

Biotreatment of Combustion Gas

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ABSTRACT

In the present paper, the possibility of using sulfur oxidizing denitrifying organisms for NO_x treatment in biotrickling filters is evaluated. In this approach, nitric oxide (NO) is used as an electron acceptor and various sulfur species are used as electron donors. Preliminary laboratory study showed that NO removal efficiency was between 25-90%, depending on the conditions of biotrickling filter (empty bed residence time (EBRT), gas composition). As expected the higher the EBRT, the better the removal of NO. More than 90% NO removal was achieved at an EBRT of 189 seconds. However, oxygen in the inlet gas inhibited the NO removal. At 0.5% oxygen the removal dropped from 12.4 to 7.7 g/m³ h.

Overall, the research shows new possibilities for using autotrophic organisms in biotrickling filters for the treatment of combustion gases from power generation equipment.

INTRODUCTION

Nitrogen oxides (NO_x) are among the most damaging air pollutants to date. The common form of NO_x generated during coal combustion is nitric oxide (NO). This odorless and colorless gas reacts with oxygen and water to form acid rain. Nitric oxide is also a key precursor in photochemical ozone depletion. In 1998, NO_x emission in the US was estimated to be 1.98×10^{10} kg/year, almost 50% of which came from fuel combustion in electric utility and industrial power or heat generation.⁴ More stringent regulations and concerns over NO_x emission may serve as an incentive for developing new techniques, which are more economical and efficient.

Current NO_x control technologies based on chemical techniques such as adsorption, selective catalytic reduction, etc. are expensive. So the development of novel methods to reduce the amount of NO_x emission is required.

Biological treatment of NO_x contaminated gas may offer an economic alternative for reduction of NO_x in combustion gases. NO_x biotreatment can follow an oxidative route (nitrification) leading to nitrate or a reductive route (denitrification) leading to nitrogen gas. The latter is the most interesting, as it does not result in any water contamination with nitrate. Denitrification is in fact a dissimilatory process, which allows microbes to use oxidized nitrogen compounds as alternative electron acceptors for energy production. Typically, this process refers to nitrate respiration--nitrate is reduced to nitrite, nitric oxide, nitrous oxide, and nitrogen gas consecutively.⁶ Denitrification has been successfully used to remove nitrate and nitrite in wastewater treatment plants. However, recent studies have also reported the application of denitrification for removing NO_x from waste gas streams as well.^{2,7,10} The advantage of denitrification is that NO_x is reduced stepwise to environmental friendly nitrogen gas (N₂).

Of all biotreatment processes, the biotrickling filter seems to be the most suitable for NO_x control. The main advantage of biotrickling filter is the ability to treat hot air streams and acid producing contaminants¹, which makes it possible to handle combustion gas with a minimum of air preconditioning. Moreover one may speculate that thick biofilm growing on the packing of biotrickling filters may protect microbes from toxicity of NO_x and/or provide

anaerobic microniches that favor denitrification.

Reductive NO_x biotreatment can be divided into two main categories depending on the sources of carbon and energy. In heterotrophic systems, NO_x reduction is coupled with the oxidation of organic carbon (chemoorganoheterotrophs). On the other hand, in autotrophic systems, energy is provided by oxidation of inorganic substances such as sulfide, sulfur, iron etc., while the carbon for growth comes from carbon dioxide or carbonate (chemolithoautotrophs).

Several heterotrophic bioreactor systems have been reported to remove NO_x from gas stream. Barnes et al.⁷ demonstrated the biological removal of NO_x in compost biofilter, enhanced by feeding lactate or glucose, indicating that heterotrophic denitrification took place. This study also suggested that pH may be a key factor to obtain a successful NO_x removal.

du Plessis et al.¹⁰ successfully used a biofilter with thick biofilm to treat NO_x contaminated gas under aerobic conditions while toluene is used as an energy source. A comparison of packing materials of biofilters and/or biotrickling filters was illustrated by Flanagan et al.² With a supplement of organic carbon, this study found that compost was the best packing material for NO_x removal. Extended studies of toluene-degrading biofilters conducted by Woertz et al.¹⁴ showed a potential of using heterotrophic fungi for NO_x removal in biofilters. Interestingly, the fungal mechanisms responsible for NO_x removal in the biofilter may involve nitrogen assimilation, as NO_x removal was inhibited by the accumulation of ammonium in the biofilter, a known major inhibitor of assimilatory nitrate reduction.

