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Nitrification using polyvinyl alcohol-immobilized nitrifying biofilm on an O_2-enriching membrane

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Abstract

A combination of cell immobilization and membrane aeration approaches was used in a biological reactor to treat NH_4^+ in wastewater. Nitrifying microorganisms, immobilized by polyvinyl-alcohol (PVA) and attached to the surface of a silicone membrane tube, were used to develop a novel reactor for nitrification. The immobilized biofilm had a rubber-like elasticity and resisted shear stress over 5 months of operation. The reactor removed 95% of ammonium, added at 1.97 g N m^{-2} d^{-1}, with O_{-2} enriching the membrane.

Introduction

NH_4^+ removed from wastewater by membrane aeration bioreactors has become a common technology. For example, Brindle *et al.* (1998) designed a reactor in which nitrifying bacteria grew on a supporting membrane and where O_2 was supplied from the bottom of the biofilm and the O_2 utilization efficiency was therefore much higher than that obtained by traditional aeration methods. Among the materials used to construct the membrane, silicone membranes are non-porous but with high gas permeability (Côté *et al.* 1988) and can be operated at a high gas pressure thus contributing to high transfer efficiency (Ahmed & Semmens 1992). Moreover, the O_2 transfer rate was higher when the permeable membrane was operated with a biofilm, for example with nitrifying bacteria on the outside (Rothemund *et al.* 1994). Cell immobilization techniques have recently been extended to biological wastewater treatment systems. Chen & Lin (1994) reported many materials such as polyacrylamide, sodium alginate, agar and polyvinyl alcohol have been extensively applied in cell immobilization.

In the beginning of this study, nitrifying bacteria were directly cultivated on a gas-permeable membrane. However, the biofilm was unexpectedly sloughed off. Polyvinyl alcohol (PVA) was then introduced to entrap nitrifying microorganisms on the membrane and thus prevented such a loss of the biofilm. Moreover, immobilizing microorganisms yields a high cell density medium and can be used easily to separate solids from liquids in a settling tank. Immobilizing cells in PVA with the presence of starch or calcium alginate were found to improve gas permeability by modifying the structure, and thus favor the entrapment of microorganisms in matrix of the PVA (Chen *et al.* 1996).

In this study, PVA-immobilized nitrifying biofilm attached to the surface of a silicone membrane tube was used as the basis of a bioreactor for nitrification of synthetic wastewater. A silicone membrane was used as both an O_2 diffuser and a nitrifying bacteria carrier, and PVA performed as an immobilizing agent to strengthen the nitrifying biofilm on the silicone membrane. The effects of the partial pressure of O_2 and NH_4^+ loading on PVA-immobilized nitrifying biofilm reactor were considered. The results of

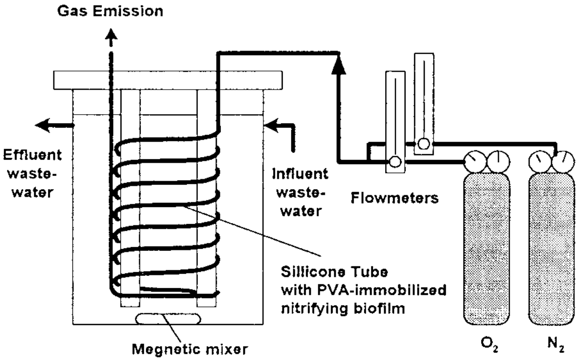

Fig. 1. Schematic diagram of experimental device of PVA-immobilized nitrifying biofilm reactor.

a model simulation of the reactor are also presented here.

Materials and methods

Synthetic wastewater

Synthetic wastewater that contained $(NH_4)_2SO_4$ (118–707 mg l^{-1}) and other nutritents including KH_2PO_4 (8.5 mg l^{-1}), K_2HPO_4 (21.8 mg l^{-1}), $Na_2HPO_4 \cdot 7H_2O$ (33.4 mg l^{-1}), $CaCl_2 \cdot 2H_2O$ (27.5 mg l^{-1}), $MgSO_4 \cdot 7H_2O$ (22.5 mg l^{-1}), $FeCl_3 \cdot 7H_2O$ (0.25 mg l^{-1}), and $NaHCO_3$ (500 mg l^{-1}) was used to culture nitrifying microorganisms and the biofilm.

