

Evaluation of Increased Denitrification in an Anoxic Activated Sludge Using Zeolite

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Abstract—Zeolite added activated sludge unit (ZU) under anoxic conditions improved nitrate removal efficiency by 48% (i.e., equivalent to approximately 10 mg/l) greater than that of a conventional activated sludge unit (CU) regardless of varying C/N ratio ranging from 0 to 4.8. For a C/N ratio of 4, no significant differences of denitrification rate were found between two units showing a range of 6.7 to 6.9 mg NO₃⁻-N/g VSS (volatile suspended solids) hr. However, a C/N ratio decrease to 1.6 was ascribed to considerable differences in denitrification rate showing 4.15 mg NO₃⁻-N/g VSS·hr for the ZU, which was 39% greater than that of the CU presenting at 2.98 mg NO₃⁻-N/g VSS·hr. It was decided that the presence of greater concentration of MLVSS (mixed liquor suspended solids) in the ZU can be efficiently used for enhanced denitrification as a potential carbon source due to autolysis, although a lower concentration of COD (i.e., less than 1.6 of C/N ratio) is introduced.

Key words: Acetylene Inhibition, Activated Sludge, Denitrification, Zeolite

INTRODUCTION

Microbial denitrification, denitrification rate and rate coefficient are generally employed to estimate denitrification capacity [Hallin and Pell, 1994; Çeçen and Gönenç, 1994]. Zeolite is well known as a biofilm carrier due to its high cationic exchange capacity on NH₄⁺ in contrast to other media such as talc, activated carbon, Al₂(SO₄)₃, FeCl₃ and SiO₂ [Jeong et al., 2001; Kim et al., 2002]. It was revealed that the magnitude of nitrification could be improved as high as 30% compared to that of a conventional activated sludge [Olah et al., 1989; Piirtola et al., 1998]. Addition of zeolite to the activated sludge can reduce sludge generation as low as 1/4 to 1/7 because sludge density and settling property have been improved [Lee et al., 2001]. However, the effect of zeolite on denitrification capacity has not yet been reported. The aim of this research was thus to study the effect of zeolite addition in an activated sludge on its enhanced denitrification capacity.

MATERIALS AND METHODS

1. Description of Denitrification Reactor and Experimental Condition

To demonstrate the effect of zeolite on its denitrification capacity, two sets of experiments were performed. One was performed in a powdered zeolite activated sludge unit (ZU), and the other in a conventional activated sludge unit (CU). Reactors to be used in the test were composed of an anoxic basin (3 l) and a clarifier (2 l). The schematic diagram of the system is shown in Fig. 1.

Synthetic wastewater was prepared, of which chemical components are illustrated in Table 1. The experiments were conducted at two different concentrations of substrates in terms of peptone, glu-

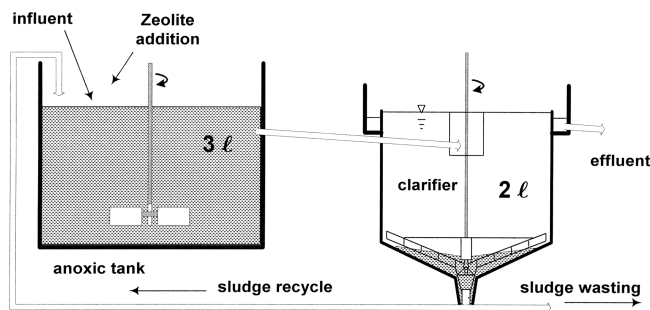


Fig. 1. Schematic diagram of denitrification system.

tamate, and ammonium acetate being differentiated and others the same.

Powdered zeolite was daily introduced at 400 mg/l into the anoxic basin. Zeolite addition was ended up when its concentration in the reactor had reached 4,000 mg/l. Its cationic exchange capacity was 1.28 meq/g and its size ranged from 10 to 100 μm of which effective diameter was 19.75 μm. The experiments were initially performed at 240 mg COD/l and 50 mg NO₃⁻-N/l for 3 hr of hydraulic retention time (HRT). Solids retention time (SRT) was controlled at 10 days as the nominal amount of sludge was daily withdrawn. To investigate the effect of denitrification capacity on varying ratio of COD/NO₃⁻-N, COD loading was solely decreased from 240 to 80 mg COD/l for a duration of 15 days in terms of 75 to 90 days after the test being initiated.

