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Performance evaluation of biofilters packed with carbon foam and lava for nitric oxide removal

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Abstract

Long-term (>8 months) results of nitric oxide (NO) removal in biofilters, respectively, packed with lava and two different pore sizes of carbon foam (24 pores/cm (PPC) and 18 PPC) were measured. During the operation, NO removal efficiency, pressure drops, pH dependence and removal profile were evaluated. NO removal efficiencies were above 93.8%, 79.4% and 58.6% in the biofilters, respectively, packed with 24 PPC carbon foam, 18 PPC carbon foam and lava. The lava-packed biofilter demonstrated higher buffer capacity for change of pH. However, with sufficient nutrient and buffer solution feeding, the biofilter packed with carbon foam showed a higher NO removal efficiency. The pressure drops of the biofilter packed with carbon foam did not exceed 11 mm H_2O/m. The low-pressure drops made it possible by using carbon foam as packing to conveniently prevent the clogging and channeling problems associated with conventional biofilter operations.

Keywords: Biofilter; Nitric oxide; Lava; Carbon foam; Air pollution control

1. Introduction

Nitrogen oxides are emitted from most combustion processes and play a key role in the photochemically induced catalytic production of ozone, which results in summer smog and has increased levels of tropospheric ozone globally [1]. Release of nitrogen oxides also result in nitric acid deposition and increases, at least locally, the radioactive forcing effects [2]. Rapid economic development has the potential to increase significantly the emissions of nitrogen oxides in Asia [3–6]. Therefore, the technology of reducing nitric oxide (NO), a major component of nitrogen oxides, has attracted wide research attention. The major drawback of conventional post-combustion controls, such as selective catalytic reduction, selective non-catalytic reduction, adsorption and scrubbing (absorption), is high costs in treating large volumes of gas containing low-to-moderate concentration NO.

Biofiltration is one of the most important biological processes for waste gas treatment and odor control [7]. Packing material has great influence on the performance of biofilters [8–10]. The widely used packing media in biofiltration are natural organic materials, such as peat, compost, or mixtures of these materials with bark, leaves and wood chips. In practice, these packing materials have shown the common disadvantage of being strongly subject to aging phenomena and natural unhomogeneity, which may result in bed shrinkage and other problems [11].

Over the past 10 years, the compost-based biofilters have been being replaced by lava packing or synthetic packing biofilter systems [12]. The use of inert material as filter bed allowed a better gas distribution inside the reactor than organic carriers [13], though it is necessary for an initial inoculation with microorganisms as well as a periodical nutrient supply. In addition, biofilters with lava and synthetic media have a long-packing lifetime (at least 10 years). Biofilters with lava are preferred because of greater experience in use, but biofilters with synthetic media are more promising in the future because of their lower weight, smaller size and robustness. These synthetic biofilter materials have also been installed during the past couple of years [14–16].

Carbon foam is an attractive alternative material to traditional materials due to its unique properties. The cellular material can be simultaneously optimized for stiffness, strength, thermal conductivity, active surface area and gas permeability [17]. They are thermally stable, low in weight and density, chemically pure,

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resistant to thermal stress and shock, and are relatively inexpensive [18]. Especially, the carbon foam structure has thin ligaments but no closed cells that provide maximum specific surface area with significant pressure drops. In addition, the three-dimensionally interconnected open-cell utilizes the entire volume of the structure, to spread emissions throughout the volume, even with a channeled inlet flow. The tortuous flow promotes faster, more efficient treatment of mass transfer-limited gas streams.

The major biotechnologies for NO removal can be classified into two categories: (i) denitrification; (ii) nitrification. Previous investigations on denitrification revealed that NO could be removed efficiently in a biofilter [19]. However, denitrification is a dissimilatory reductive process that appeared only in the absence of oxygen (O_2). And it may be costly to remove O_2 in the application.

Nitrification is the process in which NO is oxidized to nitrate. Biofilter packed with Celite and lava, was investigated for nitrifying NO removal [20]. Little difference in performance was observed between biofilters, respectively, packed with Celite and lava despite much larger specific surface area of the former. The internal pore structure of Celite was unavailable for effective NO removal because the thin biofilm only covered the surface of open pores, which drastically reduced the diffusion of poorly soluble NO into the interior. Chen et al. [21] also found that NO biodegradation in biofilters was greatly limited by mass transfer due to its low Henry's constants. The open cell carbon foam with three-dimensional microstructures may promote the tortuous flow and the mass transfer to achieve higher removal efficiency.

