Simultaneous removal of NO\textsubscript{X} and SO\textsubscript{2} in exhausted gas through landfill leachate

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Simultaneous removal of NO\textsubscript{X} and SO\textsubscript{2} from exhausted gas were investigated by studying co-culture of sulfate reducing bacteria and anaerobic denitrifying bacteria, separated from landfill leachate. When H\textsubscript{2}S, generated by sulfate reducing bacteria was chosen as the sole electron donor for anaerobic denitrifying bacteria, the co-culture system demonstrated a faster NO removal rate, higher stability and better permanence. When the feed gas flow rates of N\textsubscript{2} and SO\textsubscript{2} were maintained constant at 0.1 m\textsuperscript{3}/h and 16 ml/min respectively, the maximum NO-removal rate could be achieved at over 92% with NO feed gas kept between 2-6 ml/min, while the SO\textsubscript{2} removal rate was always above 95%. Long-term continuous removal of NO exhibited an evident periodicity of five days, however, the fluctuation range of NO-removal was decreasing. Moreover, the decrease of the gas flow rate and the increase in NO inlet concentration could contribute to a higher NO-removal rate.

**Keywords:** Anaerobic denitrifying bacteria, Co-culture, Combined removal of NO\textsubscript{X}/SO\textsubscript{2}, Landfill leachate, Sulfate reducing bacteria

Simultaneous desulfurization and denitrification was achieved with the two-culture-in-series of the sulfate-reducing bacteria (SRB) and nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB) in wastewater or flue gas treatment, and all of them required two separate reactors. Recently, some systems were developed to culture two different bacteria in a single reactor: (i) a bioreactor consisting of a tubular polymeric gel immobilizing *Nitrosomonas europaea* and *Paracoccus denitrificans* populations\textsuperscript{1-3}, (ii) a membrane aerated biofilm reactor combining nitrification and denitrification\textsuperscript{4,5}, (iii) a process combining the anammox reaction\textsuperscript{6,7} with partial ammonia oxidation in biofilms or a controlled oxygen supply\textsuperscript{8-12}, (iv) a single-stage nitrogen-removal process using a composite matrix containing nitrifying and sulfur-denitrifying bacteria\textsuperscript{13}, (v) a NO\textsubscript{X} removal process integrated physicochemical and biological method\textsuperscript{14}. Although the former four bioreactors achieved high nitrogen-removal efficiencies, they were only applicable to wastewater treatment and had sensitive operating conditions\textsuperscript{13}. Due to high operating temperature, expensive complexing agent and low gas treatment capacity, the last one’s wide use was limited. Therefore, there is still a need for a simple, low-cost, and single-stage bioreactor, which is capable of simultaneous remove sulfur and nitrogen compounds from both wastewater and flue gas.

The aim of this work is to investigate the applicability of combined NO\textsubscript{X}/SO\textsubscript{2} removal using the landfill leachate as the inoculum in a traditional biotrickling filter, as the landfill leachate is particularly rich in sulfate reducing bacteria and anaerobic denitrifying bacteria.

**Materials and Methods**
Preparation of SRB, anaerobic denitrifying bacteria and co-culture—Elective culture of sulfate-reducing bacteria (SRB) was prepared by incubating glass-stoppered bottles, completely filled with a SRB selective medium (B in Table 1), and inoculated with the landfill leachate at 30°C for 48 h. Then 2/3 of the liquid was replaced with the fresh SRB medium. The replacement was repeated until the culture turned black with a strong odor of hydrogen sulfide. And then the enrichment of SRB was obtained successfully. The volume ratio of inoculum to medium is 1:10.

By the same method, the enrichment of anaerobic denitrifying bacteria was successfully obtained anaerobically in its selective medium (A in Table 1) when the culture produced gas immediately after the

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addition of fresh medium, accompanied by the disappearance of thiosulfate and nitrate. It was found that the liquid sample from the medium contained a considerable quantity of element sulfur according to Dalsgaard and Bak’s method.

The co-culture was prepared by transferring SRB and anaerobic denitrifying bacteria (volume ratio of 1:1) into the mix medium (C in Table 1).

Combined removal of NO\textsubscript{x}/SO\textsubscript{2} experiments—The co-culture and mix medium with the volume ratio of 1:10 were transferred into the NO\textsubscript{x}/SO\textsubscript{2}-removal biotrickling filter (10 in Fig. 1). Similarly, SRB and anaerobic denitrifying bacteria with their corresponding mediums were transferred into the SO\textsubscript{2}-removal biotrickling filter and NO-removal biotrickling filter, respectively (1 and 9 in Fig. 1). In order to ensure the filters were anoxic, each of the filters was flushed with N\textsubscript{2} until the gas phase had been exchanged 20 times\textsuperscript{15}. Then the pumps were started and made them working continuously under anoxic conditions for 30 days at 100 L/h liquid-flow. Meanwhile, 1/2 of the liquid were replaced with fresh mediums every 4 days until a certain thickness of biofilm was achieved on the packings.