2. Batch Test for Denitrification Rate and Analytical Methods

Denitrification rate was observed in the same manner as given by Hallin and Pell [1994] using the batch test employing an acetylene inhibition technique. The test was simultaneously conducted for both units (i.e., ZU and CU). At first, 80 ml of sludge taken from each unit was transferred to 165 ml of a glass flask (Wheaton), which

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was then sealed with a gas-tight screw cap. The headspace in the gas flask was anaerobically purged with N_2 gas (99.9%, Myungsung) at three consecutive times followed by purging with acetylene (99.99%, Myungsung) at 10 kPa and then sealed with a PTFE lined septum. 5 ml of 75 mg/l of ammonium acetate was added into the flask through the septum. In the mean time, COD was varied from 0 to 200 mg/l at 50 mg NO_3^- -N/l. Finally, they were incubated at 20 °C in a water bath (UA-100G, Eyela), which was shaken at 200 rpm for 12 hours. 1 ml of gas sample in the headspace was withdrawn with a gas-tight syringe (5 ml, Hewlett-Packard) at 3, 6 and 12 hours time interval after the test was initiated. Nitrous oxide concentration was consequently quantified by a gas chromatograph equipped with a thermal conductivity detector (TCD, Varian Co.). Gas chromatography column was CTR I packed in $10' \times 1/8''$ stainless steel (Alltech). Microbial concentration in the reactor was monitored by observing mixed liquor volatile suspended solids (MLVSS). Concentrations of other water quality parameters (i.e., TKN, NH_4^+ -N, NO_3^- -N, MLSS, MLVSS and COD) were obtained by Standard Methods (APHA, AWWA and WEF 1998).

RESULTS AND DISCUSSION

1. The Evaluation of Denitrification Rate through the Batch Test of Acetylene Inhibition Technique

Denitrification rate was not significantly different from the two units (i.e., ZU and CU) at more than 100 mg COD/l (i.e., 2 COD/ NO_3^- -N) as shown in Fig. 2. However, for less than 80 mg COD/l, the denitrification rate observed from the ZU was greater than that of the CU. Namely, the ZU revealed 1.55 and 1.96 mg N_2O -N/g VSS·hr for the ratio of 0 and 1 of COD/ NO_3^- -N, whereas the CU exposed the lower denitrification rate as 1.13 and 1.75 mg N_2O -N/g VSS·hr, respectively.

2. The Comparison of Denitrification Kinetics between Both Units

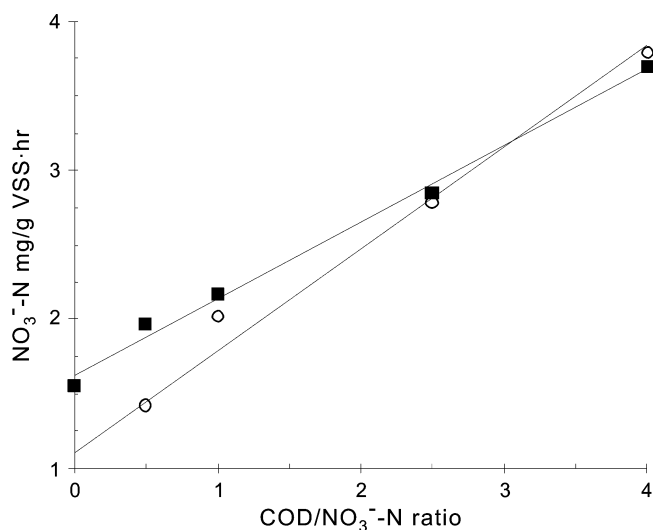


Fig. 2. Denitrification rate according to varying concentrations of substrate through acetylene inhibition technique. It was computed from gas production of N_2O and microbial concentration after 6 hours of incubation in a batch test. ■ ZU; ○ CU.

Taking biofilm kinetics into account, the denitrification rate can be represented by the following nth order reaction kinetics depending on the concentration of microbes and limiting reagents such as substrate and nitrate [Harremoës et al., 1975; Henze et al., 1995].

$$\frac{dC}{dt} = -kC^n \quad (1)$$

where C represents the nitrate concentration, n the order of reaction, k the reaction rate coefficient and t the reaction time. For the second order reaction, Eq. (1) becomes

$$\frac{1}{C} = \frac{1}{C_i} + kt \quad (2)$$

According to the Eq. (2), the slope of k can be calculated from the plot of $1/C$ against t.

