Global NEST Journal, Vol 10, No 2, pp 241-248, 2008

BIOLOGICAL REMOVAL OF NOx FROM SIMULATED FLUE GAS IN AEROBIC BIOFILTER

R. JIANG
S. HUANG*
J. YANG

College of Environmental Science and Engineering
South China University of Technology
Guangzhou, 510006, China

Received: 05/10/07
Accepted: 21/12/07

*to whom all correspondence should be addressed:
e-mail: chshuang@scut.edu.cn

ABSTRACT
A bench-scale biofiltration system was developed to evaluate the NOx removal efficiency under high oxygen concentration. The system had been running for 120 days and kept on a steady NOx removal rate above 80%. A stable NOx removal with an efficiency of more than 80% from the gas phase can be obtained by the bioreactor concept, when flue gas containing NO (400-600 ppmv) and a certain O_2 concentration (0-20%). In the blank experiment, less than 35% NO was removed as oxygen increased. The tendency of the three curves about NO removal rate with various O_2 concentrations was mainly similar but some differences in the highest and lowest removal rate happened in the definite O_2 concentration range. Oxygen was shown to have a significant effect on NOx removal at the first two or three days when oxygen concentration increased sharply. The higher concentration NO influent gas contained, the longer time the microflora need to regain activities. Compared with humidifier, microbial regenerator which was incorporated in biofilter can improve aerobic denitrifying bacteria activity by applying alternating oxic–anoxic conditions in the presence of nitrate and nitrite. Oxidation-Reduction Potential (ORP) and Dissolved Oxygen (DO) were used to control the dose of carbon source.

KEYWORDS: NOx; NO; Aerobic denitrification; Nitrification; Aerobic biofilter system.

INTRODUCTION

Nitrogen oxide emissions are a concern because they contribute to the formation of acid rain and can indirectly affect human health due to the formation of ground level ozone. As a fact electricity generation from coal has increased with the economical development in the world. Total electricity supplied during 2004 reached a record level of 0.44 billion kilowatt-hours (kWh) in China. This was a 12.8 % increase from 2003. Fossil fuel based generation from utility and non-utility sources accounted for 80% of this production. Nitrogen oxide (NOx) emissions from China's electric industry alone were greater than 6.65 million tons during 2004 (Wang, 2006). On the basis of predicting the increasing thermal power total capacity, it will reach 7.13 million tons during 2010. For this reason cost-effective strategies to control nitrogen oxides (NOx) from coal-fired power plant combustion gases must be developed.

Various methods exist to reduce NOx emission. The description herein will focus on post-combustion technologies in which NOx is removed from the gas stream after formation. To date, mainly chemical processes like selective catalytic reduction (SCR) are used for NOx emission abatement. But SCR has two significant problems—catalyst deactivation and residual ammonia (NH_3) in the flue gas (Pham and Chang, 1994). Biofilter, a biological process, may offer an alternative technology to reduce NOx emissions.

Biological removal of gas phase pollutants is emerging as a novel treatment method. Biofilters have been applied for the treatment of off-gas streams containing volatile ethanol, toluene,

petroleum hydrocarbons and reduced sulfur compounds (Christen and Domenech, 2002; Acuna *et al.*, 1999; Morgan-Sagastume and Noyola, 2006). Therefore, biological NOx removal techniques using denitrification may represent promising alternatives for the conventional SCR techniques. Whereas, the previous reports in this field do not address or solve the possible negative effect of oxygen on NOx removal, considering the presence of 3-8% oxygen in the flue gas (Brady *et al*., 2001). The biogeochemistry cycling of nitrogen is well defined that the denitrification process occurs under anaerobic conditions since oxygen inhibits the removal of NOx compounds by denitrifying bacteria. It may be noted that a biofilter was able to remove NO at a level greater than 50% in an oxygen-free condition, but below 20% efficiency using 2% oxygen at inlet gas-stream (Brady *et al.*, 2001). To overcome this problem, novel aerobic denitrifying bacteria are required that could be used for constructing aerobic denitrifying processes. Patureau (Patureau *et al.*, 1997) have shown that there was no specific natural ecological niche for aerobic denitrifiers but as soon as selective pressure such as alternating aeration condition was applied, this flexible nitrate-oxygen metabolism was amplified. In special conditions, aerobic denitrification does occur and might have evolved several times (Patureau *et al.*, 2000).

