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Nitrogen Removal from Dye-Industry Wastewater using Pile Fabrics as Biomass Carriers

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Abstract

Wastewater from the dye industry contains high level of organic nitrogen derived from urea. Thus, an effective nitrogen removal process is needed to reduce effluent nitrogen concentration. We have developed a new nitrogen removal process using non-woven biomass carriers. In this study, we used pile fabrics, which are products of the local industry in the Wakayama prefecture, instead of non-woven materials as biomass carriers to improve nitrification rates. Several pile fabrics were then used for nitrification and continuous nitrification/denitrification experiments. The specific NOx-N production rate using an acrylic pile fabric was 3.4 times higher than that of non-woven carriers. About 75% nitrification efficiencies were obtained under a T-N loading rate of 0.5 kg-N/m^3/day and a HRT of 10 hours during continuous nitrification using acrylic pile fabrics. Furthermore, continuous nitrification/denitrification experiments were carried out using acrylic pile fabrics in a base cloth with a mesh structure to improve the diffusion rates. Little biomass accumulated on the pile fabric surfaces so a high diffusion rate through the pile was maintained for long periods. Denitrification efficiencies of 56 and 77 % were achieved at HRTs of 12 and 19 hours, respectively, with influent concentrations of 200 mg/*l* T-N and 450 mg/*l* TOC.

Key words: pile fabrics, biomass carrier, nitrification, denitrification, dye-industry wastewater

INTRODUCTION

Deterioration of water quality due to eutrophication persists in three closed inland seas (Tokyo Bay, Ise Bay and Seto Inland Sea). In these areas, there is control of the total pollutant loads, chemical oxygen demand (COD), total nitrogen (T-N) and total phosphate (T-P). In the northern part of Hinomisaki in Wakayama prefecture, these items are controlled. The dye industry is one of the largest industries in the northern part of Wakayama prefecture. Large amounts of urea and organic matter are contained in dye wastewater, so COD and T-N loads are at very high levels. Generally, dye wastewater is treated by processes such as activated sludge, coagulation and sedimentation. However, effluent qualities in the dye industry are within regulation values but sometimes effluent COD and T-N concentrations are very close to the effluent standards. The improvement of the wastewater treatment is desired.

The most common technology for treating nitrogen is the biological nitrification/ denitrification process. The growth rate of nitrifying bacteria is very low, so a long sludge retention time is required. To increase the concentration of nitrifying bacteria in a reactor and thus improve nitrification efficiency, approaches such as immobilizations[1,2] and membrane bioreactors (MBR) with filtrations[3,4] have been developed. In addition, the immobilization of both nitrifying and denitrifying bacteria in common biomass carriers for simultaneous nitrification and denitrification in a single aerated unit operation has been explored.[5-7]

We have developed a new nitrogen removal process using non-woven biomass carriers. By placing the biomass carrier unit into an existing aerobic tank,[8,9] 56 % nitrogen removal efficiency could be achieved under a hydraulic retention time of about 1.3 days and a nitrogen loading rate of 0.2 kg-N/m^3/day. In experiments with pilot scale reactors in a dye factory, we achieved approximately 40% nitrogen removal efficiencies and 70% organic carbon removal efficiencies under a hydraulic retention time of 1.5 days and a nitrogen loading rate of 0.2 kg-N/m^3/day.[10] However, a number of practical problems remain in the application of this wastewater treatment system. One problem is the need for improvement of nitrification rates. In our experiments, it took about 1.5 days for oxidation of organic nitrogen to nitrate in dye wastewater. Another problem is the low rate of substrate diffusion through the non-woven materials unit. We have also observed clogging of non-woven materials during long-term operation. We have attempted to improve nitrification and denitrification efficiencies and achieve stable long-term treatment by improving diffusion rates. We have also substituted pile fabrics for non-woven materials as biomass carriers. In this study, several pile fabrics were used for nitrification and continuous nitrification/denitrification experiments.

MATERIALS AND METHODS

Seed Sludge Activated sludge from the Wakagawa domestic sewage treatment plant in Wakayama city was used as seed sludges. This plant received domestic sewage and effluent from the chemical and dye industries.