Immobilization nitrifying sludge by polyvinyl alcohol

Nitrifying sludge from a wastewater treatment plant was initially acclimated by synthetic wastewater in a 10-l laboratory-scale aeration tank at 30 °C, with a pH between 6.5 to 8 for 4 weeks. To immobilize microorganisms, PVA (16 g), alginic acid sodium salt (1.2 g) and water (100 ml) were mixed by stirring and heating. Then the mixture was cooled to room temperature, and concentrated nitrifying sludge (100 ml) from the culturing tank was added thereto the mixture with adequate mixing (Chang & Tseng 1998). A 6-m-long silicone membrane tube (outer diam. = 2.5 mm, inner diam. = 1.5 mm) was coated with the final mixture and then soaked in the solidifying agent (50% w/v $NaNO_3$ and 2% w/v $CaCl_2$) for 1 h. When the biofilm solidified around the silicone membrane tube, it was extracted and rinsed with tap water.

Setup of PVA-immobilized biofilm reactor

Figure 1 shows the laboratory-scale bioreactor for investigating of nitrification in a continuous stirred tank reactor (CSTR). The silicone membrane tube (6 m length) is wrapped around an acrylic resin base and placed in a 3-l tank. A mixture of O_2 and N_2 filled the lumen of the silicone membrane tube; the end of the tube was kept open. The reactor (except the device for supplying gas) was placed in a water bath to maintain the temperature. The ratio of the biofilm volume to the reactor volume was approx. 0.017.

Results and discussion

Test of gas permeability

The device illustrated in Figure 1 but without a PVA coating and the presence of bacteria was used to determine the efficiency of gas permeability of silicone membrane tube. The dissolved oxygen (DO) of the bulk solution reached 25 mg l^{-1} in 20 min when supplied with O_2, but reached only 7.5 mg l^{-1} in the same time using air. The O_2 transfer rate (OTR) by air (12.1 g O_2 m^{-2} d^{-1}) was 25% of that of O_2 (48.1 g O_2 m^{-2} d^{-1}), which is close to that of the amount of O_2 in air. This finding can be interpreted as the concentration gradient effect of O_2 diffusion.

O_2 permeability was again tasted for the membrane coated with PVA (no microorganisms). O_2 used the same flow rate as in the previous test. With PVA outside the membrane, the O_2 flux decreased by 75%, and the OTR reached 11.7 g O_2 m^{-2} d^{-1} in 20 min. According to Suzuki *et al.* (1993), the OTR of the membrane with a biofilm should exceed that without a biofilm. Thus, immobilized nitrifying bacteria in the PVA can be inferred to have utilized O_2 at a rate between 11.7 and 48.1 g O_2 m^{-2} d^{-1} when O_2 was applied to the reactor.

Effect of partial pressure of oxygen (Po_2)

According to Fick's law of diffusion, a higher O_2 concentration gradient associated with a higher OTR. During this experimental run, O_2 and N_2 were blended to different O_2 partial pressures, and supplied to the lumen of the silicone membrane tube. Figure 2a shows the results. Higher nitrification rate and efficiency were achieved with a higher O_2 partial pressure. As shown in Figure 2c, a higher O_2 partial pressure also

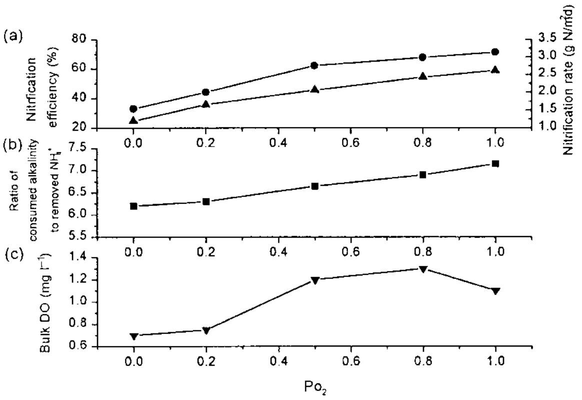

Fig. 2. Effect of O_2 partial pressure (Po_2) on nitrification by the biofilm. (a) •, Nitrification efficiency (NH_4^+ removed NH_4^+ inflow conc.), ▲, nitrification rate; (b) ■, ratio of consumed alkalinity to removed ammonium (w/w); (c) ▼, bulk DO (operation status: NH_4^+ load = 3.83 g N m^{-2} d^{-1}, pH = 6.9–7.7, temp. = 30 °C, HRT = 8 h).

