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Removal of Nitrogen Oxides from Exhaust Gas of Boilers *via* Aerobic Denitrifying Bacteria Using New Device

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In this paper, the removal efficiency of NO_x by aerobic denitrifying bacteria in bio-filter and bio-trickling filter was described, respectively and the removal mechanism of NO_x was explored. The result showed that the bio-trickling filter was more proper than the bio-filter when dealing with NO_x. The new device-the combination of the bio-filter and bio-trickling filter was employed to test the application of aerobic denitrifying bacteria in the removal of NO_x. Effects of the inlet concentration of NO_x, empty bed residence time (EBRT) and liquid flow on the removal efficiency of NO_x were investigated in the new device. And the removal efficiency of NO_x up to 94.2 % was obtained at oxygen content of 13 %, inlet NO_x concentration of 1100 mg/m^3, nutrient fluid flow of 15 L/h and empty bed residence time of 35 s.

Keywords: Bio-filter, Bio-trickling filter, Removal, Aerobic denitrification, New device.

INTRODUCTION

The main sources of air pollution are the combustion processes of fossil fuels used in power plants, vehicles and other incineration processes. Key combustion-generated air contaminants are sulfur oxides, particulate matter, carbon monoxide, unburnt hydrocarbons and nitrogen oxides (NO_x). NO_x emitted from incineration processes consists of 95 % nitric oxide (NO) and 5 % nitrogen dioxide(NO_2)[1,2]. Nitric oxide is a precursor for tropospheric ozone depletion and the main constituent in photochemical smog. It may also react with moisture in the air to form nitrous acid, which has been implicated in acid rain[3,4].

With the rising social dissatisfaction with the state of the environment, the environmental awareness of political circles significantly grew. As a result more rigorous environmental laws are introduced by the Gothenburg, Kyoto and China had raised the restrictions regarding NO_x emission to 100 mg/m^3 by GB13223-2011[5].

Conventional post-combustion technologies for NO_x removal include selective catalytic reduction, selective non-catalytic reduction, adsorption, scrubbing and so forth[6-8]. All these are effective methods, but they often suffer from some problems, such as the catalysts are easily poisoned and hazardous wastes should be disposed, which makes the new technologies that are economical and environmental producing necessary[9,10]. The bioprocesses are proved to be effective methods for the treatment of gas with relatively low concentration of pollutants, reliable and low-cost techniques that have proved to be most appropriate for the prevention of air contamination with NO_x in general[11,12].

It has been widely accepted that the denitrification process requires completely anaerobic conditions, because some tests had shown that when some bacteria were exposed to oxygen, they would lose their denitrifying capacity. But generally the flue gas vent out from the coal-fired power plants includes not only NO_x but also O_2. Recently, the discovery of aerobic denitrifying bacteria made the NO_x removal process under the aerobic conditions a promising option.

There are two groups of biological waste gas purification systems which can provide appropriate conditions: bio-trickling filters (BTF) and bio-filters (BF)[13,14]. They can be distinguished by the behaviour of the liquid phase (which is either continuously moving or stationary in the contact apparatus) and of the micro-organisms (which are either freely dispersed in the aqueous phase or immobilized on a carrier or packing material). In this paper, the bio-filter and bio-trickling filter were combined to test the removal efficiency of NO_x by aerobic denitrifying bacteria under aerobic conditions.

EXPERIMENTAL

Bio-trickling filter and bio-filter media: The nutrient liquid was recirculated from the bottom to the top of the column using a booster pump (liquid flow of 15 L h^{-1}) to provide the aerobic denitrifying bacteria with moisture and minerals necessary for growth. And the nutrient liquid included the following contents: disodium succinate, 5 g/L; $Na_2HPO_4 \cdot 7H_2O$, 3 g/L; KH_2PO_4, 1.5 g/L; $MgSO_4 \cdot 7H_2O$, 0.1 g/L; NaCl, 4,7 g/L; trace element solution, 2 mL/L; pH 7-7.5.

The trace element solutions for the bacterial growth consisted of the following components: EDTA, 50 g/L; $ZnSO_4$, 2.2 g/L; $CaCl_2$, 5.5 g/L; $MnCl_2 \cdot 4H_2O$, 5.06 g/L; $FeSO_4 \cdot 7H_2O$, 5 g/L; $(NH_4)_6Mo_7O_2 \cdot 4H_2O$, 1.1 g/L; $CuSO_4 \cdot 5H_2O$, 1.57 g/L; $CoCl_2 \cdot 6H_2O$, 1.61 g/L; pH 7.

