Novel Nitrogen Removal Process Using Attached Activated Sludge

WATARU TAKATSUJI^{1*}, MOTONOBU NAKAOKA^{1*}, YUKIHIRO SAKAI¹,
and KENJI FURUKAWA²

¹Industrial Technology Center Wakayama Prefecture / 60, Ogura, Wakayama city, 649-6261, Japan

²Department of Civil Engineering and Architecture, Faculty of Engineering, Kumamoto University
/ 2-39-1, Kurokami, Kumamoto city, 860-8555, Japan

Abstract

In a conventional activated sludge aeration tank, organic nitrogen was almost completely converted to ammonium but very little was converted to oxidized forms of nitrogen (nitrite and nitrate). Nitrification and denitrification in the aerated unit process, though, was achieved by using three submerged cells with porous sides consisting of nonwoven materials for retention of biomass. When synthetic wastewater with nitrogen only in organic form was fed directly into a cell (as opposed to the surrounding aeration tank), T-N decreased from 42 to 30 mg/l and TOC levels, from 110 to 10 mg/l. Because virtually all activated sludge was attached to cell walls, there was essentially no excess sludge wastage over 100 days of operation. Denitrification efficiency using the novel apparatus was shown to be effected by TOC and alkalinity in the influent wastewater as well as dissolved oxygen levels and the method of influent feed. When wastewater was fed simultaneously into two cells, versus only one, the T-N removal efficiency improved from 34% to 45%. Effluent T-N was shown to decrease with a decrease in DO in the aeration tank and careful control of TOC and alkalinity levels in the wastewater feed allowed for nitrogen removal efficiencies as high as 75%.

Key words : nitrification, denitrification, activated sludge, support-surrounded cell, microbial attachment, polyester nonwoven material

INTRODUCTION

The ecosystems of enclosed ocean environments in Japan such as Tokyo Bay, Ise Bay and the Seto Inland Sea are very sensitive to pollution, which has led to strict control of chemical oxygen demand (COD) emissions to these water bodies. However, problems such as eutrophication have persisted at many locations due to influxes of inorganic nutrients and thus regulations on nitrogen and phosphorus in effluent discharges have been enacted for the Seto Inland Sea. Wastewaters from food and dye industries, in particular, are exceptionally high in nitrogenous compounds and may require extensive treatment prior to

discharge to meet regulatory standards.

Ammonium can be removed by physical-chemical treatment methods such as stripping at a high pH, carbon adsorption and chlorination. However, when the nitrogen is in reduced organic forms or when there is a high biochemical oxygen demand (BOD), biological treatment may be necessary. Conventional treatment such as activated sludge, though, does not effectively convert organic nitrogen all the way to gaseous forms and thus modifications to incorporate aerobic and anaerobic stages are required to achieve biological denitrification. The growth rate of nitrifying organisms that convert ammonium to nitrate under aerobic conditions is very slow, thus requiring a long

* Corresponding Author

sludge retention time. To increase the density of nitrifying organisms in a reactor and thus improve the nitrification efficiency, processes such as microbial attachment^{1,2)}, immobilization^{3,4)} and cross-flow filtration⁵⁾ have been considered. In addition, the immobilization of both nitrifying and denitrifying organisms in a common medium (coimmobilization) for simultaneous nitrification and denitrification in a single aerated unit process has been explored⁶⁾. However, a practical and economically favorable methodology for incorporating denitrification into an activated sludge process has not yet been developed.

In this study we report on the development of an effective nitrogen removal process that can be coupled with activated sludge. In this bench-scale system, both nitrification and denitrification are accomplished in one aeration tank using a novel apparatus that consists of cells with porous walls for microbial attachment that are submerged in a conventional activated sludge phase. Dividers around the cells consist of polyester nonwoven material that serve as a biomass retention matrix for slowly growing nitrifying organisms in the surrounding activated sludge. Total organic carbon (TOC) loadings, dissolved oxygen (DO) levels and substrate feeding methods were evaluated and optimized to achieve efficient denitrification of an influent wastewater with nitrogen predominately in organic forms.