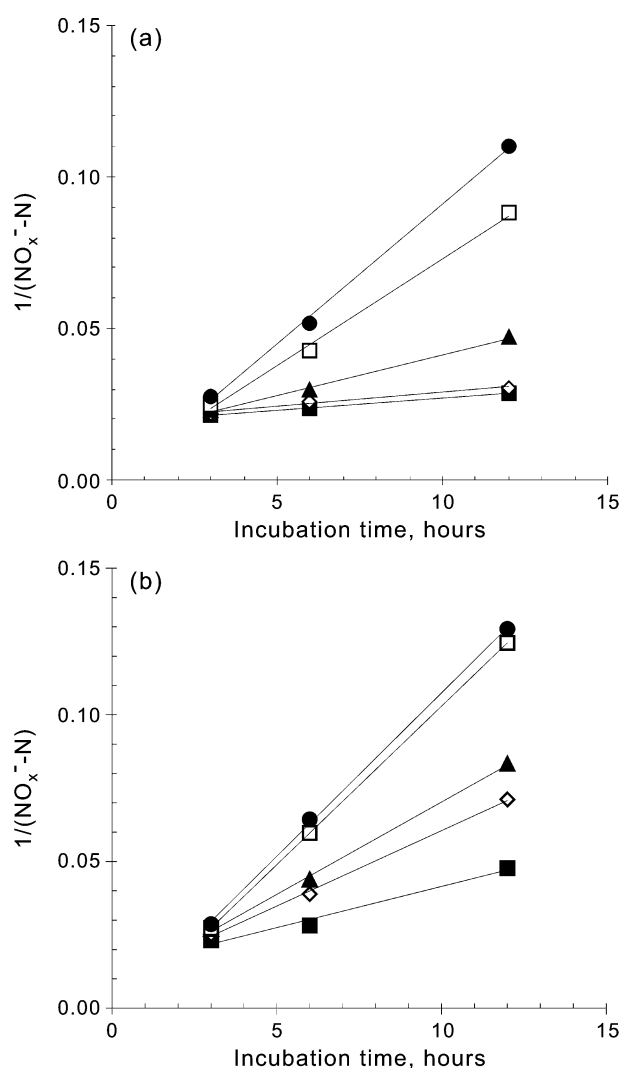


Fig. 3. $-\ln[(NO_x^- - N)/(NO_x^- - N)_i]$ vs time in varying substrate concentrations. It was computed from gas production of N_2O after 3, 6, and 12 hours of incubation according to acetylene inhibition method in a batch test. ■ COD/N ratio=0; ◇ COD/N ratio=1; ▲ COD/N ratio=1.5; □ COD/N ratio=2.5; ● COD/N ratio=4. a). $-\ln[(NO_x^- - N)/(NO_x^- - N)_i]$ vs time in the CU. b). $-\ln[(NO_x^- - N)/(NO_x^- - N)_i]$ vs time in the ZU.

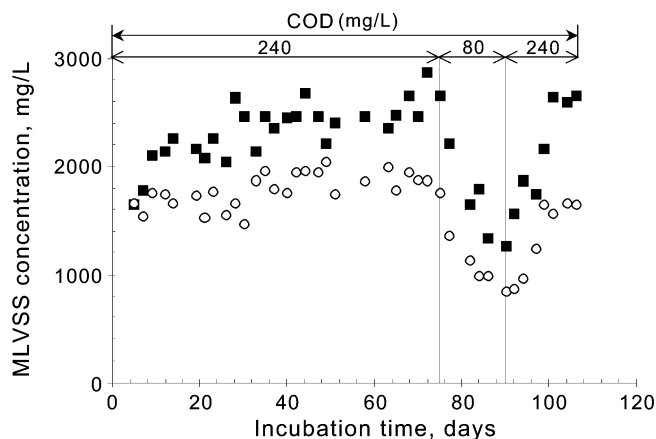


Fig. 4. Comparison of microbial concentration between the ZU and the CU according to varying loads of COD during continuous test of period. 0 to 75 day=COD 240 mg/l (C/N: 4.8); 75 to 90 day=COD 80 mg/l (C/N: 1.6); 90 to 110 day=COD 240 mg/l (C/N: 4.8) at 50 mg/l NO_3^- -N; ■ ZU; ○ CU.