In the present study, development of a new biofiltration system for the effective treatment of NOx from synthetic gas-streams in a bench-scale biofilter under a high concentration of oxygen was described. The performance of the system was monitored under selected operating conditions.

2. METHODS

2.1 Biofiltration system

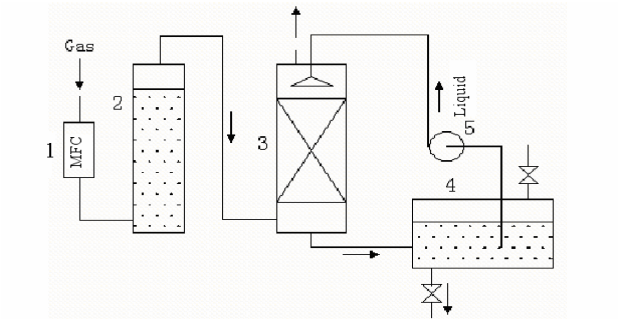

Figure 1. Sketch of biofiltration

1. mass flux control; 2. humidified column; 3. bioreactor; 4. microbial activity regenerator; 5. pump

A schematic of the system was shown in Figure 1. The biofiltration systems were consisted of humidified column, bioreactors and microbial regenerators. The biofilter was constructed using a 50 cm length × 8 cm i.d. glass process pipe. Ceramic balls (Φ4 - 6 mm) were used as medium inoculated with post-domesticated aerobic denitrifying bacteria and nitrifying bacteria. Before entering the bioreactor, gases were passed through a humidified column to adjust of the humidity. Then synthetic gas-streams were directed into the biofilter from the bottom and let off from the top. A pump was used to supply biofilter with nutrients and moisture from the top of the bioreactor. Leachate was collected into the microbial activity regenerator where it was refreshed with new nutrients and was recycled to the reactor. The microbial activity regenerator was equipped with the multi-function water quality monitor which measured oxidation-reduction potential (ORP), and dissolved oxygen (DO).

2.2 Inoculum preparation

Aerobic denitrifying organisms were enriched from farm active sludge obtained in Guangzhou, China. Nitrifying bacteria was isolated and enriched from the second sludge sample obtained from an anoxia-anaerobic-oxic wastewater treatment process at the Liede waste water treatment plant (Guangzhou, China). All sludge samples were taken in the summer.

Enrichment and isolation of nitrifying bacteria were employed in a common method (Brierley and Wood, 2001). A special method for screening and characterizing natural aerobic denitrifiers that produce N_2 gas by reducing NO_3^- under oxic conditions was described as follows: 0.5 g active sludge were transferred to 200 ml of screening medium and incubated at 30°C for 3 d. Fresh screening medium was inoculated with 5 ml of culture and incubated under the same conditions. These procedures were repeated three times.

The resultant bacterial suspension was streaked on bromothymol blue medium plates with 8.5 g of sodium succinate per liter and incubated at 30°C for 1 to 3 d. Resulting blue colonies were isolated and screened as follows (second screening): The bacteria were transferred to 200 ml of Luria-Bertani medium (1% tryptone, 0.5% yeast extract, 0.5% NaCl, pH 7.2) with 10 mmol $NaNO_3$. The flask was sealed with a butyl rubber stopper and rotary shaken at 120 revolutions per min at 30°C (precultured). The atmospheric air in the headspace was not replaced, so the initial conditions were aerobic. Then 2%, 4%, 6%, 8% O_2 and 400 ppmv NO were used to replaced air, respectively. Ar was pumped to form positive pressure. Aerobic denitrification by the bacteria was measured by determining the time-dependent production of NO_3^- and the amount of residual O_2, NO in the headspace gas. Then well cultivated nitrifying multi-species which were domesticated in the traditional method were added in a volume proportion with denitrifying cultures (3:7), and used to inoculate biofilter reactor later.

2.3 Biofilter set-up and maintenance

In the start up period, the biofilter was only fed with a recycling liquid nutrient stream supplemented with 250 mg l^{-1} $N\text{-}NO_3^-$ and 1 l^{-1} C-carbon source. After the start-up period, the reactor was continuously loaded with artificial flue gas containing NO (50–600 ppmv), O_2 and N_2 in a residence time of 60 s. The injected gas was kept at the same rate of 1L min-1. At first the gas contained 50 ppmv NO and N_2, then NO was added in 50 ppmv every five days gradually until it reached 600 ppmv. Following the influence of O_2 was determined by a gradual increase of the O_2 concentration starting with a concentration of 0.2%.