This study aimed to evaluate the feasibility of using carbon foam as an alternative filter material for long-period operation in the biofiltration of air streams contaminated by NO. NO removal performance, pH dependence, filter media clogging/channeling and removal profile were evaluated in the biofilter packed with carbon foam. And another biofilter packed with lava was tested to compare their respective characteristics.

2. Materials and methods

2.1. Packing materials

Two carbon foams (Ultramet, Pacoima, CA, USA) (Fig. 1a) with different pore sizes were tested: 18 pores/cm (PPC) and 24 PPC. The average specific surface areas of the two different porosities were 2345 and 3655 m^2/m^3, respectively. The bulk densities are 0.047 and 0.048 g/cm^3, respectively. The carbon foam was machined into 7.62 cm long by 5.08 cm diameter cylinder sections.

The porous basaltic lava samples (Fig. 1b) in this study were obtained from Jilin Province, China. After being crushed, particles in the size range of 3–5 mm were selected as carriers for the biofiltration experiment. The specific surface area of the lava is 735 m^2/m^3, and its stones were boiled in demineralized water before use.

2.2. Inoculation and cultivation system

Activated sludge from Hangzhou Urban Wastewater Treatment Plant, Zhejiang Province, China, was used as an inoculum source. The activated sludge and inorganic nutrients were added into a 2 L conical flask, into which the air was blown continuously. The inorganic nutrients include $NaNO_2$ (1.2 g), $FeSO_4$ (0.4 g), K_2HPO_4 (0.4 g), $MgSO_4$ (1 g), NaCl (4 g) and $NaCO_3$ (2 g), of which $NaNO_2$ served as the only nitrogen source for nitrifying bacteria [22]. When nitrate was detected, the carbon foams were inoculated with bacterial suspension. The carbon foams were placed on a metal screen in a 20 L polyvinyl chloride (PVC) container, with a recirculating drip unit to develop a biofilm on the surface. Lava was packed in one of the biofilter columns, in which the bacteria suspension sprayed from the top of the column to develop the biofilm on the lava surface. The bacteria suspension and the supplied nutrition are identical to that sprayed on carbon foam. The concentrations of $NaNO_2$ and $NaNO_3$ were measured on a daily basis. When NO_2^-–N concentration was below 10 mg/L, the solution was renewed.

2.3. Biofilter design and operation

The biofilter system, illustrated in Fig. 2, consisted of three 5.08 cm inner diameter acrylic columns, each with a threaded PVC cap at the base. The biofilters named BF-I, BF-II, BF-III were, respectively, packed with 18 PPC and 24 PPC carbon foams and lava to the height of 30.48 cm. Before being plugged into the columns, the carbon foams had been inoculated and the biofilm was developed during the 2 months in the cultivation system. Each column was designed with five regularly spaced gas-sampling ports along the depth of the column. To

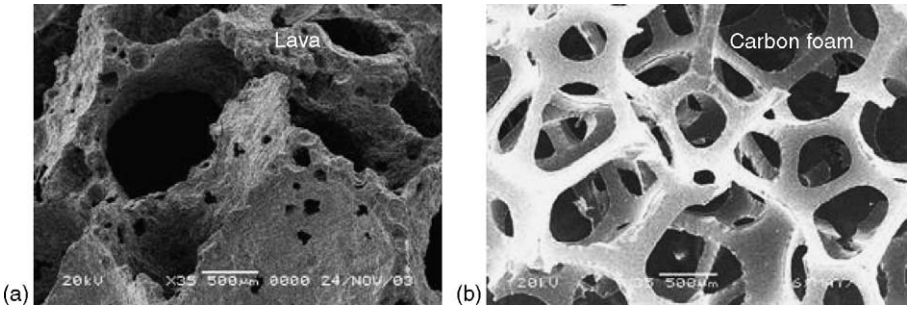

Fig. 1. The SEM photo of lava and carbon foam (24 PPC), 35×.