On the other hand, autotrophic systems for the removal of NO_x have only been reported in a small number of papers compares to NO_x treatment is heterotrophic systems.^{2,7,10,11} However, based on the substantial amount of work from nitrogen removal in aqueous phase, autotrophic NO_x removal from gas streams should be possible. Lee and Sublette¹¹ demonstrated that the facultative anaerobe, *Thiobacillus denitrificans* can be cultured in anaerobic reactors using nitric oxide (NO) as a terminal electron acceptor and Hydrogen sulfide as electron donor with reduction of NO to elemental nitrogen. However, further efforts to combine NO and SO₂ removal from combustion gas, based on direct contact to a co-culture of sulfate reducer, *Desulfovibrio desulfuricans*, and sulfur oxidizer, *Thiobacillus denitrificans*, failed¹¹. The original idea was to use sulfate reducing bacteria to convert sulfate to sulfide and use the latter as electron donor for denitrification, however the authors found some flaws, including an inhibition of *D. desulfuricans* by NO, an inhibition of *T. denitrificans* by oxygen present in reactor and finally inhibition of NO removal by nitrate.

As mentioned above, heterotrophic organisms have been used in biofilters to remove NO_x from gas streams, however, the approach often resulted in large amounts of biomass accumulation in the bed leading to excessive pressure drop and clogging of the system. When this happens, several measures are needed to remove excess biomass from clogged reactors, which will increase operating cost and affect the long-term performance. The autotrophic approach, in which the pollutant-removal mechanism depends on slow growing bacteria seems to be more promising in term of biomass control and system stability. Moreover, as will be explained further, the autotrophic denitrification can possibly be combined with the treatment of sulfur dioxide, another important pollutant present in combustion gas.³ Hence, in the present paper, the basic concept for using sulfur oxidizing denitrifying bacteria for NO_x control is presented and recent experimental proof of concept is shown.

CONCEPT

The basic concept is presented in Figure 1. In short, bacteria use electrons from thiosulfate for denitrification in the biotrickling filter. The oxidation of thiosulfate results in sulfate, which is then converted to hydrogen sulfide by sulfur reducing bacteria (SRB) in the post treatment unit. Next, hydrogen sulfide is converted to elemental sulfur (or thiosulfate) under microaerophilic conditions. The degree of sulfur oxidation reached in the post-treatment unit depends on the supply of oxygen. Too much oxygen will result in unwanted sulfate production. Elemental sulfur may be desirable, as it will allow recovering the sulfur for recycle in the process, for disposal, or for sale. On the other hand, Thiosulfate might be more convenient as it is soluble and will not cause solid deposits when recycled in the treatment system.

However, the combustion gas may also contain sulfur dioxide (SO_2). SO_2 may be treated in autotrophic biotrickling filter as follows. First SO_2 is absorbed in the trickling liquid and chemically reacts with water to form sulfate or sulfite. Sulfite is converted biologically to hydrogen sulfide and then elemental sulfur or thiosulfate using electrons provided by the organic carbon (COD). Such treatment of SO_2 with quasi-equimolar production of elemental sulfur has recently been demonstrated in our group.¹³ Both hydrogen sulfide, elemental sulfur and thiosulfate can possibly be recycled to the biotrickling filter and serve for NO_x removal. However, careful selection of the conditions and feed locations is required to avoid hydrogen sulfide emissions from the system as it would cause an odor problem.