caused the DO value to increase in the bulk solution, however, the maximum DO value was below 1.3 mg l^{-1}. Such a low DO value in an aerobic nitrification reactor is surprising. Dissolved O_2 levels of approx. 2–3 mg l^{-1} are typically recommended for nitrification (Benfield & Randall 1980). However, the bulk DO in a permeable membrane reactor could be very low, even close to anoxic, since O_2 is consumed by microorganisms attached to the membrane before reaching the outside layer (Timberlake *et al.* 1988). Although the previous test of O_2 permeability of the tube yield a high DO value, most O_2 that penetrated the membrane was consumed by the biofilm and only a little was released to the bulk phase. Inside the biofilm, NH_4^+ diffused from the bulk solution toward the membrane; O_2, however, diffused in the opposite direction. The opposing substrate (NH_4^+ and O_2) diffusion directions yield a larger active volume in the biofilm than that in a conventional biofilm reactor. Moreover, effluent-treated water with low DO can avoid large impact on denitrification in a two-stage system (Chang & Tseng 1999). This shows the potential to develop a simultaneous nitrification and denitrification reactor.

Figure 3 shows model simulation results of the effects of partial pressure of O_2 applied to the reactor. In the simulation, Po_2 was given from 0.2 (using air) to 1 (using O_2). From Figure 3a, a higher Po_2 corresponded to less effluent NH_4^+, and in Figure 3b, higher Po_2 increased the concentration of effluent nitrate. The simulation results reasonably matched the experimental data.

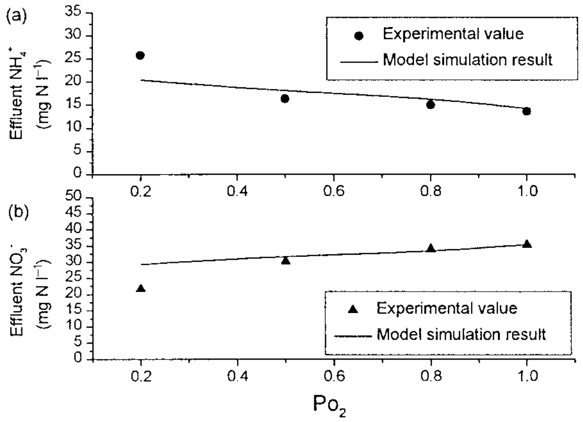

Fig. 3. Model simulation results at various oxygen partial pressure (Po_2). (a) Effluent NH_4^+ concentration; (b) effluent NO_3^- concentration (simulation assumptions: inflow NH_4^+ = 50 mg N l^{-1}, Po_2 = 0.2–1, HRT = 8 h).

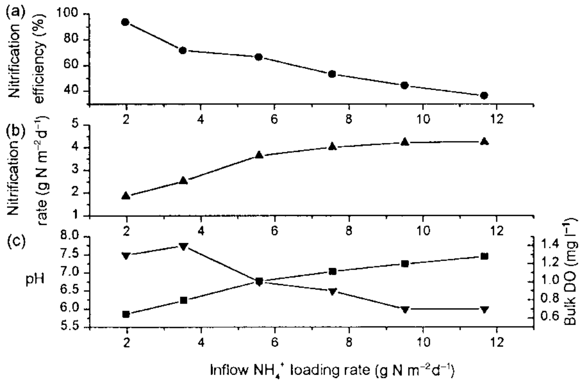

Fig. 4. Effect of NH_4^+ loading on nitrification by the biofilm. (a) •, Nitrification efficiency (NH_4^+removed/NH_4^+ influent conc.); (b) ▲, nitrification rate (c) ■; pH, and ▼, bulk DO (operation status: Po_2 = 1 (using O_2), pH = 5.9~7.5, temp. = 30 °C, HRT = 8 h).

Alkalinity reduced by nitrification

For every gram of ammonium nitrogen removed during nitrification 7.14 g of alkalinity (as $CaCO_3$) is theoretically consumed. However, NH_4^+ can also be removed from wastewater by microbial assimilation, which process consumes less alkalinity serves as carbon source for the autotrophs (Benfield & Randall 1980). From Figure 2b, the ratio of consumed alkalinity to removed ammonium nitrogen (w/w) ranged from 6.2 to 7.15 as Po_2 increased from zero to one. This result shows that most NH_4^+ removed via nitrification if sufficient O_2 is supplied. Otherwise, some NH_4^+ removal may be replaced by microbial assimilation, causing the ratio to drop.