Initial nitrification rate at start-up using pile fabrics as biomass carriers Six types of pile fabric made from different materials (5 cm x 5 cm, 6 pieces, manufactured by Ohyapile Co., Ltd., Hashimoto, Japan) were used as biomass carriers (Fig. 1). These pile fabric biomass carriers were set to plastic frames and placed into an aerobic tank (9 cm x 29 cm x 19 cm, working volume 3.85 *l*) containing a synthetic dye wastewater (Table 1) and activated sludge with an initial mixed liquor suspended solids (MLSS) concentration of 80 to 100 mg/*l*. The synthetic dye wastewater was then fed into the aeration tank with a hydraulic retention time (HRT) of 24 hours. One week later, NOx-N (NOx-N

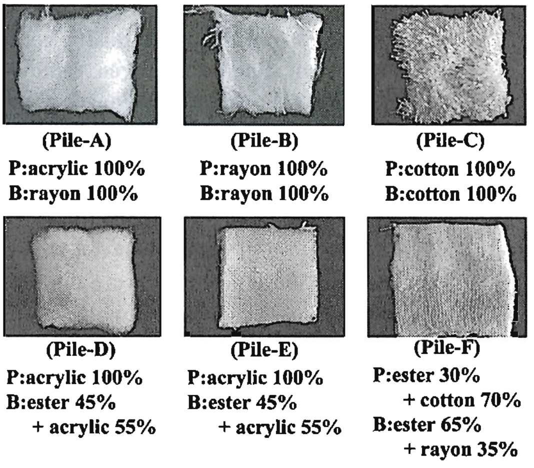

Fig. 1 Photographs of pile fabrics biomass carriers
P: material of the pile part of pile fabrics
B: material of the base part of pile fabrics

Table 1 Composition of synthetic dye wastewater

Components	Concentrations*1
Urea	0.40 g/*l*
$NaHCO_3$	0.40 g/*l*
Sodium Alginate (5%)	1.72 g/*l*
Starch	0.20 g/*l*
H_3PO_4 (85%)	7.4 mg/*l*
Cibacron Red P-B (33%)	6 mg/*l*
Procion Blue P-GR (40%)	5.2 mg/*l*
Kayacion Yellow P-M3R (33%)	6 mg/*l*
m-Nitrobenzensulfonic acid sodium (20%)	0.20 g/*l*
Tap water	1.0 *l*

*1: concentrations in tap water of 1 *l*

= NO_2-N + NO_3-N) concentrations were measured. We carried out the same experiments using a non-woven material (5 cm x 5 cm, 9mm thickness, MB-T9-P, a polyester material coated with a copolymer, 4-vinylpyridinestyrene) manufactured by Japan Vilene Co., Ltd. (Tokyo, Japan).

Biomass attached to the carriers at start-up The six types of pile fabrics shown in Fig. 1 were dried at 80℃ for one hour and weighed after cooling in a desiccator (W_1). The carriers were then placed in beakers containing 500 m*l* of activated sludge (MLSS 5,000 mg/*l*) from the dye industry and mixed at room temperature for 20 hours. The biomass carriers were then retrieved and dried at 80℃ for one hour and the sludge mass determined by weighing after cooling in a desiccator (W_2). A blank solution was created by removing solids from a 500 m*l* sample of dye industry activated sludge by centrifugation (8,000 rpm, 5 min) and filtration (0.2 μm filter). Biomass carriers were also weighed with this blank solution (W_0). The masses attached to biomass carriers (Sw) were obtained using equation (1). The same experiments were carried out using non-woven materials.

$$Sw = (W_2 - W_0) - W_1 \quad (1)$$

Nitrification rate under steady state condition using acrylic pile fabrics as biomass carriers Fig. 2 shows photos of acrylic pile fabrics used as biomass carriers for continuous nitrification experiments. The material was acrylic fibers with pile diameters of 1 mm. The length of Pile-G and Pile-H were 1.0 cm and 3.0 cm, respectively. The densities, which were numbers of piles per $1cm^2$, of each pile fabric are also shown in Fig. 2. Six acrylic pile fabrics of 5 cm x 10 cm, as shown in Fig. 3-A, were set to plastic frames and placed in the aerobic tank (3.85 *l* working volume) shown in Fig. 3-B. Activated sludge from the Wakagawa sewage treatment plant was attached to the acrylic pile fabric samples under aeration for 24 hours. Synthetic dye wastewater was fed as a pre-culture with a hydraulic retention time of 1 day. The nitrification rate under steady state condition was measured as follows. Each biomass carrier was retrieved from the aerobic tank and placed in a bottle containing 1.5 *l* of synthetic influents (see Table 2 for compositions) for nitrification studies under aerobic conditions. Changes in amounts of NOx-N were measured during 24 or 25 hours and dry weights of biomass carriers were measured at the end of experiments. Amounts of NOx-N were calculated with NOx-N concentrations. The specific NOx-N production rates were calculated with NOx-N concentrations and projected areas of carriers. The same experiments were carried out using non-woven materials.