MATERIALS AND METHODS

Influent wastewater The synthetic wastewater used in most experimental runs is described in Table 1. For some select runs, raw wastewater with a high urea content from a dye industry in Wakayama city was utilized. The water quality of this industrial wastewater prior to treatment is partially described in Table 2.

Sludge seeds Activated sludges from a domestic wastewater treatment plant in Wakayama that also received discharges of chemical industries and from a treatment plant of the dye industry that provided the raw wastewater (see above) were utilized as sludge seeds in this research. The sludges and wastewater were separated using a

centrifugal filter (Hitachi CF15D), which was rotated at 8,000 rpm for 5 min, and then the sludges were washed twice with phosphate buffer (10 mM, pH 6.8) prior to use.

Nonwoven materials Three nonwoven materials (nonwovens; MB-T9, MB-T9-P and T-9P) manufactured by Japan Vilene Co., Ltd., were utilized. MB-T9 was made of polyester; MB-T9-P was a polyester material coated with a copolymer, 4-vinylpyridine-styrene; and T-9P was made of polyolefin. All nonwovens were obtained in sheets of approximately 9 mm thickness.

Frame for support-surrounded cell (SSC)

Nonwoven sheets (5 cm by 10 cm each, 27mm thickness (3 sheets of 9mm thickness)) were attached to both side panels of a frame as shown in Fig. 1. The distance between the sheets in the SSC interiors was either 2.4 cm (type-A cell) or 3.3 cm (type-B cell). Water-soluble substrates and air (oxygen) in the aeration tank can only pass to the interior of a cells through the nonwoven sheets on the cell walls.

Selection for activated sludge and nonwoven

An activated sludge with high nitrification efficiency was previously selected by batch operation. The activated sludge was combined with 3 l of raw industrial wastewater (see Table 2) in the 5-l aeration tank to a mixed liquor suspended solids (MLSS) concentration of 2,000 mg/l. The mixed

Table 1 Composition of synthetic wastewater

Components	Concentration(mg/l)		
	case 1	case 2	case 3
Polypeptone	200	400	800
Meat extract (Bacto)	300	600	1200
MgSO ₄ ·7H ₂ O	10	20	40
CaCl ₂	7	14	28
NaCl	5	10	20
KCl	7	14	28
NaHCO ₃	105	210	420

Table 2 Water quality of raw wastewater from the dye industry

pH	7.2
T-N	220 mg/l
TOC	200 mg/l

Fig. 1 Frame for nonwoven support-surrounded cell (SSC)

liquor was then aerated at 7 liters (of air) per minute. Next, nonwovens for attachment of nitrifying organisms were evaluated during continuous operation. Nonwovens or SSCs with nonwovens were placed into the 5-l aeration tank with an air flow of 7 liters (of air) per minute for 24 h, containing 3.85 l of synthetic wastewater and activated sludge with a MLSS concentration of 100 to 200 mg/l. Thereafter, the synthetic wastewater was fed into the aeration tank at a hydraulic retention time (HRT) of 24 h.

Reactor startup and operation Three SSCs, with nonwovens attached, were then placed directly in the activated sludge of the aeration tank with 3.8 l of synthetic wastewater and aerated at 7 liters (of air) per minute for 24 h. By this procedure, within 24 hr all of the activated sludge, which was initially present at 150 mg/l, was apparently attached to the nonwovens on the SSCs. Thereafter, the synthetic wastewater was fed continuously to the aeration tank at a HRT of 24 hr. The wastewater was fed either into the main body of the aeration tank or directly into the interiors of the SSCs as shown in Fig. 2. DO was adjusted stepwise between 8.6 and 5.5 mg/l during the testing period and TOC was increased stepwise from 56 mg/l (case 1, see Table 1) to 400 mg/l (case 3).

Fig. 2 Schematic diagram of bench scale reactor using SSC. 1-3; SSC, 4; aeration instrument, 5; aeration tank, 6; influent storage tank, 7; feed pump, 8; effluent

Analytical methods $\text{NH}_4\text{-N}$ and $\text{NO}_x\text{-N}$ were determined in accordance with Japanese Industrial Standards⁷. Total-N, TC and IC were analyzed by gas chromatography (Sumigraph GCT-12). Organic-N was determined by calculation from known total-N, $\text{NH}_4\text{-N}$ and $\text{NO}_x\text{-N}$. TOC was determined by calculation from known TC and IC. Oxidation-reduction potential (ORP) was determined using a RM-20P meter, DO with a DO-21P meter, and pH with a HM-30V meter, all three from DKK TOA Co.

