# Performance of nitrogen removal and biofilm structure of porous gas permeable membrane reactor

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**Abstract** A porous gas permeable membrane can supply oxygen effectively, utilizing the high ability of oxygen uptake of nitrifying biofilm. If the membrane with the biofilm is applied to wastewater treatment, simultaneous denitrification occurs, but control of the biofilm thickness is necessary to maintain the high efficiency of the treatment.

In this research, small fluidized cylinders were tested as the media for slough off of excess biofilm, and the performance of nitrogen removal was investigated supplied with municipal wastewater. The results showed that the nitrogen removal efficiency was well kept for a long period with the method tested, especially the nitrification rate in the range of 1.1 to 3.1 gN/($m^2$ d), and that the biofilm formed a stable structure of double layers, that is, an inner firm nitrifying biofilm and an outer loose denitrifying biofilm.

**Keywords** Biofilm; denitrification; gas permeable membrane; nitrification; nitrogen removal; oxygen supply

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## Introduction

The porous gas permeable membrane, which is made of a hydrophobic material and forms three-dimensional fine mesh structures, can let gas go through but prevents water permeation. Because of this feature, the membrane can be used both for the separation of pressurized water and non-pressurized air and for the supply of oxygen from the air to the water through the film by diffusion. The method of oxygen supply using the membrane might lead to low energy consumption because it does not require high air pressure.

Several researchers (Cote *et al.*, 1988; Timberlake *et al.*, 1988; Debus *et al.*, 1994; Wilderer, 1995; Ahmed and Semmens, 1996) have reported the efficiencies of oxygen transfer and wastewater treatment with gas permeable membranes, but they mostly used silicone rubber as the membrane and pressurized air or pure oxygen.

Suzuki *et al.* (1993) used the porous gas permeable membrane and non-pressurized air, and reported the effect of biofilm formed on the membrane. When nitrifying biofilm was formed on the membrane, the oxygen supply efficiency was increased, because the high oxygen uptake rate of the nitrifying biofilm reduced the resistance of oxygen transfer in the liquid phase. They also reported that simultaneous nitrification and denitrification was possible, when the membrane with nitrifying biofilm was put into synthetic wastewater and denitrifying biofilm was formed on the nitrifying biofilm. However, control of the thickness of the denitrifying biofilm was necessary to keep the nitrogen removal rate high.

In this research, the application of the gas permeable membrane to municipal wastewater treatment was attempted with the method of slough off of excess biofilm, and the performance of nitrogen removal was investigated together with the structure of the biofilm formed on the membrane.

## Experimental methods

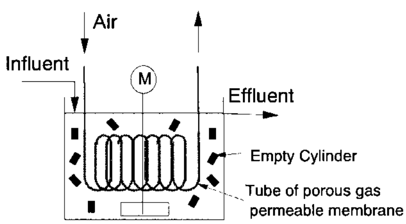
A porous and waterproof tube made of polytetrafluoroethylene (PTFE) was used for the experiment (Table 1). The surface of the tube was roughened with sandpaper to permit

**Table 1** Characteristics of gas permeable membrane

| | |
|---|---|
| Material | polytetrafluoroethylene (PTFE) |
| Inner diameter | 3 mm |
| Membrane thickness | 0.5 mm |
| Porosity | 50% |
| Pore size | 2 $\mu$m |
| Max. waterproof pressure | 90 kPa |

**Table 2** Experimental conditions

| | Run 1 | | | Run 2 | | |
|---|---|---|---|---|---|---|
| | a | b | c | a | b | c |
| Term (d) | 28 (0–28) | 94 (29–122) | 47 (123–169) | 43 (170–212) | 42 (213–254) | 14 (255–268) |
| Influent | Raw municipal wastewater | | | Raw municipal wastewater | | |
| HRT (h) | | | | | | |
| Prior cell (Condition) | 3(Anaerobic) | 3 (Aerobic) | 1 (Aerobic) | – | – | |
| Tube reactor | 6 | 6 | 10 | 10 | 10 | 10 |
| Nitrification cell | 3 | 3 | 2 | 2 | – | – |
| Empty cylinders in tube reactor | | | | | | |
| Existence | Always | Always | Always | Always | 2 d/week | 1 d/week |
| Volume fraction | 2 % | 2 % | 2 % | 5 % | 2 % | 2 % |
| Air supply | Always | Always | Always | Always | Always | Stopped 2 h/week |
| Flow rate (mL/min) | 600 | 600 | 600 | 600 | 600 | 600 |