2.4 Analyses

The flowing rate of gases was controlled by mass flux control. The concentration of NO, NO_2, O_2 was analyzed by using a flue gas analyzer (Quintox KM9106, Kane-May Company). The lower detection limit of it was 1ppmv. Nitrate and nitrite were analyzed by an ion chromatography (DX-500, Dionex Corporation). ORP, DO and pH were measured with a multi-function water quality monitor (Mnlti 340i, Germany WTW). In this study, the degree of confidence used was 95%, and all the experimental results represent the mean of at least five experiments. It was evaluated from a t-distribution table.

3. RESULTS

3.1 The total performance of the biofilter

Figure 2 outlined the biofilter performance as well as a manner that mimicked conditions in a wet scrubbed flue gas stream. The system had been running for 120 days and kept on a steady NOx removal rate above 80%. Influent gas was supplied to the biofilters from the bottom in an upward, continuous one-pass mode of operation. The liquid recycle rate was set at a nominal 45 ml min^{-1} until the modified total suspended solids had reach 0.45 mg g^{-1}. For the first operation of 60 d, the normal pressure drop ranged in 400-600 Pa m^{-1}, then the pressure drop increase sharply to a level (4 kPa m^{-1}) greater than the normal condition when the bed depth from bottom was always 40 cm. This happened because a thick biofilm shiver had blocked the spacing in the biofilter. After the start-up period, the reactor was continuously loaded with artificial flue gas containing NO (50–600 ppmv).The influence of O_2 was determined by a gradual increase of the O_2 concentration starting with a concentration of 0.2%. The liquid recycle rate was set at a nominal 5 ml min^{-1} for a gas influent rate of 60 l h^{-1}. From Figure 2, it showed that clogging of bio-packing tower was a key problem in the long term and stable operation of the NOx removal system.

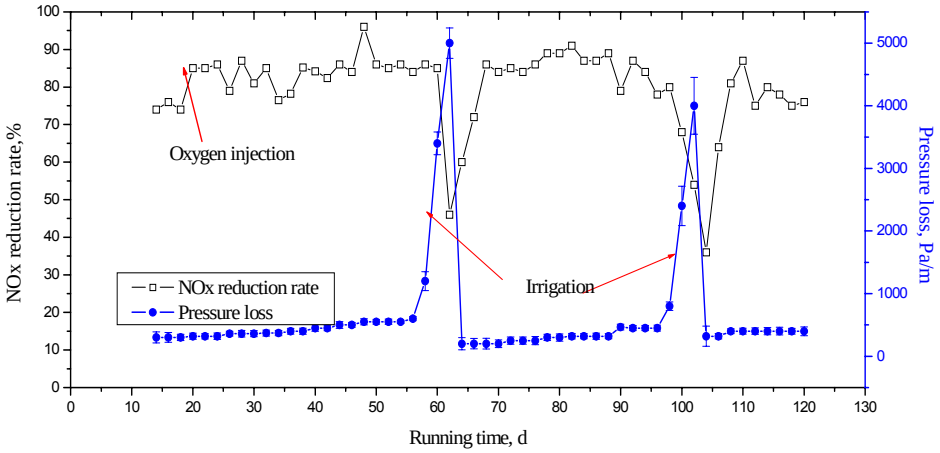

Figure 2. The Total performance of the biofilter

3.2 Effect of oxygen on NOx removal

As was shown in Figure 3, stable NO removal with an efficiency of more than 80% from the gas phase can be obtained by the bioreactor concept when treating with flue gas containing NO (400-600ppmv) with varied O_2 concentrations(0-20%). Adsorption studies were conducted comparing NO removal in a cultivated experiment and a blank experiment. To assess potential abiotic loss of NO in the biofilter, a blank experiment was developed with sterilized medium. In the blank experiment, as the oxygen increased, at least than 35% NO was removed when 20% oxygen existed. The reason was that more NO was oxidized in a high oxygen condition and transferred into liquid from the gas streams. The contrast in NO removal efficiency between the blank experiment and the bioreactor was considered to be due to the biological contribution.