RESULTS AND DISCUSSION

Nitrogen conversions at the dye-industry treatment plant The concentrations of nitrogenous compounds over a six-month period in the influent, aeration tank and effluent of the wastewater treatment plant of the dye industry are summarized in Table 3. Nitrogen in the influent was almost entirely organic-N, primarily urea, which was readily converted to $\text{NH}_4\text{-N}$ in the aeration tank. It has been considered that the removal of nitrogenous compounds in dye-industry wastewaters could be accomplished in a two-stage process: the oxidation of $\text{NH}_4\text{-N}$ to $\text{NO}_x\text{-N}$ by nitrifying organisms under aerobic conditions and subsequently the reduction of $\text{NO}_x\text{-N}$ by denitrifying organisms under anaerobic conditions ultimately to nitrogen gas.

Selection of nitrifying activated sludge

As shown in Fig. 3, the conversion of $\text{NH}_4\text{-N}$ to $\text{NO}_x\text{-N}$ using the sludge of the domestic wastewater treatment plant of Wakayama city increased to an efficiency of 45% during 8 hr of operation. Using the sludge of the wastewater treatment plant of the dye

Table 3 Concentrations of nitrogenous compounds in influent, aeration tank and effluent of the dye-industry wastewater treatment plant

Month	Influent			Aeration tank			Effluent		
	Organic-N mg/l	NO _x -N mg/l	NH ₄ -N mg/l	Organic-N mg/l	NO _x -N mg/l	NH ₄ -N mg/l	Organic-N mg/l	NO _x -N mg/l	NH ₄ -N mg/l
9	217	1.1	16	6	0.037	197			
10	194	1.2	16	88	0.24	135			
11	150	1.4	7				0	0.30	221
12	195	1.6	5				18	0.06	153
1	205	1.0	3.6				46	0.05	171
2	200	1.1	1.9				37	0.13	138

Fig. 3 Nitrification efficiency of raw wastewater from a dye industry using activated sludges from the Wakayama domestic treatment plant and the dye-industry treatment plant.

Symbols: ○, Wakayama domestic treatment plant; ●, Dye-industry treatment plant
 Nitrification efficiency = $\frac{\text{Effluent NO}_x\text{-N}}{(\text{Influent organic-N and NH}_4\text{-N})} \times 100$

industry, however, conversion efficiency remained near zero over 9 hr. Considering that conversion of NH₄-N to NO_x-N is the rate-limiting step for nitrogen removal, the activated sludge of the Wakayama domestic treatment plant was selected for use in all subsequent experiments.

Evaluation of nonwoven carriers The time courses of effluent total-N and NO_x-N concentrations during continuous flow treatment of synthetic wastewater using MB-T9 and MB-T9-P nonwovens for attachment of activated sludge are shown in Fig. 4. Using MB-T9-P, effluent NO_x-N concentrations approached 30 mg/l following 7 days of treatment under aerobic conditions and after an additional 4 days with no aeration or additional feed, total-N levels decreased from

Fig. 4 Time courses of effluent nitrogen concentrations during continuous treatment of synthetic wastewater using attached activated sludge. Activated sludge (initial MLSS = 100 mg/l) was attached in MB-T9 and MB-T9-P (5 cm by 10 cm, 6 sheets each).
 For MB-T9: ●, T-N; ▲, NO_x-N
 For MB-T9-P: ○, T-N; △, NO_x-N

about 60 to 40 mg/l. Nitrification efficiency was slightly higher using MB-T9-P than MB-T9. The time course of total-N and NO_x-N concentrations using the type-A SSC process with MB-T9 and T-9P nonwovens for attachment of activated sludge are shown in Fig. 5. Using MB-T9, effluent NO_x-N concentrations were about 25 mg/l following 10 days. Using T-9P, however, NO_x-N was only about 14 mg/l after 16 days. Due to the greater nitrification efficiency, MB-T9-P was used as the biomass attachment medium in all subsequent experiments.