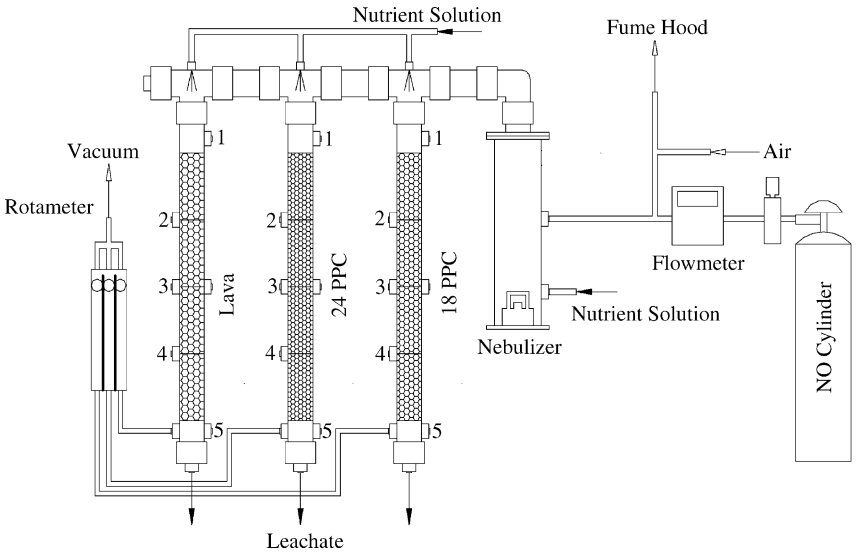

Fig. 2. Schematic of biofilter.

limit the liquid loading to the biofilters, an ultrasonic nebulizer unit capable of delivering a fine humidified aerosol to the biofilters was utilized and located in a separate column. The aerosol column consisted of a 5.08 cm inner diameter acrylic column with mixed NO and air entering near the base. The mixed gas, which was entrained in the aerosol, entered the three columns, providing water and nutrients to maintain the bacterial population. A mass flow controller and three rotameters were used to regulate NO concentration and the flow rate of the mixed gas entering the aerosol column. Over the top of each biofilter column, a spray nozzle was set-up. The spray system was used to transport buffer solution ($NaHCO_3$, 6 mg/L) to maintain a stable pH value (7.0–7.5) within the biofilter. When the pH of leachate from the biofilter was below 6.5, the buffer solution was sprayed, with a total amount of about 2 L/d and a total spraying time of 2 h/d. When the waste gas was not supplied, the nutrient solution, which was the same as the inorganic nutrition for cultivation and inoculation, was added (about 1 L/d, 4 h/d) to maintain biomass growth. The entire biofilter system was maintained in a constant temperature room at 23 °C.

After the investigation on bio-nitrification, the biofilter packing was disinfected to determine the effect of adsorption in the removal process. The packing material was taken out and sterilized at 121 °C for 20 min. After that, the packing was refilled into the biofilter. The adsorption process was conducted with inlet concentration at 98–102 mg/m^3 and EBRT 3.5 min.

2.4. Analytical methods

Nitrite and nitrate were measured according to the method stated in "Standard Methods for the Examination of Water and Wastewater" [23]. NO concentrations were analyzed by NO/NO_2 analyzer 42CHL (Thermo Electron Corporation, USA) on-line.

Surface area and average pore size were measured using a Brunauer–Emmett–Teller (BET) isotherm (ASAP 2010, Micro Meritics, USA), and chemical composition was determined by an energy dispersive atomic X-ray analyzer (PV 9900, EDAX International Corporation, USA). Pressure drops of the filter bed were monitored by a water manometer.

All experiments were repeated three times. The data shown in the corresponding figures are the mean values of the experiments.

