickling filter packed with plastic Pall rings was used to treat odor gas containing hydrogen sulfide (H_2S) of lower than 190 ppm and H_2S removal efficiency reached 100% at a very short empty bed residence time (EBRT) of 11 s [9]. However, NO_x removal by biofiltration is a relatively new subject. Under aerobic conditions in a biofilter, NO_x can be oxidized into nitrate by both nitrification and chemical oxidation, and nitrification is the main process for NO_x removal at a lower inlet NO_x concentration [10]. Under anoxic conditions within a biofilter, NO_x can be reduced to inert nitrogen gas by denitrification for a higher NO_x removal efficiency [11–13]. With wood compost in a biofilter, more than 90% NO was removed by denitrification with lactate as carbon source at an EBRT of 2 min [11]. With soil compost in a bench-scale biofilter, removal efficiency of nitrogen dioxide was almost 100% [13]. Under aerobic conditions of oxygen concentration greater than 17%, NO removal efficiency of 97% was also achieved with water-soluble carbon source as denitrification electron donor in a toluene-treating biofilter packed with porous silicate pellets [12]. All these results showed that biofiltration is a promising technology for NO_x removal.

However, there are two major drawbacks with existing biofilters and biotrickling filters, that is, uneven distribution of

* Corresponding author. Tel.: +86 571 88320386; fax: +86 571 88320276.
E-mail address: jchen@zjut.edu.cn (J. Chen).

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ingredients and difficulty to control excess biomass. To overcome these problems, the rotating disc contactor (RBC) was applied for the abatement of volatile organic compounds in waste gas, presenting wonderful performance, and was later renamed as a rotating drum biofilter (RDB) for waste gas purification [14–16]. When used to treat diethyl ether, RDB can achieve a stable removal efficiency of 99% for more than 6 months without any biomass control measures with a loading rate of not higher than 2 kg COD m^{-3} day^{-1}, and biomass is almost evenly distributed within the same media depth [14]. All these were studied in treating VOCs, but there was no knowledge of RDB on NO_x removal.

In this paper, a bench-scale RDB by denitrification was used to investigate NO removal from a synthesized gas, aiming to evaluate the effects of EBRT based on the drum volume and drum-rotating speed on RDB performance. The effect of inlet oxygen concentration on NO removal mechanisms was also discussed.

2. Materials and methods

2.1. Bioreactor design

The schematic diagram of RDB system is presented in Fig. 1. This system was composed of inlet part, inspection part and RDB part. NO waste gas was synthesized using nitrogen and nitric oxide during the startup and operation at different drum-rotating speeds and EBRTs. When studying the effect of inlet oxygen concentration on NO removal efficiency, oxygen was fed in the inlet gas stream. NO and NO_2 in the inlet and outlet gases could be measured online simultaneously.

The RDB consisted of a covered aluminium chamber, in which the layer of spongy media was mounted on aluminium drum frame with impermeable plates at both ends. The media was an open-pore reticulated polyurethane sponge, used to support the growth of biofilm in RDB. The sponge was made by Shanghai Xinyuan Sponge Ltd. (Shanghai, China) and its parameters were as follows: porosity, 93.87%; pore size, 2.5 pores/cm. The axial length of the spongy media was 250 mm, and the outer and inner diameters were, respectively, 400 and 260 mm with the total media volume of 14.4 L.

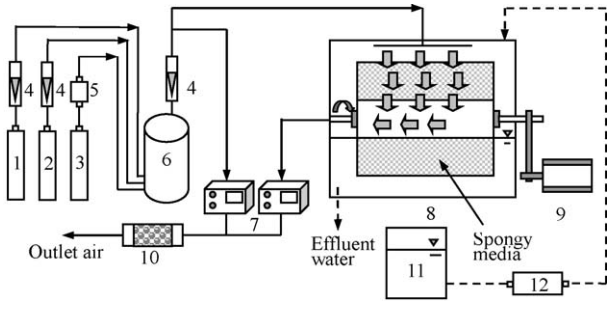

Fig. 1. Diagram of the experimental system. (1) N_2 cylinder; (2) O_2 cylinder; (3) NO cylinder; (4) rotameter; (5) flowmeter; (6) gas mixed container; (7) NO/NO_x analyzer; (8) RDB; (9) motor; (10) tail gas absorber; (11) nutrient solution; (12) pump.