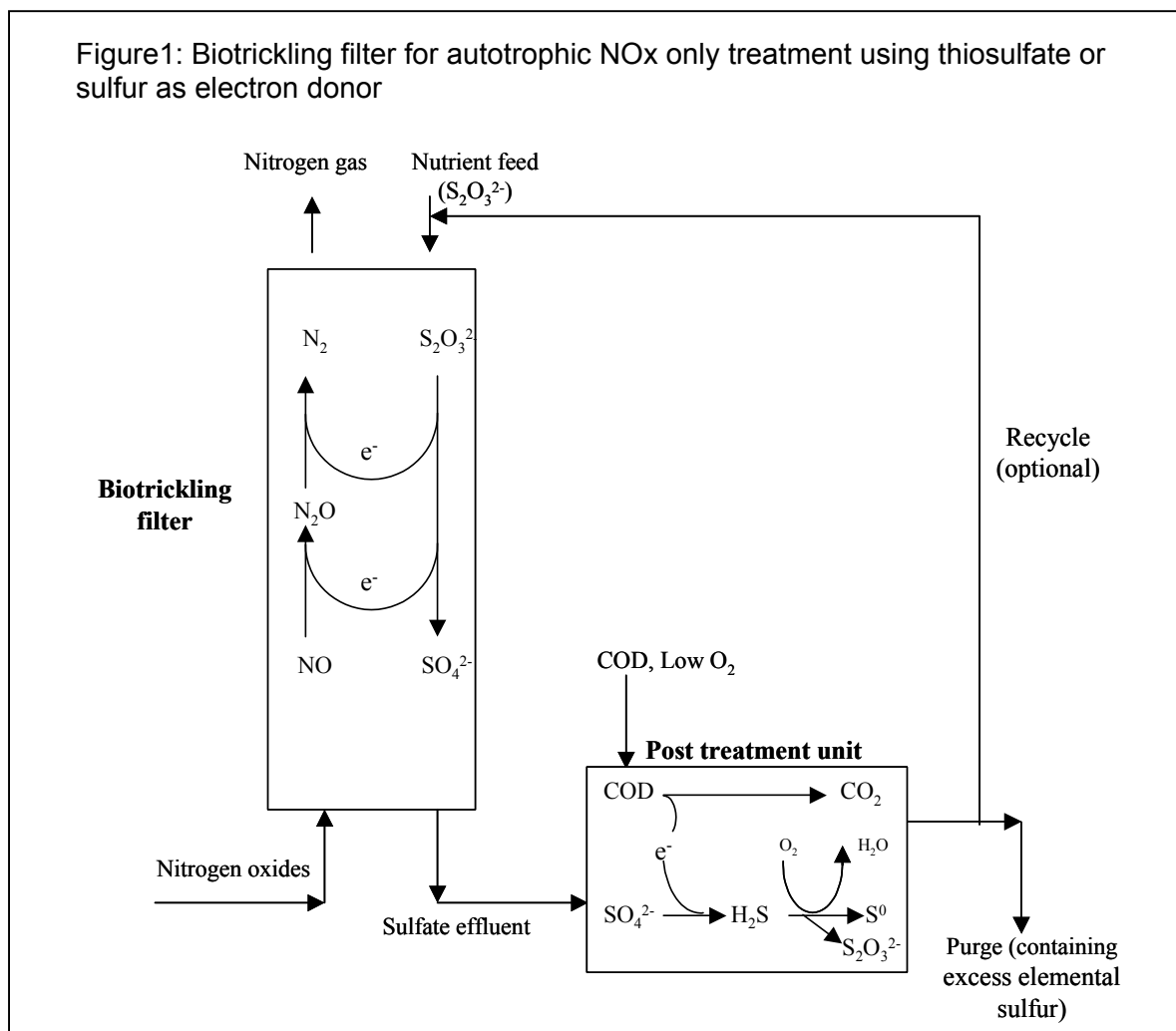
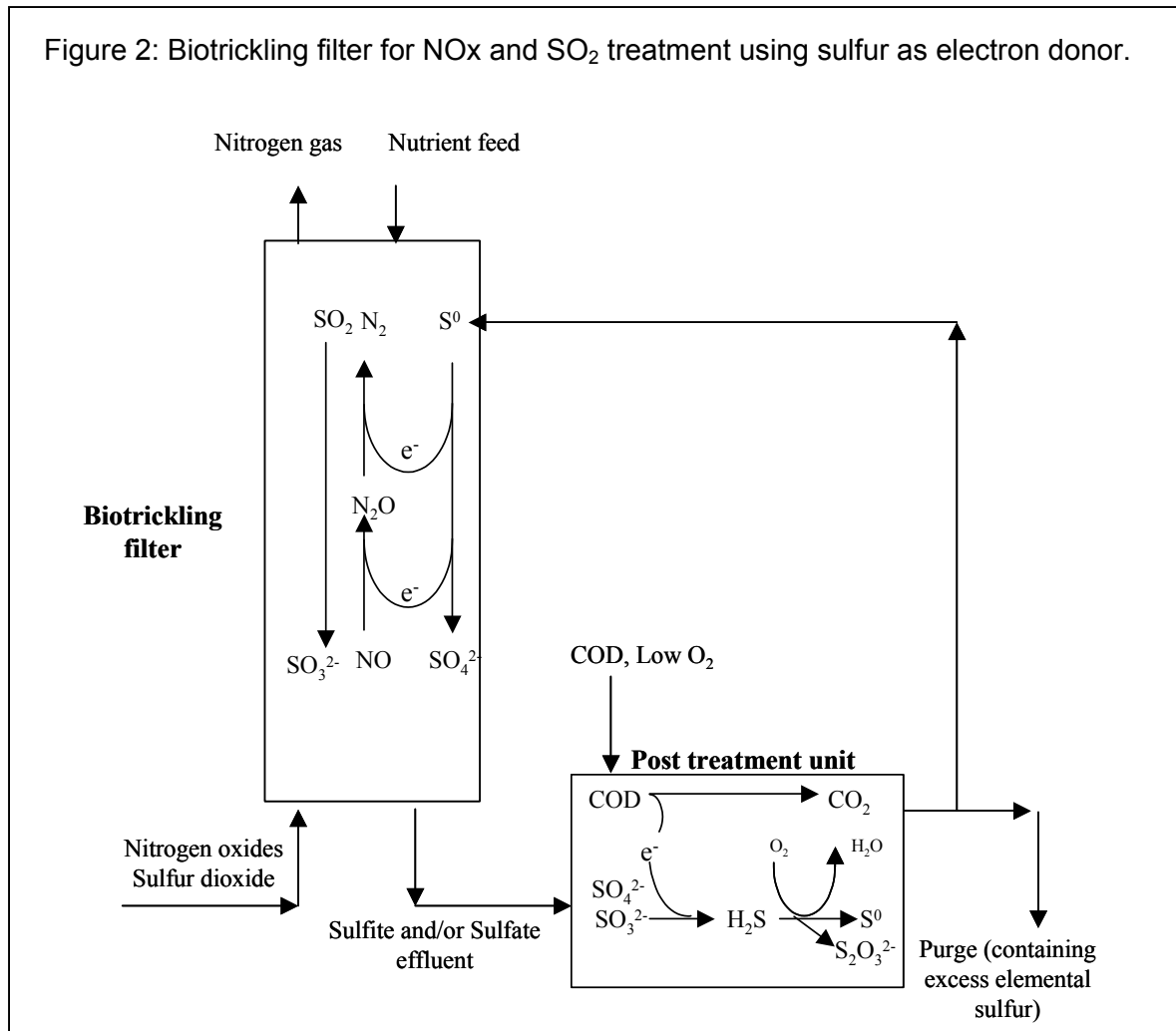