3. Results and discussion

3.1. Inoculation results

After inoculation and cultivation for a period, NO_2^- was nitrified and the results of nitrification capacity versus time were shown in Fig. 3. The acclimation tests showed that the nitrified NO_2^-–N increased slowly during the first 20 days. From the 21st day, the nitrification capacity began to increase abruptly; within the later 30 days, the amount of NO_2^-–N converted to NO_3^-–N, respectively, increased to 253 mg/(L d) and 135 mg/(L d) in carbon foam and lava inoculation systems. In the last 10 days, the nitrification capacity reached a plateau and, presumably, a maximum biomass was obtained. Ammonia con-

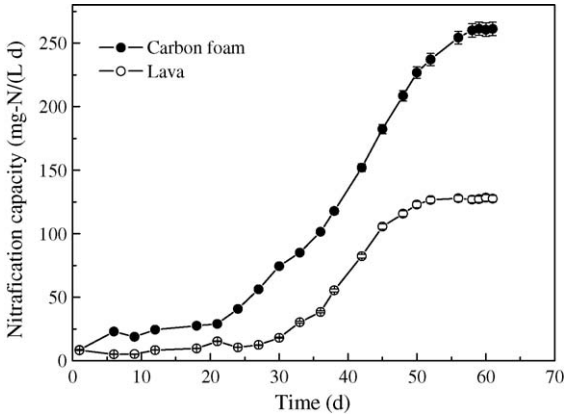

Fig. 3. Nitrification capacity of nitrite vs. time in inoculation system.

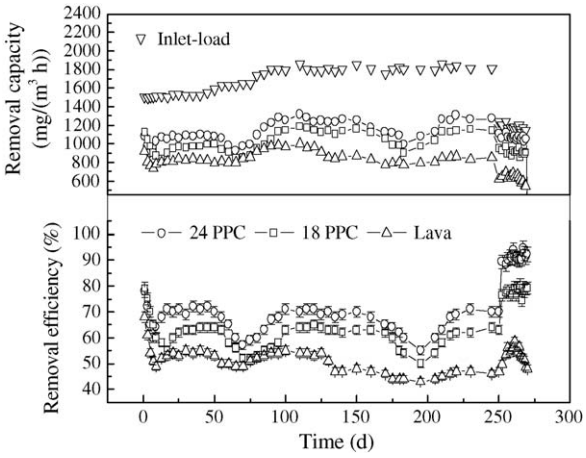

Fig. 4. Variations of the NO removal efficiency and capacity for three biofilters during the operation time.

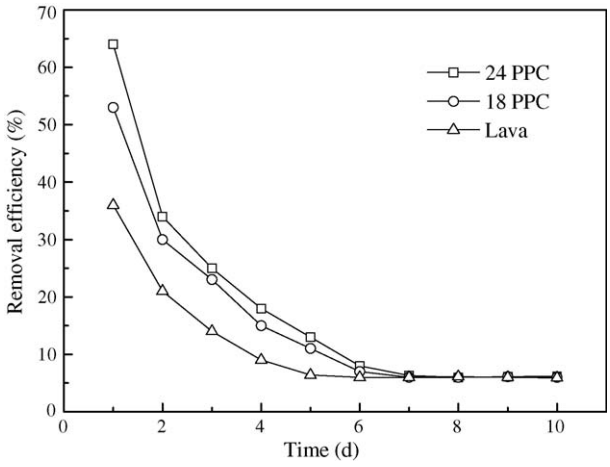

Fig. 5. Adsorption removal efficiency on the packing surface.

centration was measured during the inoculation, but it was very low at about 0–0.030 mg/dm. The fact that almost no ammonia was detected in the samples suggested that all NO_2^-–N was oxidized to NO_3^-–N. Total-N decreased by 16% and 9.3% within 12 h on the 50th day. The reduction of total-N could be attributed to several factors, such as biomass assimilation, denitrification in anoxic microenvironments, removal of nitrogen via sampling and volatilization. The growth of nitrifying organisms was indicated by the rapid conversion of NO_2^-–N to NO_3^-–N.

3.2. NO removal performance

NO removal efficiencies of biofilters, respectively, packed with carbon foams and lava are shown in Fig. 4. The data describes the results of about more than 8 months' continuous operations. Inlet NO concentration is in the range of 87.0–107.9 mg/m^3 in the initial 250 days. In the last 20 days, inlet concentration decreased to 65.4–72.4 mg/m^3. The empty bed residence time (EBRT) was kept at about 3.5 min. With inlet concentration decreased from about 100 to about 70 mg/m^3, the removal efficiency increased from 72%, 65% and 56% to 93.8%, 79.4% and 58.6% in BF-I, BF-II and BF-III, respectively. However, the removal capacity decreased. Previous investigations [24] found that a steady removal efficiency of 80% was attained at a specified inlet NO concentration of about 1000 mg/m^3 and an EBRT of 2 min in a biotrickling filter. However, the concentration of outlet gas was still as high as 200 mg/m^3.