Continuous treatment using SSC process

The time courses of total-N, NO_x-N and TOC transformations using the type-A SSC

process over a 100-day period of operation are shown in Fig. 6. As shown, when the synthetic wastewater was fed into the aeration tank, after 8 days effluent $\text{NO}_x\text{-N}$ concentrations increased to 40 mg/l, which was nearly equal to the effluent total-N; denitrification, though, did not occur. However, because denitrification had been shown to occur during periods when the activated sludge was not aerated, denitrifying organisms were thought to be present in significant numbers in the SSC unit process. After 23 days of operation, the synthetic wastewater feed was switched directly to the interior of SSC-1 and, as shown in Fig. 6-a, this resulted in the effluent total-N level dropping from approximately 42 to 30 mg/l. In this manner, nitrification and denitrification were achieved in the same unit process employing aeration. The effluent TOC concentration was consistently about 10 mg/l during the 100 days of operation as shown in Fig. 6-b. As shown in Fig. 7, when influent is fed into the aeration tank, $\text{NO}_x\text{-N}$ may be slightly reduced to N_2 because of the lack of TOC in the SSC interior (i.e., an anaerobic condition). However, when influent is fed directly to the

SSC interior, $\text{NO}_x\text{-N}$ is more effectively reduced to N_2 coupled with decreasing TOC. A photograph of the aeration tank is shown in Fig. 8. When three sets of SSCs were set into the aeration tank, the activated sludge in the tank almost instantly attached to the nonwovens. After 15 minutes, the solution in the aeration tank became clear, which was maintained throughout the 100 days of

Fig. 5 Time courses of effluent nitrogen concentrations during continuous treatment of synthetic wastewater using the SSC (type A) process with MB-T9 and T-9P. Activated sludge (initial MLSS = 200 mg/l) was attached on three SSCs. Influent was fed directly into the aeration tank.
For MB-T9: ●, T-N; ▲, $\text{NO}_x\text{-N}$
For T-9P: ○, T-N; △, $\text{NO}_x\text{-N}$

Fig. 6 Time courses of changes in nitrogen and TOC using the SSC (type A) process with MB-T9-P. Symbols: ○, effluent T-N; △, effluent $\text{NO}_x\text{-N}$; □, effluent TOC.
—, average of effluent T-N after 23 days;
---, average of influent T-N. ■, no aeration and no feed.

Fig. 7 Nitrogen conversion mechanisms using the SSC process with nonwoven sheets under different loading conditions

Fig. 8 Photographs of the SSC unit process (type A)

treatment. As the activated sludge can be kept in the tank using the SSC process, it is evident that the solids retention time (SRT) is very long and that nitrification efficiency is enhanced and that very little excess sludge is produced.

Influence of DO and step-feed on the SSC process When the synthetic wastewater

was fed into SSC-1 at 3.8 l/day over a period of 48 days, the level of DO in the aeration tank was decreased stepwise from 8.6 to 5.5 mg/l. The synthetic wastewater was then fed directly into the interior of both SSC-1 and SSC-2 at 1.9 l/day, each, and effluent total-N, NO_x-N and TOC concentrations and ORP in the aeration tank during the ensuing runs were as shown in Table 4. Effluent total-N decreased with a decrease in DO in the aeration tank, but only a very slight difference was observed between DO levels of 6.7 and 5.5 mg/l. Total-N levels decreased from 38 to 25 mg/l with decreasing DO levels corresponding with a nitrogen removal efficiency of 34%. ORP in the aeration tank throughout the treatment period (66 days) was between 100 and 185 mV. ORP in the interior of the SSCs without direct wastewater feed was about 100 mV, which was essentially the same as that in the aeration tank; however, with direct wastewater feed into the SSCs, the interior ORP level dropped to -200 mV. Only when the wastewater was fed directly to the SSC interiors did a significant reduction of NO_x-N to N₂ occur. When wastewater was fed into the interiors of SSC-1 and SSC-2, effluent total-N decreased from 38 to 21 mg/l, which corresponds to a nitrogen removal efficiency of 45%.