Figure 2: Biotrickling filter for NOx and SO₂ treatment using sulfur as electron donor.



MATERIALS AND METHODS

Biotrickling Filter Setup and Operation

A prototype system was setup following the schematic shown in Figure 1. The reactor was made out of clear Schedule 40 PVC pipe (ID=4 cm, Ryan Herco, Burbank, CA). The total length of the reactor was 60 cm and the bed height was 50 cm. The reactor contained 0.63 L of packing made of open pore polyurethane foam cubes (4 × 4 × 4 cm cubes, specific surface area of 600 m²/m³; density of about 35 kg/m³) cut to cylindrical shape to fit the reactor internal diameter. The trickling liquid was sprinkled over the packed bed at a rate of 0.8 m/h (1 L/h) from the top of the reactor. A relatively low trickling rate was selected to minimize possible mass transfer limitations towards the attached biofilm and to produce the highest possible concentration of absorbed pollutant in the trickling liquid. Selecting a low trickling rate also minimized the liquid consumption, as the liquid was not recycled as usually done in biotrickling filters. The biotrickling filter effluent was collected from the bottom of the reactor and fed to the post-treatment unit. The gas inlet and outlets ports were located at the bottom and top lids of the reactor, respectively.

The biotrickling filter was operated at room temperature (20-24 °C). The pH inside the reactor was maintained at 6.8 ± 0.2 by adding sodium carbonate (0.5 g/L) to the liquid being trickled. The liquid trickled consisted of a mineral medium with the following composition (in g/L in demineralized water) K₂HPO₄ (1); KH₂PO₄ (1); MgCl₂ (0.25); CaCl₂ (0.52); Na₂CO₃ (0.75) Na₂S₂O₃ (0.5) and trace metal solution 1ml/L. There was no external carbon

source supplied to the biotrickling filter except for CO₂ and carbonate.

Simulated flue gas was prepared by mixing a metered flow of approximate 10% CO₂, 90% N₂. Oxygen and NO gas was added to make up the compositions as required. The total gas flow rate was varied to achieve empty bed residence times (EBRT) in the reactor ranging from 20 to 190 s.

Post-treatment Unit

The post-treatment unit was made out of clear Schedule 40 PVC pipe (ID=15 cm, Ryan Herco, Burbank, CA) fitted with a gas tight cap. A schematic of the unit is shown in Figure 1. The total height of the treatment unit was 15 cm with a working volume of 1.7L. A glucose solution (30 g/L in deionized water) was supplied to the system at a flow rate corresponding to S-SO₄²⁻:COD ratio of 1:1.5. Gentle mixing of the reactor contents was achieved by using a magnetic stirrer. The post-treatment reactor was maintained at a temperature of 35 ± 2 °C using a hot-stir plate. The pH of the system was maintained at 7-8 by adding Na₂CO₃ whenever required. To improve the biomass holding capacity in the reactor, 20 cubes of polyurethane foam (see above for characteristics) were added to the reactor. A metered stream of air was supplied to the post-treatment unit for oxidizing sulfate to elemental sulfur.