The tendency of the three curves about the NOx removal rate with varying O_2 concentrations were mainly similar but for some difference in the highest and the lowest removal rate happened in the definite O_2 concentration range. The highest NOx removal efficiency was 89,2%, 88,5%, 89,6% respectively, when the experiment parameters were setting as following: 600 ppmv NO and 3.6% O_2, 500 ppmv NO and 4.8% O_2, 400 ppmv NO and 12% O_2. There seems to be no link in the NO removal and NO concentration in term of changing oxygen concentrations. Because the removal of NOx in an aerobic biofiltration involves both biological and physical reactors, NO transference rate might be various as $O_{2(g)}$ and $NO_{(g)}$ concentrations were changed. There was a balance in $NO_{(g)}$, $NO_{2(g)}$, $O_{2(g)}$.

$$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$$

The reasonable explanation was a reversible chemical balance in NO, NO_2, O_2, and NO was more difficult to removal. Meanwhile the microbial activities depended on their sensitivity to oxygen concentrations at specific microenvironment, bioflim thickness, and so on.

3.3 Effect of running time and oxygen on NOx removal efficiency recovery

Oxygen was shown to have a significant effect on NOx removal at the first two or three days when oxygen concentration increased sharply. 80% NOx removal efficiency returned as microflora adapted themselves to a new environment. After 10 days of continuous operation the NO concentration in the influent gas was stepwise increased to around 300 ppmv, while the O_2 concentration remained constant around 0.8%. At this time, the removal rate reached 84.6%, but it decreased to about 50% when O_2 concentration increased to 8% abruptly. The same experiments were carried on with 400 ppmv and 500 ppmv NO. It took 72 hours for NOx removal rate (300 ppmv) to reach above 80% again, it took 4 days for 400 ppmv NO, and about 108 hours for 500 ppmv NO to recover (Figure 4). The higher concentration the influent gas contained, the longer time the microflora needed to regain activities.

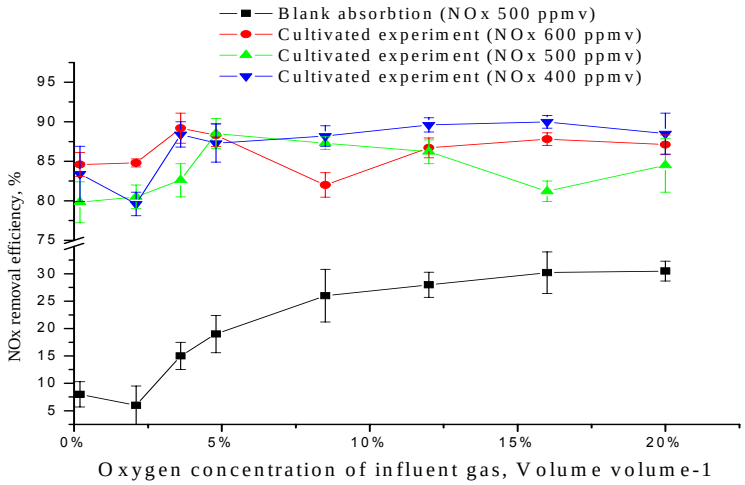

Figure 3. NO removal efficiency under different concentration of O_2

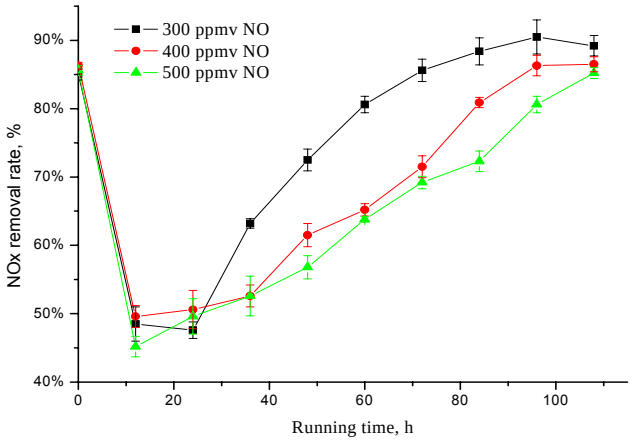

Figure 4. NO removal efficiency with running time (O_2 concentration, 8%)