Effect of influent wastewater TOC Removals of nitrogen and TOC at three

Table 4 Influence of DO and influent feed method on nitrogen conversion using the SSC process (type B)

Aeration tank					Effluent		
DO (mg/l)	feed point	ORP		temp (°C)	T-N (mg/l)	NO _x -N (mg/l)	TOC (mg/l)
		outer (mV)	inner (mV)				
8.6	①	185		21	33	9.4	20
7.5	①	155	-188 ¹⁾	23	30	13	17
6.7	①	100	-230 ¹⁾ 110 ²⁾ 100 ³⁾	24	25	16	12
5.5	①	160	-120 ¹⁾	25	27	12	13
6.9	①+②	110	-220 ¹⁾ -200 ²⁾	25	27	12	10

1) ORP in the interior of SSC-1. 2) ORP in interior of SSC-2. 3) ORP in the interior of SSC-3.
T-N, NO_x-N and TOC in influent are 38 mg/l, 0.3mg/l and 100 mg/l, respectively.

wastewater strengths (cases 1, 2 and 3; see Table 1) are shown in Fig. 9. The synthetic wastewater was fed to the inside of SSC-1 and SSC-2 at 1.9 l/day, each, and influent TOC was increased stepwise from 56 to 400 mg/l. With case 1 where TOC is 56 mg/l (IC = 55 mg/l and total-N = 39 mg/l), effluent total-N was 20 mg/l, corresponding to a nitrogen removal efficiency of 49% and $\text{NO}_x\text{-N}$ was

nearly absent in the effluent. For case 2 with a TOC of 120 mg/l (IC = 87 mg/l and total-N = 72 mg/l), effluent total-N and $\text{NO}_x\text{-N}$ concentrations were 40 mg/l and 25 mg/l, respectively, and the nitrogen removal efficiency was 44%. For case 3 with a TOC of 400 mg/l (IC = 141 mg/l and total-N = 167 mg/l), effluent total-N was 40 mg/l, corresponding to a nitrogen removal ef-

Before SSC setting

After 5 min.

After 15 min.

After 100 days.

Fig. 9 Influence of influent wastewater concentration on nitrogen conversion and TOC removal using the SSC process (type B). Three SSCs were used and influent was fed into the interiors of SSC-1 and SSC-2. DO, 5.8–7 mg/l; pH, 7.5–8.1; temperature in aeration tank, 18–25 °C.

efficiency of 75% and effluent $\text{NO}_3\text{-N}$ was 10 to 20 mg/l. Considering the relatively high alkalinity in the wastewater of case 3, the nitrifying bacteria in the activated sludge may have been able to grow more effectively in the nonwovens and a high nitrogen removal efficiency was thus achievable. Effluent TOC was maintained below 20 mg/l even with an influent TOC as high as to 400 mg/l.

CONCLUSIONS

From the results of this study, the following conclusions can be drawn:

- (1) Because organic-N in a dye-industry wastewater was readily converted to $\text{NH}_4\text{-N}$ in an aeration tank, the conversions of nitrogenous compounds via traditional oxidation and reduction processes in a single unit was considered technically feasible.
- (2) When wastewater was feed directly to the interior of a SSC, nitrification and denitrification could both be accomplished in a single aerated unit process. By directing the influent wastewater into only one of three SSCs, applied T-N decreased from 42 to 30 mg/l and effluent TOC could be maintained at about 10 mg/l. Do to complete attachment of activated sludge on nonwoven sheets, the SRT was considered to be very long. By this process nitrification efficiency was enhanced and very little excess sludge was produced.
- (3) The method of wastewater feed using the SSC process was shown to be very important for nitrogen removal efficiency. When wastewater was fed simultaneously into two SSCs, versus only one, T-N removal efficiency improved from 34% to 45%.
- (4) Effluent T-N was shown to decrease with a decrease in DO in the aeration tank, but the difference became ne-

gligible at DO levels below 6.7 mg/l. Because nitrification and denitrification were occurring simultaneously with oxidation of organic materials, careful control of TOC and alkalinity levels in the wastewater feed allowed for nitrogen removal efficiencies of up to 75%.

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(Submitted 2002. 6. 17)

(Accepted 2002. 7. 4)