Analytical Methods

Gas samples were collected from the inlet and outlet of reactor in 3.8-liter Chemware's tedlar gas sampling bag before analyzed by combustion gas analyzer (Model IMR 1400-c ,IMR Environmental Equipment, Inc., FL). Trickling liquid was collected from the reactor and feed tanks for analyzing nitrogen and sulfur species. Nitrate, nitrite and sulfide contents were determined by using analyzing kits (Vacuvial, Chemetrics Inc. VA). Sulfate and sulfite contents were analyzed as described in Standard methods (4500-SO₄²⁻, 4500-SO₃²⁻).⁹ Thiosulfate was analyzed following Kurtenacker method.⁸

RESULTS AND DISCUSSION

Biotrickling Filter Performance

The concentration of nitric oxide in inlet gas and outlet gas during startup is shown in Figure 3. Thiosulfate was used as the electron donor for denitrification leading to the removal of nitric oxide. The amount of nitric oxide removed was around 50 ppm_v at an empty bed residence time of 25 seconds, which corresponds to 17% removal. The removal trend (Figure 4) was increasing slowly, presumably due to slow growth of the denitrifying bacteria. Analysis of the biotrickling filter liquid effluent showed no nitrate or nitrite, thus indicating that the NO removed was most probably converted to N₂ gas. At this time, we believe that the formation of N₂O gas, an intermediate of denitrification, is unlikely although it can not be excluded. After 30 days, the process seemed to have reached a pseudo steady-state, i.e., no more change in the NO removal performance was observed over several days.

Figure 3: Inlet and outlet concentrations of NO in the autotrophic denitrifying biotrickling filter. EBRT = 25 sec.

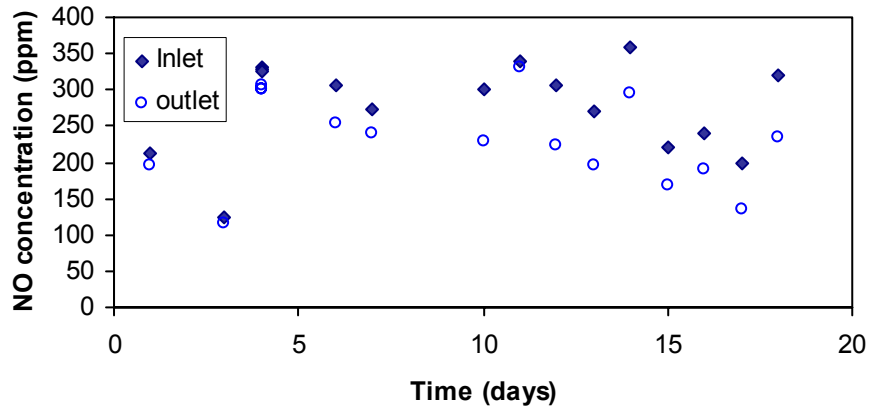
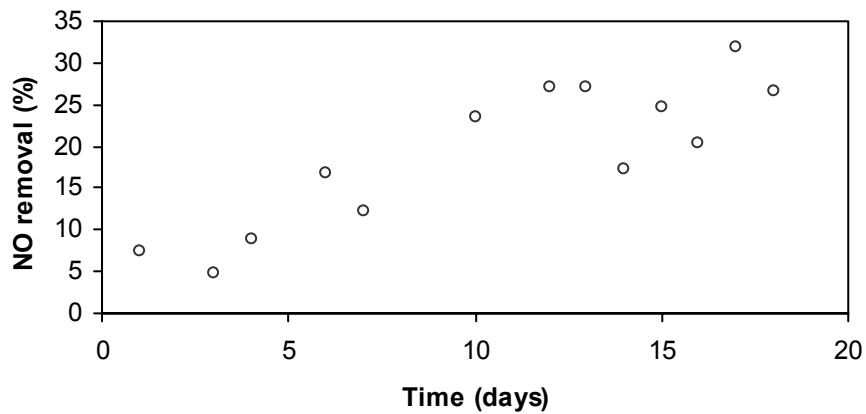