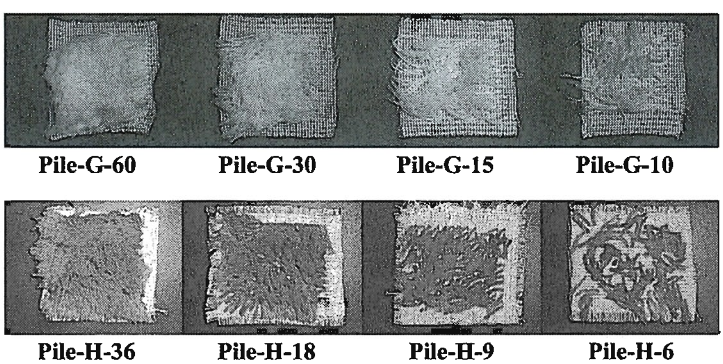

Fig. 2 Photographs of acrylic pile fabrics biomass carriers
Material; acrylic fiber
Diameter of a pile; 1 mm
Length of a pile; Pile-G: 1.0 cm, Pile-H: 3.0 cm
Last number indicates the pile per 1 cm^2

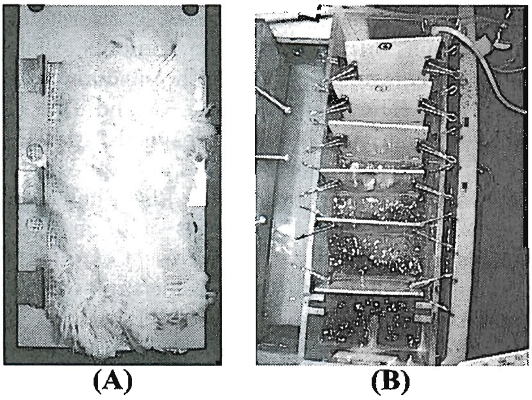

Fig. 3 Photographs of the biomass carriers (A) and continuous nitrification treatment tank (B) using acrylic pile fabrics

Table 2 Composition of synthetic influents for nitrification studies

Components	Concentrations[*1]
$(NH_4)_2SO_4$	943 mg/l
KH_2PO_4	100 mg/l
$NaHCO_3$	400 mg/l
Na_2CO_3	360 mg/l
$MgSO_4 \cdot 7H_2O$	60 mg/l
$FeSO_4 \cdot 7H_2O$	8 mg/l
$CaCl_2 \cdot 2H_2O$	8 mg/l
Tap water	1.0 l

*1: concentrations in tap water of 1 l

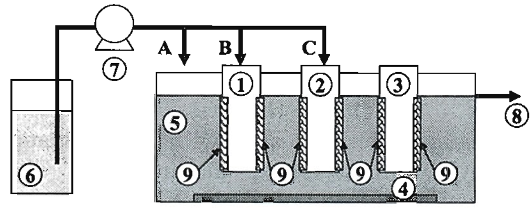

Fig. 4 Schematic diagram of continuous nitrification and denitrification treatment using acrylic pile fabricss
①-③; biomass carriers, ④; aeration instrument, ⑤; aeration tank, ⑥; influent storage tank, ⑦; feed pump, ⑧; effluent

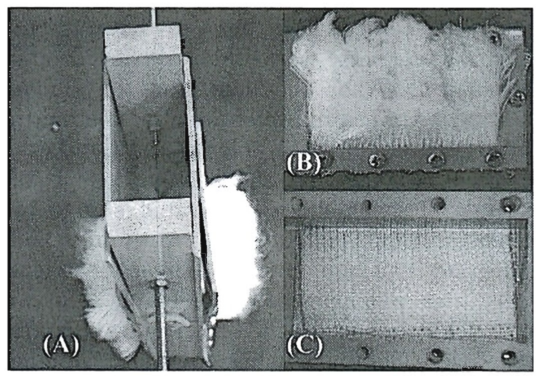

Fig. 5 Photographs of continuous nitrification and denitrification treatment using acrylic pile fabrics (Pile-H-36)
(A); biomass carriers
(B); outside, aerobic zone
(C); inside, anaerobic zone

Continuous nitrification/denitrification treatment using acrylic pile fabrics A diagram of the continuous nitrification/denitrification treatment process and photos of the biomass carrier unit using acrylic pile fabrics are shown in Figs. 4 and 5, respectively. Three biomass carrier units were set in the aerobic tank (working volume of 3.85 l) containing activated sludge from the Wakagawa sewage treatment plant and synthetic dye wastewater. Activated sludge was attached on the biomass carrier units through aeration (3 l/min) for 24 hours. Then synthetic dye wastewaters were fed to the aerobic tank under a hydraulic retention time of one day. Acrylic pile fabrics were placed on both sides of the units. This design of structure enabled the interior of the biomass carrier unit to maintain anaerobic conditions. The continuous nitrification/denitrification treatments were operated without a sedimentation tank.