3.4 Effect of the Microbial regenerator in NOx removal

To stimulate the activities of multi-culture microbial, the microbial regenerator was incorporated to create a sequential anoxic-aerobic environment. The experiment was carried out with the microbial regenerator or a liquid recycle reservoir, keeping all the other conditions the same. In this context, the role of the regenerator is evaluated. The effective volume of microbial regenerator was 1 liter. The liquid recycle rate was set at a nominal 50 ml per min^{-1} for a gas influent rate of 1 liter per minute. In this way, the reactor liquor was continuously recycled with a hydraulic retention time (HRT) of 20 mins. A multi-function water quality monitor was installed in the top, pH, ORP and DO were recorded at interval of a quarter of an hour for ten days. Compared with the microbial regenerator, the liquid recycle reservoir wasn't equipped with any monitor. Glucose was dosed at a rate of 1.728 (CH_2O) g per day for one time. In the microbial regenerator ORP and pH were used as key parameters to control carbon source dosing. Preconditioned the same amount in carbon source, nutrient fluid was adding four or five times per day according ORP value. Table 1 shows that the microbial regenerator improved higher NOx removal efficiency 5-8% than the system with the liquid recycle reservoir. In this case the microbial regenerator which was incorporated in the biofilter can improve aerobic denitrifying bacteria activity by applying alternating oxic–anoxic conditions in the presence of nitrate and nitrite. Some studies had found a bending-point on the ORP and pH curves that was linked to the major biological activities that played a role in nitrification and

denitrification. ORP was used to control the dose of carbon and trace elements because the ORP value dropped when denitrification developed completely (Paul *et al.*, 1998). ORP fluctuant range was 280-40 mv, when pH increased from 7.2 to above 7.8. DO fluctuate at 0.5-4.8 mg l^{-1} because the injected gas had a different oxygen concentration. The ORP shows a strong response to DO at low concentrations below the detection limit of most DO probes. The ORP was, therefore, recommended as control parameter for SND (Zhao *et al.*, 1999; Fuerhacker *et al.*, 2001).

Dosing started when ORP was lower than 80 mV and it switched off at ORP > 250 mV. The microbial regenerator provided an anoxic environment where the multi denitrification microbial activity recovered and high NOx removal can be maintained. The pH variation (range and rate) and ORP thresholds might denote carbon limitation for denitrification. Moreover, flexibility in carbon source dosing has potential on optimization of bacterial population. However, work was also in progress to elucidate the bending-point feature in order to improve the representative measures of this procedure.

Table 1. Contrast of the systems with microbial activity regenerator or not

O_2	System with microbial activity regenerator TSS		With the liquid recycle reservoir TSS	
	NOx removal rate packing*	mg biomass/g	NOx removal rate packing*	mg biomass/g
2%	80.2%	(0.481-0.615)/0.542	68.6%	(0.382-0.462)/0.431
5%	92.3%	(0.642-0.816)/0.775	81.4%	(0.442-0.561)/0.513
10%	82.5%	(0.498-0.685)/0.616	75.6%	(0.502-0.547)/0.522
20%	89.8%	(0.643-0.753)/0.716	80.4%	(0.413-0.575)/0.531

* Note: Sample was analyzed every five days, averaged by different sample from three sample ports.

3.5 The special microbial system in aerobic condition

To study the microbe feature in the biofilter primarily, three different types of denitrified microflora were screened by enrichment culturing of the biofilter using a nitrate broth. The feature of three kinds of microbes was shown in the Table 2. All mixed cultures were enriched and isolated from the suspend solution of biofilm adhering to the surface of ceramic balls. Figure 5 depicted two 1000x magnification micrographs of the colony on plating medium 3 days after spreading liquor taken from the microbial activity regenerator. The first micrograph showed a large number of short rods and populating the colony of the plating medium with enriched cultures described in Table 2, the first type of mixed cultures. The second micrograph indicated mostly cocci which were described in the second or the third type. Different types of denitrified cultures were observed in this study which could be explained by the existence of microenvironments within the biofilm or biomass flos in which the requirements of various types of microorganism would be met.