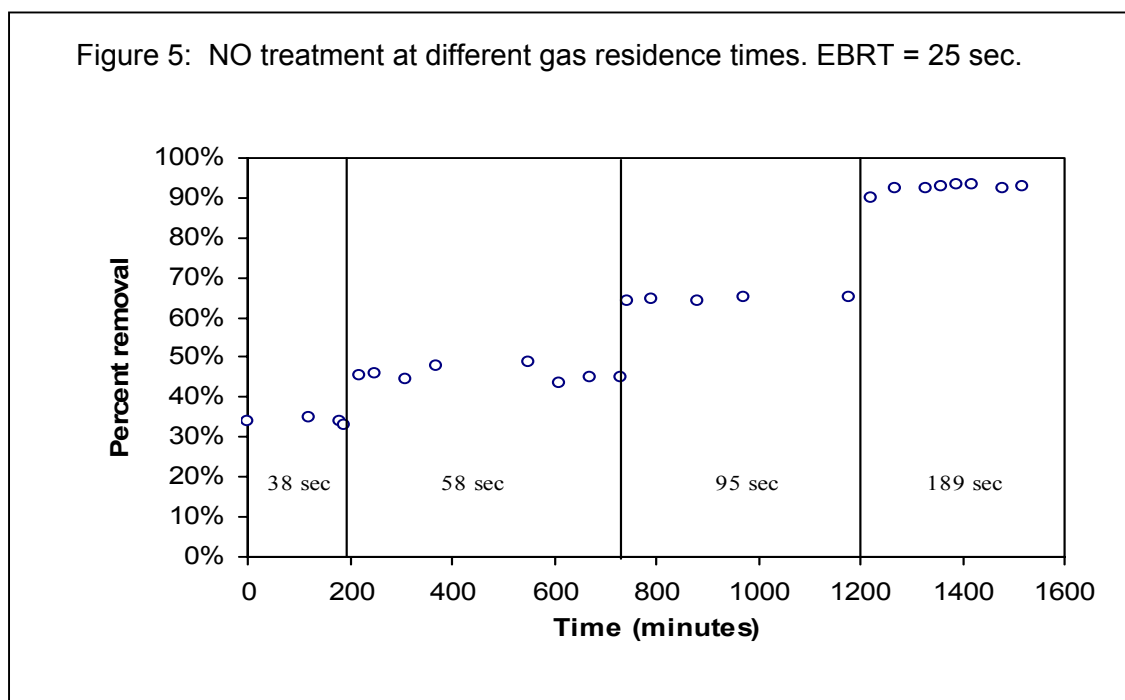
Figure 4: Removal percentage of NO in the autotrophic denitrifying biotrickling filter.



Influence of Gas Residence Time

To determine the kinetics of NO_x removal in the autotrophic biotrickling filter, the empty bed residence time of the gas was varied, while the influent concentration of NO was maintained at 300 ± 20 ppm. As expected, the percentage removal of NO_x was proportional to the gas residence time in the biotrickling filter. At gas contact times of 189 seconds, more than 90% NO removal was achieved. As shown in Figure 5, after changing the inlet concentration, the system rapidly reached a new steady state. This was expected in light of the high Henry coefficient of NO. Throughout the experiment, the biotrickling filter effluent was also monitored for NO₂ as the possible product of abiotic oxidation of NO, however even at the longer gas contact times, NO effluent concentrations remained low (<3 ppm_v).

Figure 5: NO treatment at different gas residence times. EBRT = 25 sec.



A cursory comparison of NO removal rate in autotrophic and heterotrophic biotrickling filters reveals that the latter may be faster. For example, Flanagan et al.² reported that a biotrickling filters packed with inert material bed could remove over 85% of 500 ppm NO at residence times of 70-80s, which is approximately 2.5 times faster than the removal rate of the biotrickling filter in this study. This difference may be due numerous factors. One may be the supposedly faster specific biodegradation kinetics of heterotrophic denitrifying organisms, although further proof of such difference is required. It may also be due to the fact that the results presented in this paper are from a system not yet optimized. Amongst others, refining conditions, and/or experimenting with different inorganic electron donors such as elemental sulfur, which is more reduced than thiosulfate, may improve NO removal rate in the autotrophic biotrickling filter. In any case, further characterization of the process was warranted.

Influence of Pollutant Loading and Gas Residence Time

The effects of NO load and gas residence times on the elimination capacity (EC) of NO are shown in Figure 6. In these experiments, the EBRT was maintained at either 20 s or 60 s whereas the NO concentration in the inlet gas was changed to obtain different NO loadings. The results show that the EC was affected by both NO load and EBRT. The ECs obtained from 60 s EBRT were higher than those obtained at 20 s EBRT at the same NO load. In other words high concentration-low flow was better treated than low concentration-high flow. This is a typical behavior of kinetically limited systems treating hydrophobic contaminants. As concentration is increased, a higher concentration of contaminant is achieved in the biofilm, resulting in faster specific biodegradation rates.

Figure 6: Steady state elimination capacity of NO in autotrophic denitrifying reactor at different NO loadings.