The lower part of RDB was filled with a nutrient solution that enabled the media and biofilm to be fully submerged in the solution and microorganisms to take in the nutrient as the rotating drum reached its lowest point. The nutrient solution volume in RDB was 18 L. A fresh nutrient solution was fed into RDB continuously, using a tubing pump at a rate of 2.0 L day^{-1}.

The experiment was carried out at a temperature of 28 °C and a pH value ranging from 6.5 to 7.5. After the waste gas entering the running RDB chamber through a dispersion pipe, it passed through the spongy medium coated with a moist microbial biofilm. The contaminants in waste gas were absorbed into and biodegraded by the biofilm. The purified gas exited from RDB through the outlet in the center of the drum.

2.2. Nutrients

The nutrient solution fed to the bioreactor mainly consisted of phosphate and micronutrients as follows: KH_2PO_4 0.625 g L^{-1}, K_2HPO_4 1 g L^{-1}, $MgSO_4$ 0.5 mg L^{-1}, $CuSO_4 \cdot 5H_2O$ 0.1 mg L^{-1}, $CaCl_2$ 2 mg L^{-1}, Na_2MoO_4 0.1 mg L^{-1}. Sodium bicarbonate was used as a buffer to prevent major excursions in pH of the nutrient solution. Glucose was used as electron donor and C/N (mole ratio between glucose and NO) was controlled at 2.5.

2.3. Bacterial culture

A concentrated sludge was taken from a secondary sedimentation tank at Hangzhou Qige Wastewater Treatment Plant, China. The sludge was cultured for 2 weeks in a liquid medium (glucose 2500 mg L^{-1}; soldium nitrate 1000 mg L^{-1}) and then used for seeding into RDB.

2.4. Analytical methods

During the startup and operation, the gas steams were sampled and measured three times and averaged. Especially when the parameters were changed and reactor ran stably for 1 week, the data were averaged and then plotted in the figures. N_2 used as inert background gas in the inlet gas was far higher in concentration than N_2 produced by denitrification, which made it very difficult to precisely detect the concentration of the latter. So N_2 concentration in inlet and outlet gases was not detected in the experiment.

Inlet and outlet NO and NO_2 concentrations were measured in the experiment, respectively. NO and NO_2 concentrations in inlet gas were measured by a Model 42C High Level NO–NO_2–NO_x Analyzer (Thermo Electron Co., USA). NO and NO_2 concentrations in outlet gas were measured by a Model 42C Chemiluminescence NO-NO_2-NO_x Analyzer (Thermo Environmental Instruments Inc., USA). Oxygen concentrations in the inlet and outlet gases were measured by a G1010 Oxygen Analyzer (Hitech Instruments Ltd., UK). The pressure drop of spongy media was measured by a Model YYT2000 Inclined Manometer (Hongyu Environmental and Applied Institute, Shanghai, China). The pH values were measured by a Model pHS-9V Acidimeter (Huaguang Wireless Electric Company,

Hangzhou, China). Nitrate and nitrite analysis were carried out in accordance with Standard Methods [17].

3. Results and discussion

3.1. Startup

RDB was initially started up at a drum-rotating speed of 0.5 rpm, with inlet NO concentration of 500 ppm, a gas flow rate of 0.8 $m^3\ h^{-1}$ and an EBRT of 65 s. NO removal efficiency and pressure drop during this period are displayed in Fig. 2. In the first 3 days after seeding, NO removal efficiency and pressure dropped increased slowly, and then microorganisms were gradually acclimated to the environment and their activity recovered litter by litter. During the next 7 days, NO removal efficiency increased rapidly and reached 94% on the 10th day, and then remained almost constant and so did pressure drop, which suggested that the biofilm on the media became mature.