Table 2. Feature of three kind of microbes from biofilter

Three different type of mixed cultures	Nitrate accumulation	Oxygen-resistance	Bubble behaviors
1	No	Facultative aerobes	Small bubble
2	>200 mg l^{-1}	anaerobic	No bubble
3	<5 mg l^{-1}	Facultative aerobes	Small bubble

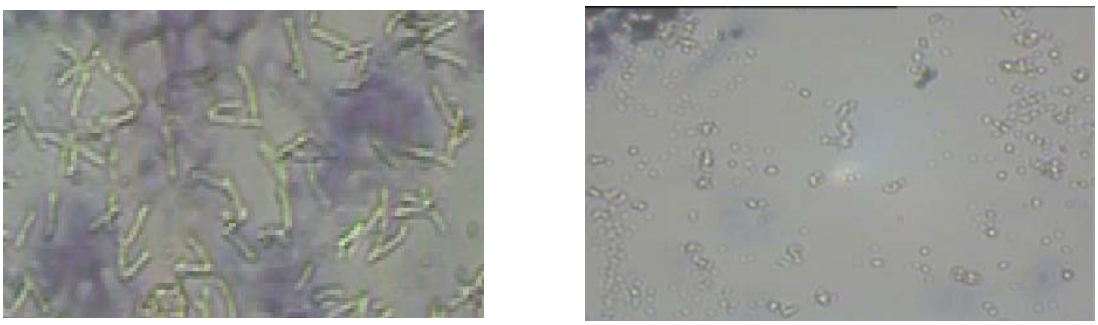

Figure 5. Biomass morphology (observed by 1,000x phase-contrast microscope) of the colony on plating medium 3days after spreading liquor taken from the biofilter

4. DISCUSSION

The removal of NO in a biofilter involves both biological and physical process. Due to the large volume of NO generated and its very low solubility (62 mg in 1 kg of water at 20 ^{o}C and an NO pressure of 1 atm), absorption of NOx can be explained with the following possible chemical reactions: There are two ways for NO removal. One way is oxidation of $NO_{(g)}$ to $NO_{2(g)}$, then $NO_{2(g)}$ is soluble in water. However , oxidation is slow at low NO concentrations, because this reaction rate is proportional to the oxygen concentration, especially under low oxygen concentration (0.8-3%). As Figure 3 indicates indirectly, the abiotic conversion was small in our aerobic studies.

The other way is the biological NO removal pathway. The mechanism of nitrogen loss can be imagined as that absorption and nitrification was the pretreatment of denitrification, whereby $NO_{(g)}$ was turned to $NO_{2}^{-}{}_{(g)}$, $NO_{2}^{-}{}_{(aq)}$, and $NO_{3}^{-}{}_{(aq)}$. Almost all of the $NO_{2}^{-}{}_{(g)}$, $NO_{2}^{-}{}_{(aq)}$, and $NO_{3}^{-}{}_{(aq)}$ were finally turned to nitrogen and biomass during denitrification, but the fluctuation of the curve in Figure 3 indicated that the transformation mechanism of NO in the biofilter was more complex than imagined. Even though no nitrite and nitrate were added to nutrient liquid, about 1-5 mg l^{-1} nitrite can be detected in the leachate. The possible pathways of NOx removal which may occur in the biofilter system were shown in Figure 6.

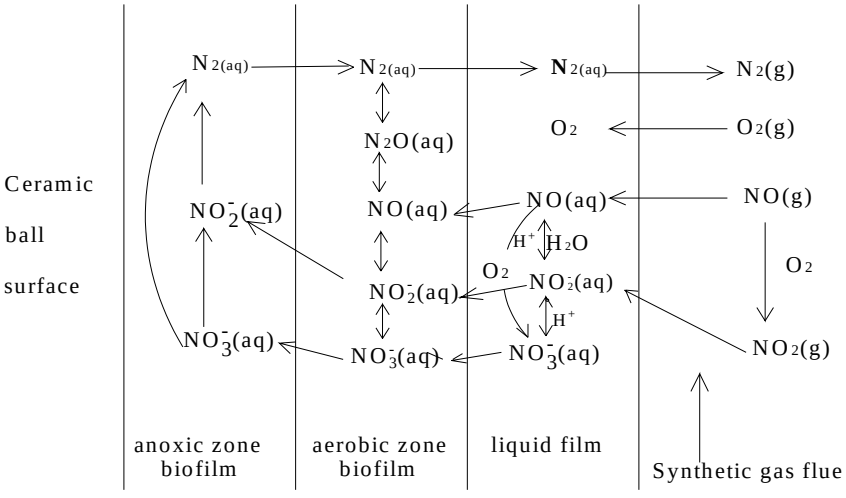

Figure 6. Possible pathway of NOx possible transformations in Aerobic Biofilter System

5. CONCLUSIONS

The biofilter could keep an a stable NO removal efficiency of over 80% for more than 120 days by the bioreactor, when treating flue gas containing NO and up to 20% O_2 concentration. Well cultivated denitrifying and nitrifying multi-species microorganism were successfully used for the NOx removal in the aerobic biofilter.