With regard to NO\textsubscript{x}/SO\textsubscript{2}-removal filter, a gas mixture (1% SO\textsubscript{2}, and balance N\textsubscript{2}) was initially introduced at 0.1 m\textsuperscript{3}/h for approx 0.5 h in order to acclimate denitrifying bacteria to utilizing H\textsubscript{2}S as the only electron donor. When the stoichiometric production of H\textsubscript{2}S was observed in the outlet gas, a gas mixture (SO\textsubscript{2}, NO and N\textsubscript{2}) was introduced into the filter. The feed gas flow rates of N\textsubscript{2} and SO\textsubscript{2} were maintained constant at 0.1 m\textsuperscript{3}/h and 16 ml/min, respectively. While the NO feed gas was kept between 2-6 ml/min. The concentration of NO in this gas mixture was increased stepwise until it reached the NO toxic level. While, mixed gas of SO\textsubscript{2} with N\textsubscript{2} and mixed gas of NO with N\textsubscript{2} could be introduced into their respective filters directly. The mediums should be replaced weekly. The filters were run at room temperature (30°C).

Chemical analyses—The pH was measured with a precision pH meter. Nitrate, nitrite, sulfate, sulfite, sulfide and the amount of protein were all determined by Merck NOVA 60 Spectroquant with the corresponding regents separately. Before that, the sample was diluted with deionized water until all the interfering ions were below the minimum limits required for Spectroquant. The concentration of NO, NO\textsubscript{2}, SO\textsubscript{2} and H\textsubscript{2}S in the inlet as well as in the outlet were determined by the KANE940 Multi-Gas Combustion Analysers.

Results and Discussion

Process of combined removal of NO\textsubscript{x}/SO\textsubscript{2}—By controlling the composition of substrates in the mix medium, success was achieved in connecting anaerobic denitrifying bacteria with SRB based on H\textsubscript{2}S — the reductive end-product of SRB, which is

Table 1—Medium composition of anaerobic denitrifying bacteria (A), SRB (B) and co-culture (C)

<table>
<thead>
<tr>
<th>Substrates</th>
<th>A (g/L)</th>
<th>B (g/L)</th>
<th>C (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{4}Cl</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>MgSO\textsubscript{4}</td>
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<td>1.5</td>
</tr>
<tr>
<td>KH\textsubscript{2}PO\textsubscript{4}</td>
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<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>K\textsubscript{2}HPO\textsubscript{4}</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Lactate</td>
<td>0</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}⋅5H\textsubscript{2}O</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
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<td>NaHCO\textsubscript{3}</td>
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<td>2.52</td>
<td>2.52</td>
</tr>
<tr>
<td>KNO\textsubscript{3}</td>
<td>2</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>FeSO\textsubscript{4}⋅7H\textsubscript{2}O</td>
<td>0.05</td>
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</tr>
<tr>
<td>Trace Element *</td>
<td>0.02</td>
<td>0.02</td>
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</tbody>
</table>

* Trace Element: Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Mn\textsuperscript{2+}, Zn\textsuperscript{2+}, Ca\textsuperscript{2+} and ammonium molybdate

Fig. 1—Schematic diagram of experimental set-up. 1-SO\textsubscript{2} removal biotrickling filter; 2-packings; 3-gas distributor; 4-preventing clogging net; 5-recycle liquid reservoir; 6-gas flow indicator; 7-pump; 8-liquid distributor; 9-NO\textsubscript{x} removal biotrickling filter; 10-combined removal NO\textsubscript{x}/SO\textsubscript{2} biotrickling filter; 11-gas demister; 12-exit gas absorber
served as the only electron donor for denitrifying bacteria. Denitrifying bacteria and SRB were immobilized on the surface of the packings in the form of fixed biofilm. In this process SO$_2$ was first reduced to H$_2$S by SRB, and then H$_2$S will support electrons for the reduction of NO to N$_2$ in denitrification by denitrifying bacteria. After long-term acclimation, SRB and anaerobic denitrifying bacteria could gradually adapt themselves to each other’s growing habits and mutual inhibition competitions were largely eliminated.

**Comparisons of no removal between denitrifying bacteria and co-culture**—The comparisons on NO removal behaviors between denitrifying bacteria and co-culture are shown in Fig. 2. The comparison experiments included stability testing, toleration of starvation and recovery rate from the bad environmental conditions. During the first 5.5 h, NO removal ability with denitrifying bacteria followed in the steps of that with co-culture, although NO inlet concentration was doubled suddenly. After the second shift-up of NO feed, denitrifying bacteria was not capable of maintaining the high NO-removal rate, while co-culture was capable of restoring from disturbance and keeping the removal stability. And after long-term starvation period, the co-culture could be achieved the high NO-removal rate within 20 h, while denitrifying bacteria didn’t display any denitrifying activity (seen from the saturation period in Fig. 2).