During the startup period, it can be seen that RDB can achieve a NO removal efficiency of about 95%. However, a more stable and higher NO removal efficiency depended on specific operating conditions.

3.2. Effect of drum-rotating speed on NO removal efficiency

The process of NO removal in RDB can be divided into two stages. First, NO is removed from the gas phase by diffusing into the liquid phase or biofilm. Second, NO is metabolized and reduced by denitrifiers.

From the process engineering point of view, the turn of the media and biofilm in RDB could enhance the gas convection and the contact between gas, liquid and biofilm. Therefore, RDB not only has the advantages of the traditional biofiltration [5,9], but also overcomes the drawbacks such as uneven distribution of nutrients, gas stream and biomass, as well as difficulty in the control of excess biomass. The mass transfer rate and microorganism activity in RDB were expected to increase with the rotation of the media. Generally, there was a water layer covering the biofilm in the RDB, which was fit for microorganisms' metabolism and growth. But the thickness of the water layer influenced the mass transfer rate of NO and the nutrient supply to the biofilm. The thicker the water layer was the higher the transfer resistance within the water layer. With the increase of drum-rotating speed in the given range, there was more chance for biofilm to be exposed to water and then the water layer became thicker, which could result in a higher mass transfer resistance and decrease the removal efficiency. Yang [15] reported that, when treating diethyl ether in a multi-layer RDB, ether removal efficiency increased with an increased drum-rotating speed in the range of 1.0–5.0 rpm. Therefore, the turn of the media and biofilm affected NO removal efficiency greatly, either positively or negatively.

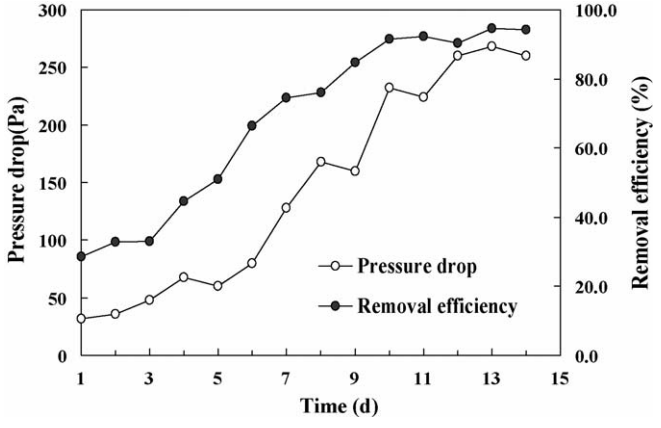

Fig. 2. NO removal efficiency and pressure drop during startup of RDB.

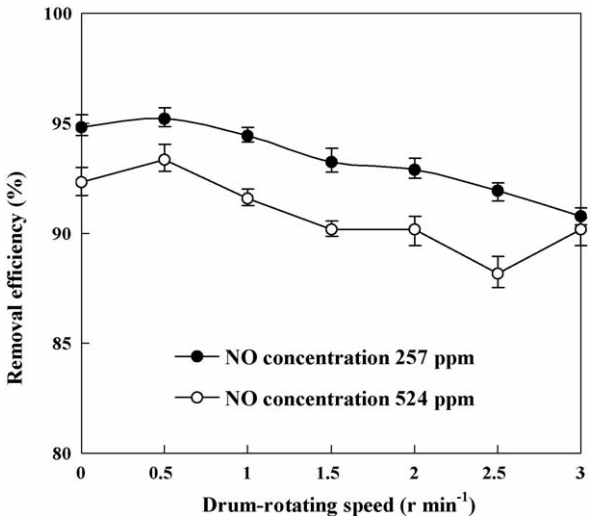

Fig. 3. Effect of drum-rotating speed on NO removal efficiency.