The rate coefficients for varying concentration of COD (i.e., 0 to 240 mg/l) at 50 mg NO_3^- -N/l were thus estimated from Fig. 3(a) and (b) for the CU and the ZU, respectively. It was calculated based on 20 °C; thereby k_{20} for the CU ranged from 0.0008 to 0.0093 l/mg·hr, while it ranged from 0.0028 to 0.011 l/mg·hr for the ZU. The denitrification coefficient observed from the ZU was exposed approximately 0.0017 to 0.0026 l/mg·hr greater than that of the CU. This may be due to the activity of denitrifiers in the ZU improving at a relatively lower C/N ratio, which could enhance the denitrification kinetics in response to the increased concentration of microbial enzymes as given in Eq. (3).

$$k = k_0 [\text{substrate}]^m [\text{enzyme of microbe}]^p \quad (3)$$

where k_0 is related to the experimental temperature by Arrhenius equation, m and p are constants.

Fig. 4 demonstrates that MLVSS concentration in the ZU was 900 mg/l greater than that of the CU exposing approximately 2,000 mg MLVSS/l.

For 240 mg COD/l which is equivalent to the ratio of 4.8 of COD/ NO_3^- -N (i.e. from 0 to 75 day), MLVSS observed from the CU was averaged at 1,640 mg/l, whereas its concentration obtained from the ZU was exposed at 820 mg/l greater than that of the CU. Even in the reduced COD concentration to 80 mg/l in terms of the ratio of 1.6 of COD/ NO_3^- -N (i.e., from 75 to 90 day), the ZU could still have higher MLVSS concentration up to approximately 50% more than that of the CU even though its concentration was rapidly decreased to 1,265 mg MLVSS/l. It demonstrated that zeolite should be used for efficient microbial media for microbes [Son et al., 2000].

3. Nitrate Removal in a Continuous Activated Sludge

Fig. 5 presents residual nitrate concentration and denitrification rate observed in the same manner as in Fig. 4. For 240 mg COD/l (i.e., 0 to 75 day), nitrate concentration was lowered by up to 79% in the ZU, which was 18% higher than that in the CU showing 19.8 mg/l. However, no significant differences of denitrification rate were found between the ZU and the CU, which ranged from 6.7 to 6.9 mg NO_3^- -N/g VSS·hr.

COD decreased to 80 mg/l (i.e., 75 to 90 day) which was attri-

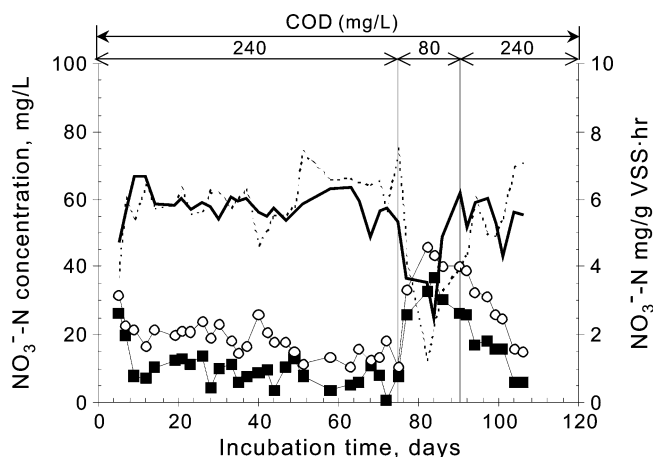


Fig. 5. Residual nitrate concentration and denitrification rate according to varying loads of COD during continuous test of period. 0 to 75 day=COD 240 mg/l (C/N: 4.8); 75 to 90 day=COD 80 mg/l (C/N: 1.6); 90 to 110 day=COD 240 mg/l (C/N: 4.8) at 50 mg/l NO_3^- -N; ■— residual NO_3^- -N concentration in the ZU; —○— residual NO_3^- -N concentration in the CU; — denitrification rate estimated in the ZU; --- denitrification rate estimated in the CU.