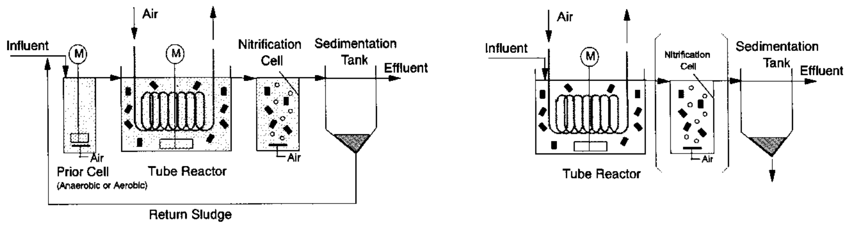



| | |
|---|---|
| Water volume | 100 L |
| Tube length | 156 m |
| Tube volume fraction | 1.96 % |
| Specific surface area | 19.6m2/m3 |

**Figure 1** Tube reactor

bacteria to attach on the surface firmly. The Reactor with the tube and its specifications are shown in Figure1. The tube wound around a supporter was set in a reactor equipped with an agitator, and air was supplied into the tube. The specific surface area of the tube in the reactor was 19.6 $m^2/m^3$.

Experimental conditions are listed in Table 2. Before the tube was applied to wastewater treatment, the tube was put in the aeration tank of a nitrification process for five days for the inoculation of nitrifying bacteria. In Run 1, the process was arranged so that the organic load to the tube was lowered by activated sludge in the prior cell or in the tube reactor (Figure 2(a)). A nitrification cell was added after the tube reactor for complete nitrification. In Run 2, the condition of high organic load was investigated with the direct supply of raw municipal wastewater to the tube reactor (Figure 2(b)). In both runs, small empty polypropylene cylinders were put and fluidized in the tube reactor to slough off excess denitrifying biofilm. In the nitrification cell, the same cylinders were added as the support




(a) Run 1 (b) Run 2

**Figure 2** Experimental apparatus

media for nitrifying bacteria. Air flow rate was set around 600 mL/min, which resulted in the air retention time in the tube of 1.8 min.

The inflow rate, water quality, air flow rate and $O_2$ and $CO_2$ concentration of discharged air were measured periodically during the experiment. In addition, batch tests were conducted before and after the tube was washed with water spray to measure the nitrification and denitrification rates for evaluation of the mass of nitrifying and denitrifying bacteria.

## Results

### Performance of nitrogen removal

The change of nitrification capacity of the tube reactor in Run 1 is shown in Figure 3 together with that of the prior cell. During Run 1a where the prior cell was anaerobic (0–28d), no nitrification occurred in the tube reactor, but after the prior cell was changed to aerobic in Run 1b (29d–), nitrification in the tube reactor could be observed. Reduced soluble organic load because of the aerobic treatment in the prior cell let nitrifying bacteria grow on the tube surface in the reactor. Even after the activated sludge lost nitrification ability because of the shorter aerobic time in Run 1c (123d–), the tube reactor showed a nitrification capacity. All through the Run, no DO concentration was observed in the tube reactor and the oxygen supplied from inside the tube was used up by the biofilm formed on the tube surface.