Oxygen was shown to have a significant effect on NOx removal at the first two or three days

when oxygen concentration increased sharply. 80% NOx removal efficiency returned as microflora adapted themselves to a new environment. The microbial regenerator where ORP and pH were used as key parameters to control carbon source dosing improved higher NOx removal efficiency 5-8% than the system with the liquid recycle reservoir.

The feasibility of designing a biofilter system exists in previous research because various nitrate-reducing microbial isolates have demonstrated denitrification at oxygen concentrations varying between 0.2 and 2.5 mg O_2 l^{-1} (Patureau *et al.*, 1997; Patureau *et al.*, 2000). However, various amounts of oxygen and fluctuate in temperature in combustion gas streams depend on post combustion. Further research related to the variables will be necessary to determine the ability of bilfilter to be capable of operating under these variable conditions.

ACKNOWLEDGEMENTS

Funding for this project was received from NSFC (the National Nature and Science Fund of China) through a sponsored project on Air Quality Improvement (Grants No. 20777019).

REFERENCES

Acuna M.E., Perez F. and Auria R.S. (1999), Microbiological and kinetic aspects of a biofilter for the removal of toluene from waste gases, *Biotechnology and Bioengeringeering,* **63**, 175-184.

Brady L.D., William A.A. and William A.S. (2001), Oxygen effects on thermophilic microbial populations in biofilters treating nitric oxide containing off-gas streams, *Environmental Progress*, **20**, 157-167

Brierley E.D. and Wood M. (2001), Heterotrophic nitrification in an acid forest soil: isolation and characterization of a nitrifying bacterium, *Soil Biology & Biochemistry*, **33**, 1403-1409

Christen P. and Domenech F. (2002), Biofiltration of volatile ethanol using sugar cane bagasse inoculated with Candida utilis, *Journal of Hazardous Material,* **89,** 253-265.

Fuerhacker M., Bauer H., Ellinger R. et.al. (2001), Relationship between release of nitric oxide and CO_2 and their dependence on oxidation reduction potential in wastewater treatment, *Chemosphere*, **44**, 1213-1221.

Gupta S.K. and Sharma R. (1996), Biological oxidation of high strength nitrogenous wastewater, *Water Research*, **30**, 593– 600.

Morgan-Sagastume J.M. and Noyola A. (2006), Hydrogen sulfide removal by compost biofiltration: Effect of mixing the filter media on operational factors, *Bioresourse Technology*, **97**, 1546–1553.

Oh J. and Silverstein J. (1999), Acetate limitation and nitrite accumulation during denitrification, *Journal Of Environmental Engineering*, **125**, 234-242.

Patureau D., Bernet N., Moletta R. (1997), Combined nitrification and denitrification in a single aerated reactor using the aerobic denitrifier *Comamonas* sp. Strain SQLY2, *Water Research*, **31**, 1363-1370.

Patureau D., Zumstein E., Delgenes J.P., Moletta R. (2000), Aerobic denitrifiers isolated from diverse natural and managed ecosystems, *Microbial Ecology*, **39**, 145-152.

Paul E., Plisson-Saune S., Mauret M., Cantet J. (1998), Process state evaluation of alternating oxic-anoxic activated sludge using ORP, pH and DO, *Water Science Technology,* **38**, 299-306.

Pham E.K. and Chang S.G. (1994), Removal of NO from flue gases by adsorption to an iron (II) thiochelate complex and subsequent reduction to ammonia*, Nature*. **369,**139-141.

Wang Z.X. (2006), Discussion on the environment protection and resources saving in power industry during the 11th Five-year Plan, *Electric Power*, **39**,97-99.

Zhao H.W., Mavinic D.S., Oldham W.K., Koch F.A. (1999), Controlling factors for simultaneous nitrification and denitrification in a two stage intermittent aeration process treating domestic sewage, *Water Research*, **33**, 961–970.