buted to reducing nitrate removal due to deficiency in carbon source. However, there were considerable differences in denitrification rate. This was observed at 4.15 mg NO_3^- -N/g VSS·hr for the ZU, which was 39% greater than that of the CU presenting at 2.98 mg NO_3^- -N/g VSS·hr. Moreover, nitrate removal observed from the ZU was 20%, equivalent to 10 mg/l, greater than that of the CU, which demonstrated the fact that the enhanced MLVSS concentration in the ZU can be more utilized as an internal carbon source by denitrifiers rather than that of the CU [Carucci et al., 1996]. After increasing COD concentration to 240 mg/l (i.e., 90 to 110 day), denitrification rate was similarly recovered by up to approximately 5.55 mg NO_3^- -N/g VSS·hr in between the ZU and the CU. However, the rapid recovery of denitrification was achieved for the ZU showing 70%, which is equivalent to 14.9 mg/l of residual NO_3^- -N observed in the effluent, while it was exposed at 47% for the CU exposing 26.1 mg/l of residual NO_3^- -N.

CONCLUSIONS

Comparison of denitrification between zeolite added and not added anoxic processes was made as COD concentration was varied while NO_3^- -N concentration was maintained at 50 mg/l. COD/ NO_3^- -N ratio was varied from zero to 4.8 such that denitrification rate was comparatively observed between zeolite added and not added processes. For the continuous flow experiments, the zeolite added system represented relatively greater denitrification performance, showing 39% higher than that of zeolite not-added system even at lower COD/ NO_3^- -N ratio.

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REFERENCES

- APHA (American Public Health Association), AWWA (American Water Works Association) and WEF (Water Environment Federation) (1998) Standard Methods for the examination of water and wastewater, 20th edition, New York, USA.
- Çeçen, F. and Gönenç, I. E., "Nitrogen Removal Characteristics of Nitrification and Denitrification Filters," *Wat. Sci. Tech.*, **29**, 409 (1994).
- Carucci, A., Ramadori, R., Rossetti, S. and Tomei, M. C., "Kinetics of Denitrification Reactions in Single Sludge Systems," *Wat. Res.*, **30**, 51 (1996).
- Hallin, S. and Pell, M., "Acetylene Inhibition for Measuring Denitrification Rates in Activated Sludge," *Wat. Sci. Tech.*, **30**, 161 (1994).
- Harremoës, P. and Riemer, M., "Report on Pilot Scale Experiments on Down-flow Filter Denitrification," Rep. 75-1, ISBN 89-425-3401-5, Department of Sanitary Engineering, Technical University, Lyngby, Denmark (1975).
- Henze, M., Harremoës, P., la Cour Jansen, J. and Arvin, E., "Wastewater Treatment. Biological and Chemical Processes," 2th edition, Springer-Verlag (1995).
- Jeong, S. W., Kim, J. H. and Seo, G., "Liquid-phase Degradation of HDPE over Alkali-treated Natural Zeolite Catalysts," *Korean J. Chem. Eng.*, **18**, 848 (2001).
- Kim, C. G., Lee, H. S. and Yoon, T. I., "Resource Recovery of Sludge as a Micro-media in an Activated Sludge Process," *Adv. Env. Res.* in press (2002).
- Lee, H. S., Yoon, T. I. and Kim, C. G., "Treatment of Municipal Wastewater with ZNR and URC Process," *J. KSEE*, **23**, 1359 (2001).
- Olah, J., Papp, J., Meszaros-kis, A., Mucsi, G. Y. and Kallo, D., "Simultaneous Separation of Suspended Solids, Ammonium and Phosphate ions from Wastewater by Modified Clinoptilolite. Zeolites as Catalysts, Sorbents and Detergent Builders," Karge, H. G. and Weitkamp, J. (eds.). Amsterdam, The Netherlands, Elsevier Science (1989).
- Piirtola, L., Hultman, B. and Lowen, M., "Effects on Detergent Zeolite in a Nitrogen Removal Activated Sludge Process," *Wat. Sci. Tech.*, **38**, 41 (1998).
- Son, D. H., Kim, D. W. and Chung, Y. C., "Biological Nitrogen Removal Using a Modified Oxic/Anoxic Reactor with Zeolite Circulation," *Biotech. Lett.*, **22**, 35 (2000).