The average nitrogen concentration profiles in the process for Run 1b and Run 1c are shown in Figure 4 and Figure 5, respectively. In Run 1b, nitrate remained in the tube reactor because of preceded nitrification in the prior cell and insufficient HRT for denitrification in the tube reactor. In Run 1c, however, the shorter aeration time in the prior cell and the longer HRT in the tube reactor enabled good nitrogen removal in the tube reactor. The highest nitrification rate in these cases was 3.1 gN/($m^2$ d).

The nitrogen removal in Run 2, where the tube reactor received raw wastewater directly without the existence of activated sludge, is shown in Figure 6. In Run 2a (170–212d)

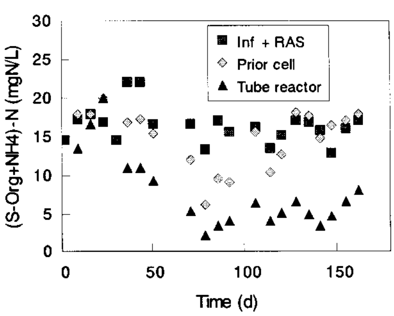



**Figure 3** Change of (S–Org+$NH_4$)–N concentration in Run 1

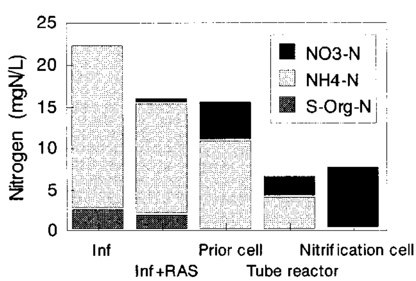



**Figure 4** Change of nitrogen concentration along flow direction in Run 1b (after 69d)

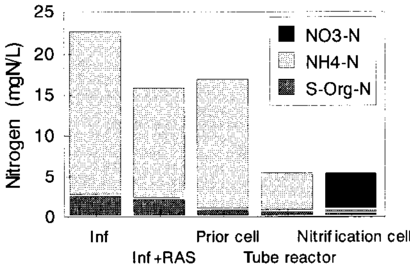



**Figure 5** Change of nitrogen concentration along flow direction in Run 1c

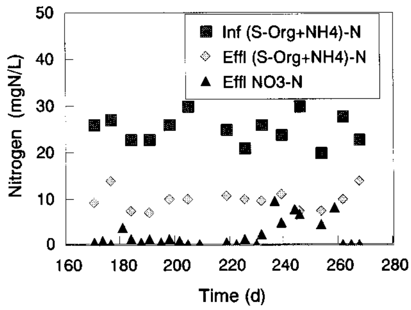



**Figure 6** Change of nitrogen concentration in Run 2

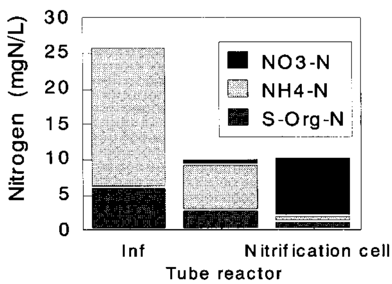



**Figure 7** Change of nitrogen concentration along flow direction in Run 2a

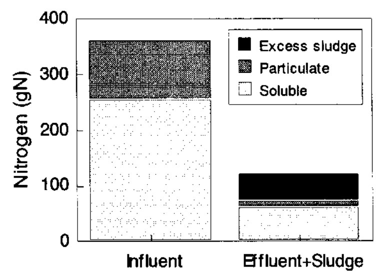



**Figure 8** Nitrogen balance in Run 1c

simultaneous nitrification and denitrification was achieved (Figure 7), but the slough off of excess biofilm seemed too intense and the frequency of placement of cylinders was reduced to two days a week (213d–). Then, nitrate began to remain in the reactor, because blood worms accumulated on the tube, grazing the denitrifying biofilm. Air was stopped two hours a week after 255 days (Run 2c) to kill the blood worms, and the denitrification ability was recovered. Through Run 2 the nitrification rate was kept more than 1.1 gN/($m^2$ d).