Fig. 3 illustrates the relationship between drum-rotating speed and NO removal efficiency at an EBRT of 43 s. When NO concentration was 257 or 524 ppm, NO removal efficiency increased with drum-rotating speed increasing from 0 to 0.5 rpm, while decreased when drum-rotating speed increased from 0.5 to 3.0 rpm. The optimal drum-rotating speed of RDB was about 0.5 rpm while NO removal efficiency was 95.2% at inlet NO concentration of 257 ppm and 93.3% at 524 ppm, respectively. Therefore, drum rotation played a positive role at the lower drum-rotating speed but a negative role at the higher speed, which suggested that mass transfer could be a key factor to influence NO removal process.

3.3. Effect of EBRT on NO removal efficiency

As mentioned above, NO removal can be described as a stepwise process going first through a sequence of mass transfer stages from the gas phase to liquid phase and biofilm, to be ultimately biodegraded in the biofilm.

The rate of mass transfer is dependent on the concentration gradient across the gas–liquid interface and can be defined as [9]:

$$\text{Mass flux} = K_1 \left(\frac{C_g}{H} - C_l \right) \quad (1)$$

where K_l is the total mass transfer coefficient, C_g the NO gas concentration, C_l the NO liquid concentration, and H is the dimensionless Henry's constant.

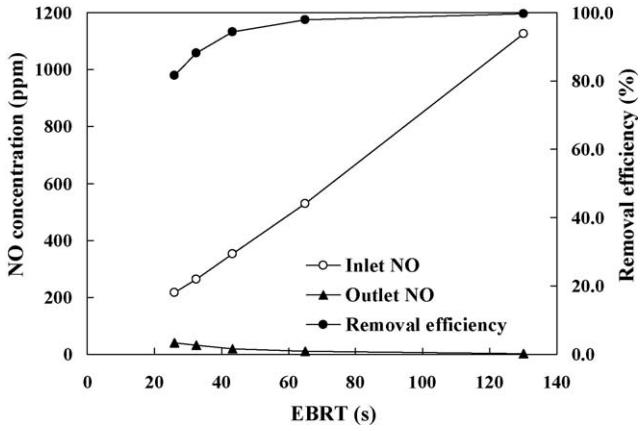

Fig. 4. Effect of EBRT on NO removal efficiency.

When the gas phase concentration is low, mass transfer is usually the limiting step; otherwise biodegradation would be rate-limiting step.

As shown in Fig. 4, at a constant feed loading rate of 59 g NO m^{-3} h^{-1}, the NO removal efficiency increased to 99.7% with the increase of EBRT and inlet NO concentration, which resulted in increasing elimination capacity. At an EBRT of longer than 65 s and inlet NO concentration of higher than 529.1 ppm, NO removal efficiency reached stable and outlet NO concentration still decreased slightly. It was concluded that both EBRT and inlet NO concentration played a key role in mass transfer rate. With the decrease of EBRT and inlet NO concentration at a constant inlet load, mass transfer rate was decreasing and subsequently mass transfer became the limiting step for NO removal.

3.4. Effect of inlet oxygen concentration on NO removal efficiency

The enzyme system capable of NO reduction, present in typical denitrifiers, is generally found under anaerobic growth conditions with N-oxides as electron acceptors [18]. But in the flue gas containing NO, oxygen concentration was often around 3–8%, which would increase oxygen dissolving in water, thus probably inhibit denitrifiers.

In the gas phase and liquid phase, NO reacted with oxygen and was chemically oxidized [19–21]. The reaction courses can be described as follows:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad (2)$$

$$4NO(l) + O_2(l) + 2H_2O(l) \rightarrow 4NO_2^-(aq) + 4H^+(aq) \quad (3)$$

When oxygen concentration increases, the reaction rate increases and more NO is chemically oxidized into NO_2 and NO_2^-. NO_2 is easier to dissolve into water and NO_2^- is easier to be reduced into N_2 by denitrifiers, which results in higher NO removal efficiency.