The experimental setup consisted of an influent gas supply system and a bench-scale device combined bio-trickling filter and bio-filter (Fig. 1). The bio-trickling filter was constructed from an 80 × 1000 mm (inner diameter × height) glass column packed with an 800 mm high plastic packing (polypropylene Pall rings which were 50 cm diameter and had an initial porosity of 90 % and a specific surface area of 206 m^{-1}). During the continuous experiment, the nutrient liquid flows down in a thin film to surround the packing material and wet the biolayer. The waste gas is forced to rise through the void volume against the nutrient liquid flow.

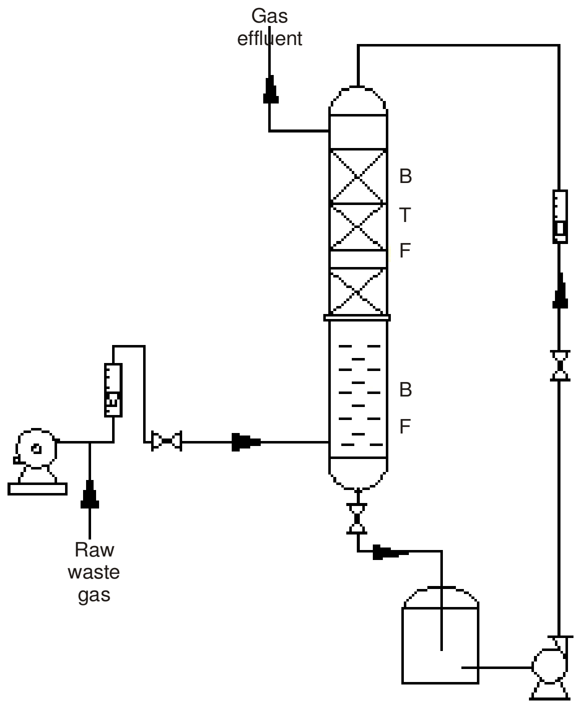

Fig. 1. Diagram of the experimental system

Generally there is 3-8 % (v/v) oxygen and SO_2 vent out from the coal-fired power plants with NO_x in the flue gas. After the flue gas was treated in a spray tower to remove the SO_2, the oxygen content will be about 8-13 %. So this experiment was carried out with 13 % oxygen in the synthesized gas which was synthesized by pure NO, N_2 and O_2 stored in respective cylinders.

In the continuous experiment, the flux of NO, N_2 and O_2 was measured by mass flow controller (MKS1479, Weiwu, China). The content of nitrogen oxides (NO and NO_2) and oxygen were measured using a flue gas analyzer (KANE 940, Germany). Nitrate nitrogen (NO_3^-–N) was analyzed through ultraviolet spectrophotometric screening method and nitrite nitrogen (NO_2^--N) was analyzed through colourimetric method using spectrophotometer (UV-2100 Spectrophotometer, UNICO, China).

RESULTS AND DISCUSSION

Comparison of different efficiencies in bio-trickling filter and bio-filter: The performance of this system was evaluated by the removal efficiency (RE) which was defined in eqn. 1, as a function of the inlet and outlet concentration of NO_x.

$$\text{RE } (\%) = \frac{(C_{in} - C_{out}) \times 100}{C_{in}} \quad (1)$$

The bio-trickling filter and bio-filter were started up with a synthesized gas flow of 50-200 L/h which contained NO concentration of 100 mg m^{-3} and 13 % O_2 when the nutrient liquid flow rate was 15 L/h and empty bed residence time (EBRT) was 2 min. After the 15 days startup period, the bio-trickling filter and bio-filter reached a pseudo-steady state. The bacteria can be observed completely cover the surface of plastic packing and the NO removal efficiency was almost steady (the NO removal efficiency was 88.9 and 81.2 %, respectively in the bio-trickling filter and bio-filter). The NO removal efficiency in the startup period of bio-trickling filter and bio-filter are shown in Fig. 2.