Compared with denitrifying bacteria, the co-culture system showed the better stability and tolerance facing the poor conditions. Because H$_2$S produced by SRB in the co-culture makes up for the deficiency of electrons in the denitrification by denitrifying bacteria, which makes the co-culture survive in the starvation period. The denitrification product of SO$_4^{2-}$, from the oxidation of H$_2$S, in turn provides enough sulfur-source for SRB growth. In addition, the liberation of alkali during the progress of desulfurization balances the acid formation of denitrification$^{16}$, which stabilizes the pH-value in the co-culture. Additionally the poise of optimal redox potentials of denitrifying bacteria may be prolonged with the aid of SRB$^{17}$. All the influencing factors mentioned above promote the mutual growth between the two species and help the co-culture overcome nutrient shortage.

**Periodicity of no removal**—In combined removal of NO/SO$_2$ experiments, the SO$_2$ removal rate maintained above 95%, while that of NO revealed an obvious periodicity, only NO removal efficiency was focused. During a cycle, everyday N-removal (NO+NO$_2$, NO$_2$ is a result of oxidation of partial NO by trace oxygen existing in N$_2$) rate increased firstly and reduced afterward as the increase of time (Fig. 3A, B, C, D and E). And the first three days of the cycle nitrogen compounds in gas were removed at the relatively high rates, and the average rates of N-removal were 82.8, 88.4 and 72.4%, respectively (Fig. 3 A, B and C). On the fourth day the rate dropped abruptly to below 40% or even approaching zero but the sixth or seventh day the removal rate was again up to more than 85% miraculously (seen in Fig. 4).

In long-term continuous experiments as seen in Fig. 4, the NO removal cycle was shortened gradually from initial 6 to 5 days to 5 to 4 days. It is found that the fluctuation range of NO removal rate was reduced and the minimal value of NO removal rate was rising gradually. Due to the periodicity of NO removal, the H$_2$S concentration in the outlet gas was fluctuated with a narrow range below 400 mg/m$^3$. By contrast, the SO$_2$ removal rate was always kept above 95% throughout the entire process.

NO-removal displayed an alternation of adaptive phase and adjustment phase in the daily NO-removal as well as in the long-term periodic removal. It is a result of the physiological regulation of bacteria as cyclical phases in response to long-term exposure to the toxic NO environment. After long-term acclimatisation, the biofilm was assimilated by the waste gas environment and bacteria’s tolerance of NO
Effect factors on NO-removal—As seen in Fig.5, the NO-removal rate with 0.15 m$^3$/h gasflow rate decreased to one-fourth or even one-sixth of that with the gasflow rate of 0.1 m$^3$/h. However, attempts were made to increase spray density by degrees to improve the NO-removal rate with 0.15 m$^3$/h gasflow, but failed. It is indicated that gas residence time is a more impact factor on the high efficiency of NO removal than spray density.

NO removal efficiency increased with increase in inlet concentration (below 4 g/m$^3$) under the condition of constant SO$_2$ and N$_2$ concentrations in the inlet gas (not shown). Instead of causing bacteriostasis, such high NO concentrations were strongly assimilated by 90%. The reasons for NO toxicity control are that (i) cytochrome c’ (a periplasmic heme-containing protein...
is capable of catalytic conversion of NO generated externally to N₂O rapidly at a certain amount of NO₁₈, and (ii) to protect against toxicity, anaerobic denitrifying bacteria has to make best use of NO as electron acceptor and control its concentration to a relatively low level¹⁹.

Further, nitric oxide, stimulating successive expression of the related denitrification enzymes without lag¹⁹,²¹ and conserving energy in respiratory chain²², will be a good substitute for nitrate or nitrite as the terminal electron acceptor. In addition, with nitrate available, NO utilization was decreased by about 75 to 80%²³,²⁴. It was found in the present study that NO removal rates were still kept high giving oxygen inlet concentration allowance of 1.5% (it would be seen from NO₂ inlet concentration in Fig.3A). This may resolve the problem that the treated wasted gas still contains a certain oxygen level, which may restrain activities of anaerobes.

Conclusions

(1) When H₂S, the end-product of SRB, was the sole electron donor of denitrifying bacteria, competition relationship between the two species was changed to synergistic relationship. It provides the possibility of simultaneous removal of NOx/SO₂.

(2) Compared with denitrifying bacteria, the experimental results showed better NO removal rate, stability, and permanence in the co-culture system.

(3) When the gasflow of N₂ and SO₂ were maintained constant at 0.1 m³/h and 16 ml/min respectively, NO removal exhibited an evident periodicity with 5 days. And the maximum NO-removal rates could be achieved over 92%, while the SO₂ removal rates were always above 95%.

(4) NO removal efficiency increased with increase in the NO concentration (below 4 g/m³) in the inlet gas. Moreover, gasflow was a more impact factor on the high efficiency of NO removal than spray density.

References