Therefore, when oxygen existing, there are two mechanisms of biodegradation by denitrification and chemical oxidation for NO removal in RDB. With the increase of oxygen concentration, chemical oxidation increases and biological denitrification would decrease for denitrifiers' inhibitation by oxygen.

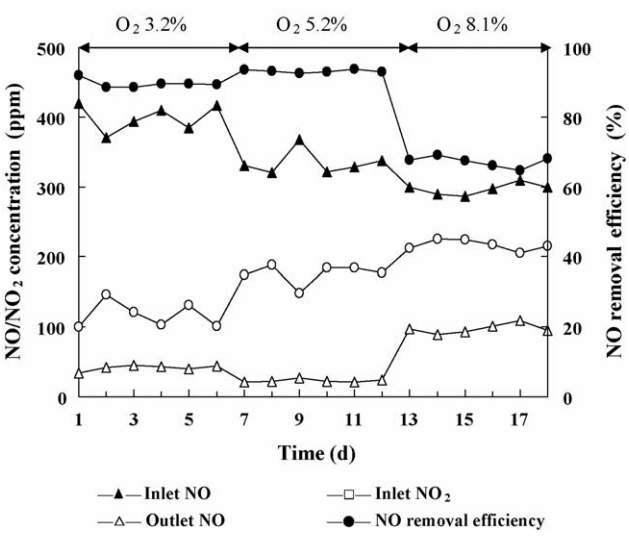

Fig. 5. Effect of inlet oxygen concentration on NO removal efficiency.

After RDB ran stably under anaerobic condition, the effect of oxygen concentration on NO removal was examined over a range of 3.2–8.1%. Fig. 5 shows that NO removal efficiency changes with time at different inlet oxygen. After three different gases (O_2, N_2, NO) were mixed in a gas mixed container, NO_2 was detected in inlet waste gas and was also shown in Fig. 5 at different inlet oxygen and NO concentrations. The experiment demonstrated that outlet NO_2 concentration was not detected at the inlet NO_2 concentration of 100–225 ppm, which showed that NO_2 was almost completely removed. At each inlet oxygen concentration, NO removal efficiency was almost constant, which presented stable operation performance. When inlet oxygen concentration increased from 3.2% to 5.2%, NO removal efficiency increased from 89.6% to 93.2%. The results showed that denitrification rate could be little affected while more chemical oxidation was resulted in at this stage. When inlet oxygen concentration increased further from 5.2% to 8.1%, NO removal efficiency decreased to 67.2%. These results explained that denitrification rate was litter affected in a low range of inlet oxygen concentration but decreased rapidly at a higher inlet oxygen concentration while chemical oxidation rate increased. So at the higher inlet oxygen concentration, chemical oxidation would be the main role in NO removal, which was in accordance with Chen and Ma [10].

4. Conclusions

A rotating drum biofilter has been applied and evaluated for NO removal from a synthesized waste gas at different EBRTs and inlet NO concentrations using glucose as electron donor. At an EBRT of 65 s and a drum-rotating speed of 0.5 rpm, NO removal efficiency was over 97.9% with inlet NO concentration of 529 ppm. Mass transfer was a key factor to decide the optimal NO removal efficiency. With the increase of drum-rotating speed higher than 0.5 rpm and the decrease of EBRT, there is an

enhancement for the gas convection and the contact between gas phase, liquid phase and biofilm, but there existed a lower rate of mass transfer and a lower NO removal efficiency at a higher drum-rotating speed. When oxygen existed, NO was removed as the function of denitrification and chemical oxidation. With the increase of inlet oxygen concentration, denitrification decreased and chemical oxidation increased and the optimal inlet oxygen concentration of about 5.2% was obtained.

For further research on NO removal in RBD, the other operating parameters need to be optimized, such as media property and carbon source. The mechanisms of NO removal by microorganisms and chemical oxidation are also well worth further study.

Acknowledgments

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