#### Nitrogen balance

In Run 1c, 80% of influent nitrogen was removed from the water, 15% of which was transformed into sludge and the remaining 65% was converted to nitrogen gas (Figure 8). In Run 2a, nitrogen removal from the water was 68%, slightly lower than that in Run 1c, among which 13% went into sludge and 55% disappeared into the air.

In both Runs, the thickness of biofilms did not increase significantly and the contribution of the biofilm growth to the nitrogen balance was negligible.

#### Biofilm structure

Maximum nitrification and denitrification rates of the biofilm on the tube were measured by batch tests before and after the biofilm was sloughed off with water spray, and the structure of the biofilm was investigated. Equal amounts of raw wastewater and tap water were put into the reactor and the change of water quality was measured. The nitrification rate was calculated from the $NH_4$–N decrease rate and the denitrification rate was obtained by subtracting the $NO_3$–N increase rate from the nitrification rate. These rates were expressed per surface area of the tube, and the rates were interpreted to correspond to the mass of nitrifying bacteria or denitrifying bacteria.

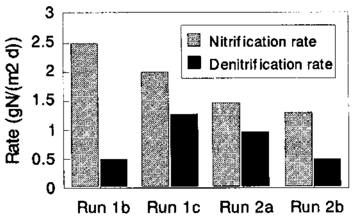



**Figure 9** Nitrification and denitrification rate of the tube before water spray

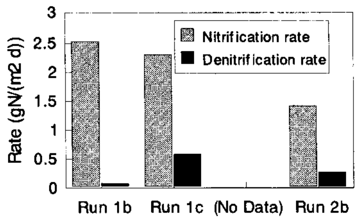



**Figure 10** Nitrification and denitrification rate of the tube after water spray

Figure 9 and Figure 10 show the nitrification and denitrification rates before and after the biofilm was sloughed off with water spray, respectively. Relatively high denitrification rates were observed before water spray for Run 1c and Run 2a, which indicates a high amount of denitrifying bacteria accumulated on the tube surface in these cases. The low accumulation of denitrifying bacteria in Run 1b can be attributed to the low soluble organic load, as shown in Figure 12, and the low denitrification rate in Run 2b might be caused by blood worm grazing. After water spray, the denitrification rates of the tube decreased to a low level, which resulted from slough off of the denitrifying bacteria. On the other hand, the nitrification rate remained high; additionally, the nitrification rates of the sloughed biofilms were basically small (Figure 11). From these results, it can be considered that denitrifying bacteria formed the outer biofilm which was easily sloughed off, and nitrifying bacteria adhered to the tube firmly forming an inner biofilm.

The nitrification capacity of the biofilm was kept over 260 days, even though the biofilm was exposed to a relatively high organic load, and this indicates that once the nitrifying biofilm is formed on the porous gas permeable membrane, it is stable as long as the denitrifying biofilm is properly controlled.

In Run 2a, the SRT of the nitrifying bacteria on the tube was estimated to be 16 days from the data of the maximum nitrification rate of the tube and nitrification capacity of the effluent which corresponded to the mass of sloughed off nitrifying bacteria. Also, in Run 2b, from the data of nitrification rates of the tube and the sloughed off biofilm, the SRT of the nitrifying bacteria was calculated to be 23 days, while the SRT of the denitrifying biofilm was estimated to be six days from the data of attached biomass and sloughed biomass. Intermittent sloughing was a better method of keeping nitrifying bacteria on the tube for a longer period.

#### Treatment mechanism

The nitrification rates calculated from the $NH_4$–N concentration were compared with oxygen consumption rates obtained from gas data (Figure 13). To make the comparison easier, the nitrification rates were expressed as oxygen equivalent by multiplying the rates by 4.57 assuming complete nitrification. Those two rates showed good agreement in Run 1, indicating oxygen in the gas phase was consumed in accordance with nitrification. However, in Run 2 the nitrification rates were a little lower than the oxygen consumption rates, and the possible reason for this is that more soluble and particulate organic nitrogen was hydrolyzed to $NH_4$–N in the tube reactor than in Run 1 which had activated sludge and a prior cell in the process.