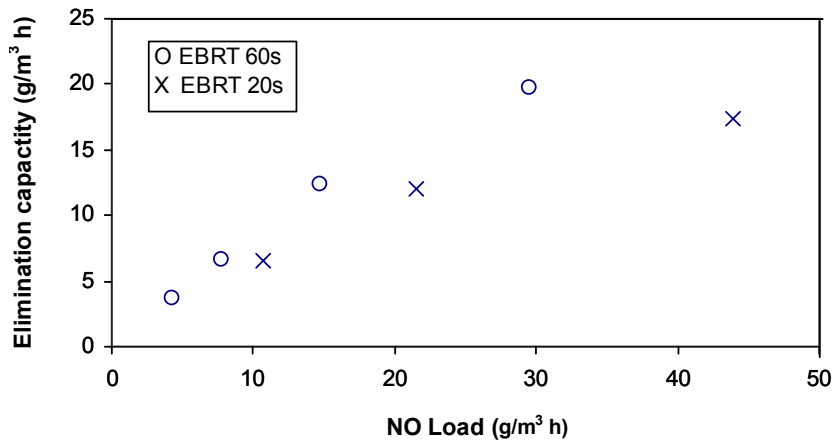
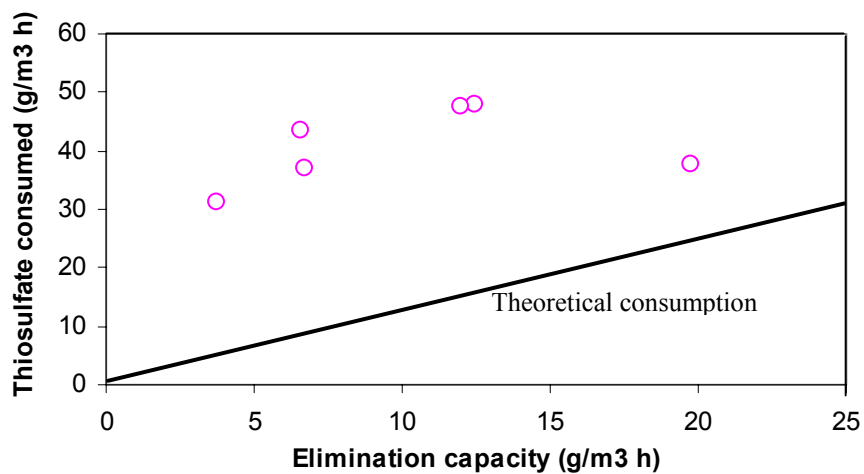


Figure 7: Comparison of the experimental thiosulfate consumption at different elimination capacities. The line represents the theoretical consumption. EBRT = 25 sec.