As shown in Fig. 2, the NO_x removal efficiency was almost the same in the bio-trickling filter and bio-filter with the NO_x removal efficiency 88.9 and 81.2 %, respectively. The bio-filter has more prominent advantages in dealing with NO_2 (because of the presence of oxygen, NO is partly oxidized to NO_2 and then dissolved in water as nitrite or nitrate); while the bio-trickling filter is better when dealing with NO. And some experiment showed that the removal efficiency could be improved more effectively when nitrate and nitrite presented in this system. So a new device that combined bio-trickling filter and bio-filter was designed to measure the NO_x removal efficiency in this paper.

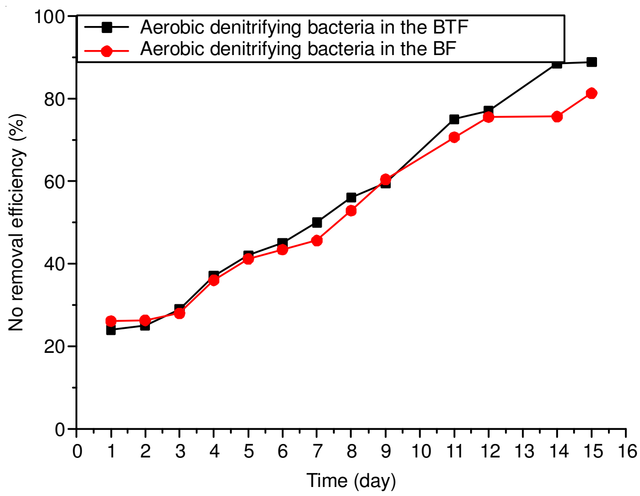

Fig. 2. Removal efficiencies of NO_x during the startup phase in bio-trickling filter

NO_x removal efficiency in the combined device: The start-up method of the new device (Fig. 1) was similar with the methods of the bio-trickling filter and bio-filter. After

15 days, the NO_x removal efficiency was increased to 90 % and stayed steady (Fig. 3). Thus it can be inferred that mature bio-film has formed on the surface of packing materials. The results of nitrate and nitrite reduction by aerobic denitrifying bacteria are shown in Fig. 4. In 3 days, the NO_3^--N had decreased from 150 mg/L to 0.009 mg/L and then the nitrate couldn't be detected. In this process, the nitrite couldn't be detected and the pH values ranged from 7.26 to 7.92 without regulation. It means that the aerobic denitrifying bacteria has more prominent advantages in removing NO_x from waste gas and maybe the simultaneous nitrification and denitrification contributes a lot[15-18].

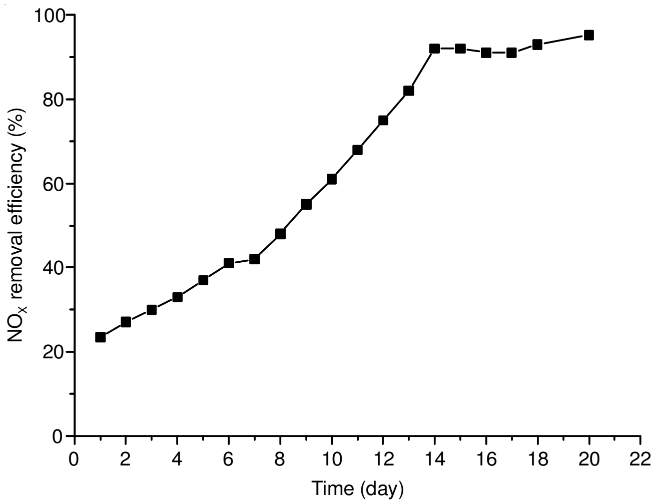

Fig. 3. Removal efficiency of NO_x during the startup phase in the new bio-filter-bio-trickling filter device

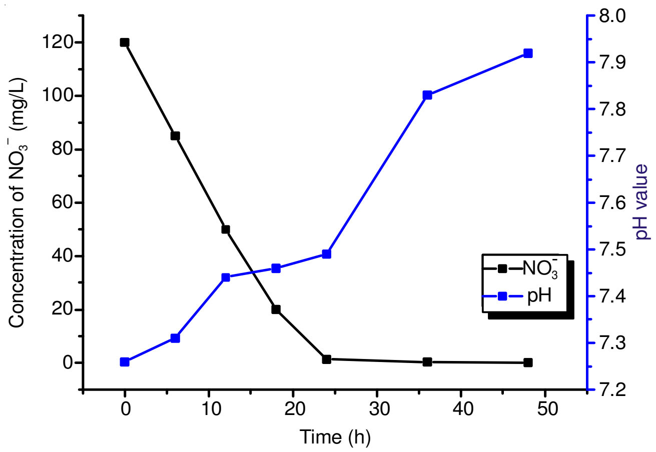

Fig. 4. Nitrate-nitrogen removal in the new bio-filter-bio-trickling filter device

After the 15 days startup period, the new device reached a pseudo-steady state which was used to evaluate the effect of some factors like the inlet concentration of NO_x, empty bed residence time (EBRT) and liquid flow on the removal efficiency of NO_x.