The activity of nitrifying bacteria is affected by water temperature; therefore, the effect of water temperature on oxygen consumption rates was examined in Figure 14. A tendency of a higher oxygen consumption rate with higher water temperature was observed in each case, but more than that the effect of soluble organic load was evident. The rates in Run 1b

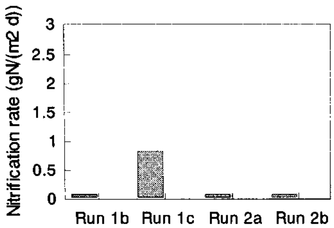



**Figure 11** Nitrification rate of the sloughed biofilm by water spray

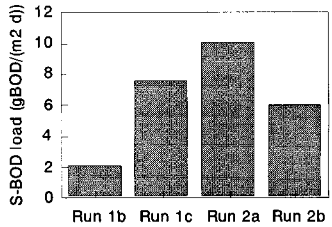



**Figure 12** Soluble organic load to tube surface

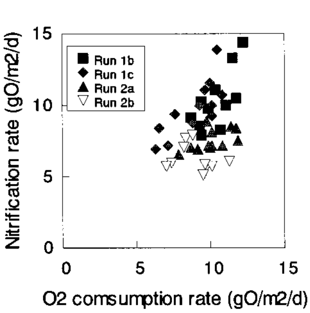



**Figure 13** Relationship between $O_2$ consumption rate and nitrificatin rate

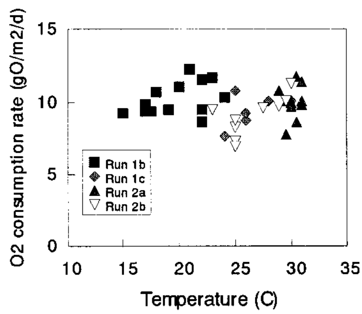



**Figure 14** $O_2$ consumption rate of tube reactor in each Run

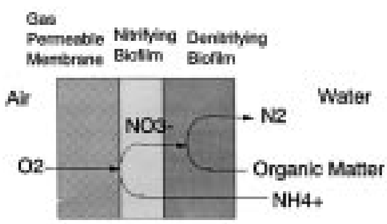



**Figure 15** Biofilm structure and treatment mechanism

where soluble organic load was low were higher than those of other cases. The reason for this is not clear, but there is a possibility that the higher organic load had some effect on the structure of nitrifying biofilm.

The relationship between the denitrified $NO_3$–N and the utilized organic matter for the denitrification could not be made clear, because COD was not measured as an index of organic matter concentration. However, if soluble BOD is used as the index, approximately 2 g of soluble BOD was removed for the denitrification of 1 g of $NO_3$–N. After oxygen was taken up and utilized by the nitrifying biofilm, CO2 was discharged from the water to the gas phase by the amount of two thirds of the oxygen consumed.

From the results above, and taking into account the biofilm structure, the treatment mechanism of the tube reactor is thought to be as follows (Figure 15); $NH_4$–N in the wastewater diffuses to the inner nitrifying biofilm and is nitrified with the oxygen taken up from the gas phase. The produced $NO_3$–N, then, diffuses to the outer denitrifying biofilm and is denitrified with organic matter in the wastewater.

## Conclusion

A porous gas permeable membrane was applied to municipal wastewater treatment, and simultaneous nitrification and denitrification was possible with biofilms forming on the membrane.

The biofilms formed a stable structure of double layers, that is, an inner firm nitrifying biofilm and an outer loose denitrifying biofilm. With a method of controlling the denitrifying biofilm thickness, the nitrification ability of the biofilm was well kept for a long time, even though the biofilm was exposed to a relatively high organic load.

Oxygen supplied through the membrane was utilized for nitrification by the inner nitrifying biofilm, and the nitrate produced was denitrified by the outer denitrifying biofilm utilizing the organic matter in the wastewater.



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