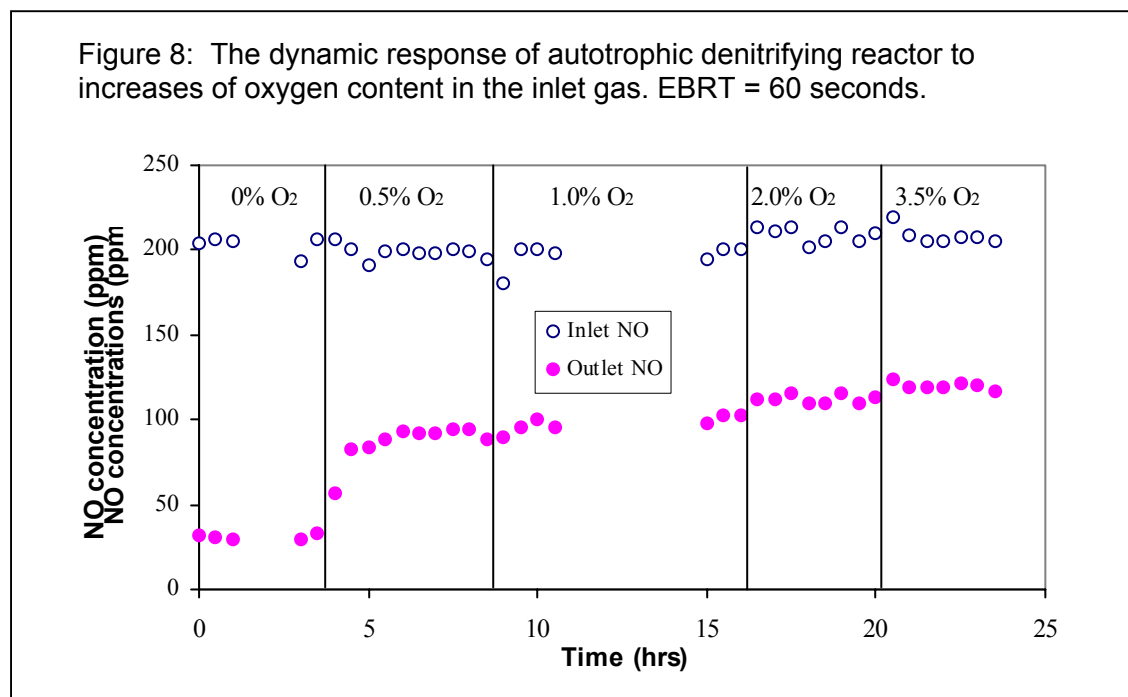


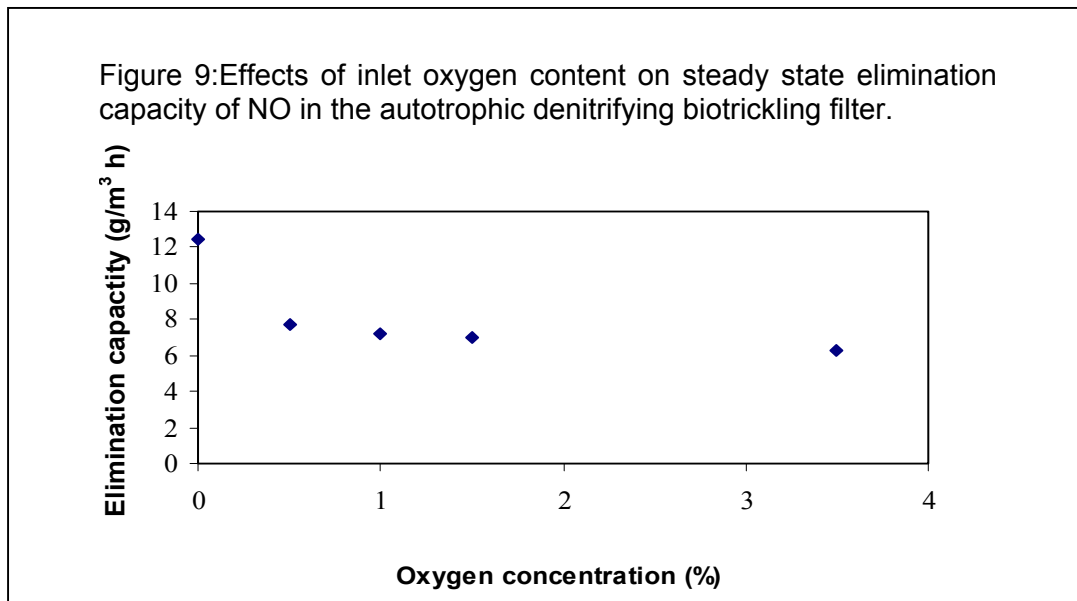
Thiosulfate plays an important role in NO_x removal using the proposed autotrophic system, since it is the only electron donor for biological reduction of NO to nitrogen gas fed to the system. The consumption of thiosulfate in the biotrickling filter reactor is shown in Figure 7 as a function of the elimination capacity of NO. The straight line represents the calculated theoretical consumption. From the figure, it can be seen that the actual consumption of thiosulfate was higher than that calculated theoretically. While the exact fate of thiosulfate and its electrons remains to be elucidated, a possible explanation is that thiosulfate is being oxidized to sulfate or sulfite by microaerophilic microorganisms using traces of dissolved present in the trickling liquid or that thiosulfate is being used for other unidentified microbial assimilatory uses.

Influence of Inlet Gas Oxygen Concentration

The influence of oxygen in the reactor is shown in Figures 8 and 9. NO concentration was maintained at 200 ± 20 ppm during the experiment, while the oxygen content of the simulated combustion gas was varied. The removal of NO decreased when oxygen was introduced in the inlet gas. This effect was most significant between 0 and 0.5% oxygen as the removal decreased from 85% to about 50%. Thereafter, a further seven fold increase of the oxygen content resulted only a modest decrease of NO removal efficiency. It is reasonable to assume that the process underwent its most profound changes –in term of process biology and biokinetics- when the oxygen content was changed from 0% O₂ to 0.5% O₂. Consistent with this assumption is the fact that when oxygen was first introduced into the system, it took up 2-3 days to reach a new steady-state, indicating that a shift in the bacterial population occurred. However, after that, new steady-states were rapidly (< 1 day) reached after each incremental increase of the oxygen content of the treated air (Figure 8)

The effect of oxygen on NO removal may be an indirect indication that NO is removed by denitrification, as it is well accepted that denitrification is favored by anaerobic conditions and inhibited under aerobic conditions. On the other hand, one may wonder why there was only little effect of increasing the oxygen content from 0.5% to 3.5%. A plausible explanation is that denitrification is occurring in anaerobic microniches, which are protected from oxygen by the outer layers of the biofilm as was discussed by Knowles.¹² Further detailed investigations of the biofilms of the biotrickling filter would be necessary to prove that this is actually occurring





CONCLUSIONS

The results presented in this paper show that autotrophic NO_x biotreatment in a biotrickling filter using thiosulfate as electron donor is possible. At this time, the process has not been optimized, and therefore, effective removal of NO still requires relatively long gas contact times. Residual oxygen was found to be an important inhibitor of the proposed process. However, the process was most affected when shifting from essentially zero oxygen to 0.5% oxygen content. Further increases in oxygen had little effect suggesting that the biotrickling filter would be able to cope reasonably well with fluctuating oxygen levels. Further research is being conducted to optimize the process optimization, as well as to address issues related to the recycle and regeneration of the electron donor, the co-treatment of SO₂, and the influence of process conditions such as temperature, biomass density, and pH.

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