The removal efficiency in all the biofilters got higher at the start and then decreased, which may result from the adsorption of NO on the packing materials. The effect of adsorption on the removal was investigated. The adsorption removal efficiency was shown in Fig. 5. It could be estimated that the most part of NO removal in Fig. 4 was due to adsorption in the initial 3 days. The carbon foam and lava both had great specific surface areas, which had strong affinity to NO. After the adsorption was saturated, the removal efficiency decreased. The removal efficiencies in Fig. 5 decreased rapidly before reaching equilibrium. However, still a little NO was removed when the adsorption was saturated.

NO is liable to be oxidized by O_2. The gas phase thermal conversion of NO to nitric dioxide (NO_2), is illustrated by the following equation:

$$2NO + O_2 \rightarrow 2NO_2 \quad (1)$$

The rate for the oxidation of nitric oxide to NO_2 can be expressed in a second order relationship by the following equation [25]:

$$d[NO]/dt = -2k[NO]^2[O_2] \quad (2)$$

where the rate constant k is equal to $k = 1.2 \times 10^3 e^{530/T}$ L^2/(mol^2 s). When there is enough oxygen, the rate of conversion of NO to NO_2 increases in the square of NO concentration.

Under the experimental conditions of inlet concentration of 65.4–72.4 mg/m^3 and EBRT of 3.5 min, the calculated chemical oxidation removal is at about 6.1–6.7%. Under Chou and Lin's experimental conditions [24], the NO removed by chemical oxidation would be 45.9% at 23 °C.

After about 10 days of cultivation, the microbe was accommodated to nitrification removal, and removal efficiency increased and then remained stable during the normal operation period in biofilters. After the 130th day, removal efficiency in BF-III decreased. That may be attributed to the excess biomass accumulation, which contributed most to the bed clogging of BF-III.

The nozzles on the top of biofilters sprayed buffer solution and inorganic nutrients at the intervals to maintain a stable pH value (7.0–7.5) and biomass. The volume of sprayed buffer solution decreased during the 55–75th day period and the 170–195th day period. The removal efficiency fell by less than 20% in BF-I and BF-II. But BF-III was little affected due to its buffering capacity [26]. The lava carrier is composed of O, Na, Mg, Al, Si, K, Ca, Ti, and Fe, whose chemical contents (wt.%) are 40.20, 3.51, 4.02, 9.03, 24.53, 1.72, 6.13, 1.43, 9.42, respectively. The alkali metal oxides, which dissolved from the lava at low pH values, neutralized the circumstance. The average pH values of leachate in BF-I, BF-II and BF-III are 6.2,

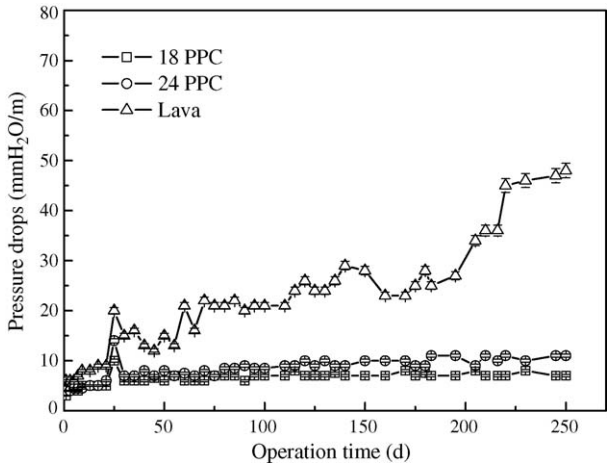

Fig. 6. Variations of the pressure drops of three biofilters during the operation time.