Effect of the inlet concentration of NO_x, empty bed residence time and liquid flow rate on the removal efficiency of NO_x: In this continuous experimental stage, the inlet NO_x concentration fluctuated between 100 to 1300 mg m^{-3} with the oxygen content being 13 % and the results are shown in Figs. 5 and 6.

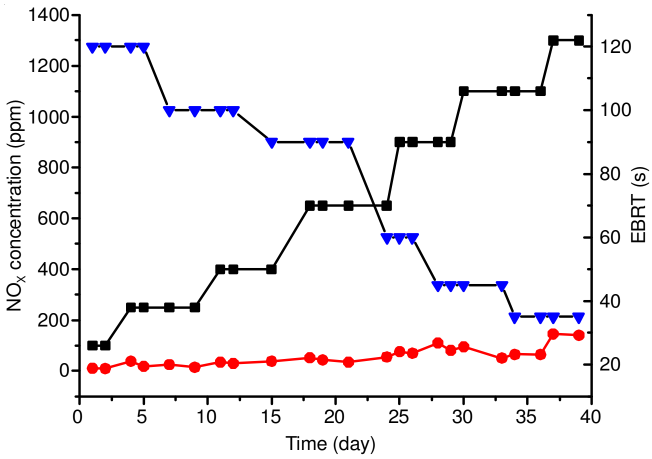

Fig. 5. Influence of the inlet concentration of NO_x, empty bed residence time on removal of NO_x in the new bio-trickling filter and bio-filter device. Symbols: inlet (■) and outlet (●) concentration of NO_x; EBRT (▲)

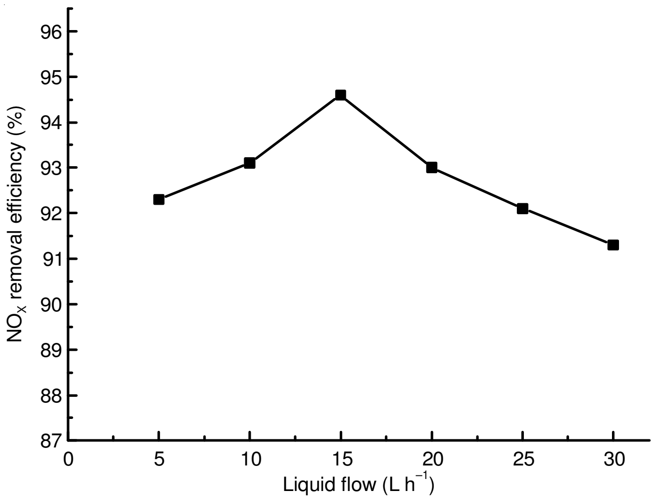

Fig. 6. Influence of the nutrient fluid flow on removal efficiency of NO_x

During this experiment, the initial NO_x concentration was approximately 100 ppm with the EBRT of 120s and the nutrient liquid flow rate was 15 L/h. The NO_x concentrations in the outlet were approximately 10 ppm which indicated that the removal efficiencies of NO_x were over 90 %. After 5 days, the NO_x concentration in the inlet increased to 250 ppm and the NO_x concentration in the outlet increased to 38 ppm which decreased to 18 ppm after 2 days. But when the EBRT was changed to 100s, the outlet NO_x concentration increased to 25 ppm. Then, the inlet NO_x concentration increased and the EBRT decreased gradually. At day 30, when the inlet NO_x concentration increased to 1100 ppm with the EBRT of 45s, the NO_x concentration in the outlet increased to 95 ppm but decreased to 50 ppm after 3 days. At day 34, the EBRT was decreased to 35s and the outlet NO_x concentration increased to 65 ppm and didn't decrease in the next 3 days. At day 37, when the inlet NO_x concentration was increased to 1300 ppm with the EBRT of 35s, the removal efficiencies of NO_x were below 90 % (Fig. 5).