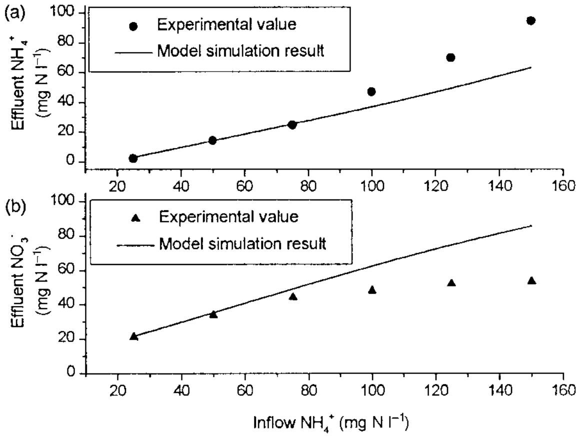

Fig. 5. Model simulation results at various inflow NH_4^+ concentration. (a) Effluent NH_4^+ concentration; (b) effluent NO_3^- concentration (simulation assumptions: inflow NH_4^+ = 25–150 mg N l^{-1}, P_{O_2}=1 (using O_2), HRT = 8 h).

Effect of ammonium loading

Different NH_4^+ loadings were sequentially applied to determine the nitrification capacity of the PVA-immobilized nitrifying biofilm. Adequate O_2 and alkalinity were supplied throughout this experimental run to avoid their becoming limiting factors. Figures 4a and 4b show nitrification efficiency to decrease with increased NH_4^+ loading, whereas the nitrification rate increased with increased loading. Nitrification efficiency reached 95% at a loading rate of 1.97 g N m^{-2} d^{-1}. However, the biofilm reached its maximum nitrification rate, as shown in Figure 4b, around a loading rate of 8 g N m^{-2} d^{-1}. The highest nitrification rate was about 4.2 g N m^{-2} d^{-1}, representing the nitrification capacity of the biofilm. Nitrification rate increased with NH_4^+ loading, and the pH value was expected to drop accordingly. However, Figure 4c shows that the pH value increased from 5.8 to 7.5, caused by the presence of much residual NH_4^+ in bulk solution. Lower DO was detected in bulk solution as NH_4^+ loading increased, which result can be explained by the consumption of more DO due to higher nitrification rate.

Figure 5 presents the model simulation results for various NH_4^+ loadings. The simulation included concentration of influent NH_4^+ from 25 to 150 mg N l^{-1}. The results did not match experimental data when concentration of influent NH_4^+ exceeded 75 mg N l^{-1}. Liu & Capdeville (1994) reported that increasing concentration of residual NH_4^+ increased the amount of free ammonia in bulk solution, inhibiting nitrification. However, the simulation here did not consider this phenomenon, causing the inaccurate prediction at higher influent NH_4^+ concentration.

Conclusion

PVA-immobilized nitrifier gel was introduced to form a layer of artificial biofilm on an O_2-enriching silicone membrane to support efficient biological nitrification of wastewater. Experiments and model simulation yield the following conclusions.

(1) Following 20 weeks of experimental runs, the biofilm still strongly adhered to the silicon membrane tube. PVA provided elasticity to strengthen the biofilm against shear stress and enhance the durability of the biofilm over a long period of operation.

(2) The effluent-treated water exhibited effective O_2 consumption and a high nitrification rate. The DO value in bulk solution was below 1.3 mg l^{-1}, which can avoid large DO impact on denitrification. This shows the potential to develop a simultaneous nitrification and denitrification reactor.

(3) NH_4^+ removal efficiency reached 95% at a loading rate of 1.97 g N m^{-2} d^{-1} when O_2 was supplied to the silicone membrane tube. The nitrification rate was comparable to that of conventional nitrifying biofilms.

(4) A model was successfully developed to simulate nitrification of the PVA-immobilized nitrifying biofilm reactor under various experimental conditions. The performance of the reactor with an influent nitrogen concentration under 75 mg N l^{-1} is predictable.

Acknowledgement

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