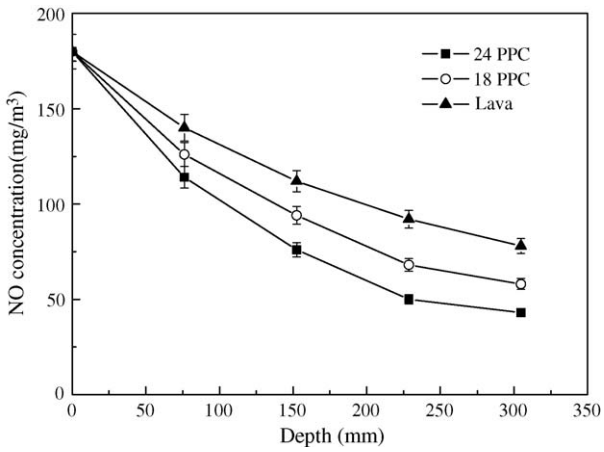

Fig. 7. The NO removal profiles on the 125th day from the top to bottom of packing material.

6.3 and 7.3, respectively. The lava showed a strong adaptability to the fluctuant conditions.

Though the microbe in BF-I and BF-II were impaired due to the change of pH, higher removal efficiencies were obtained when compared with those achieved in BF-III packed with lava. The results suggest that the high specific surface area and the open cell structure of the carbon foam are beneficial to NO removal. With sufficient nutrient and buffer solution supply, the biofilters can achieve higher and more stable NO removal efficiency throughout a long operation period.

3.3. Pressure drops and removal profile

The filter bed pressure drop is a key aspect of biofilter performance. It affects the energy consumption of the blower, which contributes most to the operation cost. The variations of the pressure drop in the filter columns are shown in Fig. 6. During this experiment, the pressure drops in BF-I, BF-II and BF-III were around 8, 11 and 50 mm H_2O/m, respectively. The variations of the pressure drop in BF-I and BF-II were negligible.

The pressure drops of the three biofilters increased a little on the 25th day, which resulted from too much buffer solution sprayed (about 5 L/d) due to a control error. Excessive water content will lead to media compaction and gas clogging, which will eventually result in flow channels because of granulometry change [27]. But the pressure drop changed little in the carbon foam-packed biofilter, due to its stiff structure and thin ligaments. During the operation, the pressure drop in BF-III kept on increasing up to about 50 mm H_2O/m. The higher pressure drop in BF-III may be caused by low porosity and the biomass growth. These pressure drops were comparable to the values of Choi et al. [28], who mentioned pressure drops of 25–27 mm H_2O/m filter bed. Overall, the biofilter packed with carbon foam showed higher removal efficiency and decreased pressure drops, which could save more operation costs when the biofilter was scaled up in the application.

Fig. 7 shows NO concentration profiles as measured on the 125th day. During the operation, when inlet NO concentration remained at 180 mg/m^3 and EBRT 4 min, NO removal efficiency remained at 76.1%, 67.8 and 56.7% in BF-I, BF-II and BF-III, respectively. The zone of biodegradation decreased along the depth of the column. The slope of the curve in Fig. 7 indicated that NO was consumed primarily in the first 150 mm column of the biofilters. Based on the NO profile measurements along the depth of the biofilter, the majority of biomass appeared to be located near the entrance of the biofilter. The localization of biomass near the entrance is consistent with the findings of other researchers [16,29]. Since there is more nitrogen source at the entrance; nitrifying organisms are growing rapidly, after a long period of liquid phase or gas phase operation, thus larger area of biofilm forms. On the other hand, higher NO concentration enhanced the mass transfer from the gas phase to the biofilm. As a result, the nearer the entrance, the bigger the mass transfer rate and the higher removal efficiency obtained. The results showed that the structure of biofilters could be improved as a cuboid shape.

4. Conclusions

Both tested packing materials, especially carbon foam, showed good performance for long-term operation. The NO removal efficiencies of the biofilter systems were above 93.8%, 79.4% and 58.6% in BF-I, BF-II and BF-III, respectively. The lava-packed biofilter had higher buffer capacity with the change of pH. However, with sufficient nutrient and buffer solution feeding, the biofilter packed with carbon foam showed a higher NO removal efficiency. NO was consumed primarily by biomass located near the entrance of the biofilter. The pressure drop of the biofilter packed with carbon foam did not exceed 11 mm H_2O/m. The low-pressure drop made it possible by using carbon foam as packing to conveniently prevent the clogging and channeling problems associated with conventional biofilter operations.

Acknowledgments

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