The nutrient liquid was continuously supplied using a booster pump to maintain the nutrients on biofilm growth. As can be seen in Fig. 6, when the nutrient liquid flow was 15

L/h, the removal efficiency of NO_x was higher. It can be considered that all the bio-trickling filter processes took place in two phases of gas and biofilm linked by a thin liquid interfacial layer and the bio-filter processes would not be affected by the changing of the nutrients fluid flow. And when the liquid flow was 10 L/h or less, it would broaden the effect of nutrients limitation on biofilm growth; when the flow was 20 L/h or more, the liquid interfacial layer would be much thick that would affect the transfer of NO_x from the gas phase to the biofilm phase.

The experimental results showed that the removal efficiency of NO_x was up to 90 % at the inlet concentration of 1100 ppm, oxygen content of 13 %, the EBRT of 35s, the nutrient fluid flow of 15 L/h.

Steady-state performance at high load of NO_x: The device was used to evaluate the stable performance in removing high load of NO_x. In this experimental stage, the inlet NO concentration fluctuated between 1000 and 1100 ppm with the inlet O_2 concentration remained constant of 13 % (v/v), the corresponding empty bed retention time (EBRT) of 35s, the nutrient liquid flow of 15 L/h. The NO_x removal efficiency reached to 94.2 % and stay steady. The results are shown in Fig. 7.

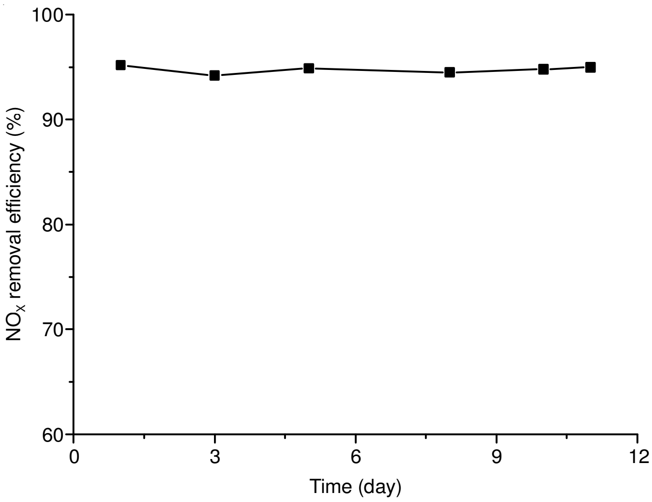

Fig. 7. Steady-state performance at high load of NO_x in the bio-filter-bio-trickling filter device

NO_x removal mechanism: It has commonly been accepted that denitrification requires completely anoxic conditions because some well studied bacteria completely shut down their denitrifying capacity upon exposure to oxygen. Oxygen is known to repress the denitrifying reductases. But in the several decades, denitrification under aerobic conditions in some bacteria has been reported, suggesting that aerobic denitrification does occur and might have evolved several times.

Robertson and Kuenen[1] suggested aerobic denitrification theory, they found the present of aerobic denitrification bacteria and pointed that the bacteria grew faster when the acetate culture provided with both nitrate and oxygen than the cultures receiving either. And then Lukow and Diekmann[16] found that most aerobic denitrification bacteria can be aerobic nitrification bacteria to make the simultaneous nitrification and denitrification possible.

Achieving the simultaneous nitrification and denitrification has considerable benefit to the experiment. Firstly, it can reduce the running cost efficiently, because the denitrification process will make the pH higher, but the nitrification process is in the opposite way. So the simultaneous nitrification and denitrification will make the pH stay steady at 7 to 8, reducing the cost of buffer. Secondly, the removal efficiency can be improved more effectively, because the aerobic denitrifying bacteria can grow faster using the nitrate and nitrite produced by aerobic nitrifying bacteria and the bio-filter processes which indicates the advantages of the new bio-filter-bio-trickling filter device.

Conclusion

The new device had more advantages in dealing with NO_x than the bio-trickling filter and bio-filter, because the bio-filter processes could produce the nitrate and nitrite and make the simultaneous nitrification and denitrification possible in the bio-trickling filter. The removal efficiency could reached to 94.2 % at the inlet NO_x concentration of 1100 mg/m^3, the inlet O_2 concentration remained constant at 13 % (v/v), the nutrient liquid flow rate of 15 L/h and the corresponding empty bed retention time (EBRT) of 35 s.

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