Analytical methods NH_4-N and NOx-N were determined in accordance with Japanese Industrial Standards (JIS K-0102, 1998). T-N and TOC were analyzed by TOC-$V_{CPH/CPN}$ from Shimadzu Co., Ltd. (Kyoto, Japan). Dissolved oxygen (DO) concentration, oxidation-reduction potential (ORP) and pH were determined using DO-21P, RP-20P and HM-20P probes, respectively (DKK TOA Co., Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Initial nitrification rates and sludge mass attached on biomass carriers at start-up using pile fabrics NOx-N concentrations and the initial sludge mass on each pile fabric biomass carrier sample were determined at

Table 3 NOx-N production and the amounts of attached sludge on biomass carrier in continuous nitrification treatment.

Biomass carriers	NOx-N production*1	Amounts of attached sludge*2
Pile-A	8.5 mg/l	96 g/m²
Pile-B	12.2 mg/l	57 g/m²
Pile-C	30.0 mg/l	58 g/m²
Pile-D	10.3 mg/l	102 g/m²
Pile-E	10.6 mg/l	68 g/m²
Pile-F	8.2 mg/l	43 g/m²
MB*3	10.4 mg/l	71 g/m²

*1; NOx-N concentrations after one week
*2; after 20 hours, 5cm × 5cm biomass carrier
*3; MB-T9-P (non-woven)

the end of each treatment (Table 3). The highest NOx-N concentration, 30 mg-N/*l*, was obtained for Pile-C. NOx-N concentrations for other pile fabrics were comparable with those of non-woven biomass carriers. The high nitrification concentration obtained for Pile-C was considered to be due to the area available for sludge attachment. The corrugated Pile-C was able to provide a larger sludge attachment area closed to the wastewater than other biomass carriers. On the other hand, the mass of sludge attached to Pile-A, Pile-D and Pile-E were similar to or higher than that of MB-T9-P. These three pile fabric materials contained acrylic fibers. Clearly, the acrylic pile fabrics were suitable for retention of more sludge on the biomass carriers. From these results, we concluded that acrylic fiber was the best biomass carrier material for attaching nitrifying bacteria and that the pile should be as long as possible to obtain height corrugation, similar to Pile-C. We then obtained other types of acrylic pile fabric with a similar form to Pile-C.

Effects of pile density on nitrification rate Changes in the amounts of NOx-N produced by using acrylic pile fabrics with pile lengths 1.0 and 3.0 cm are shown Figs. 6 and 7, respectively. Using Pile-G (pile length 1.0 cm), the amounts of NOx-N from that of acrylic pile fabrics with different pile densities had no difference from MB-T9-P (Fig. 6). Using Pile-H (pile length 3.0 cm), the amounts of NOx-N produced increased with an increase in pile density (Fig. 7). As

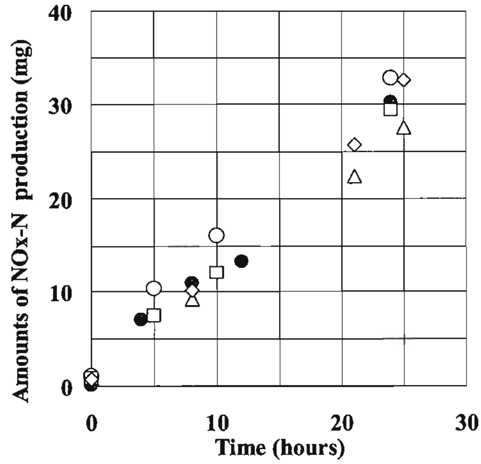

Fig. 6 Changes in amounts of NOx-N production during batch treatment of synthetic influents for nitrification studies using various density of pile fabrics with pile length 1.0 cm
Symbols: ○; Pile-G-60, △ ; Pile-G-30, □; Pile-G-15, ◇; Pile-G-10, ●; MB-T9-P

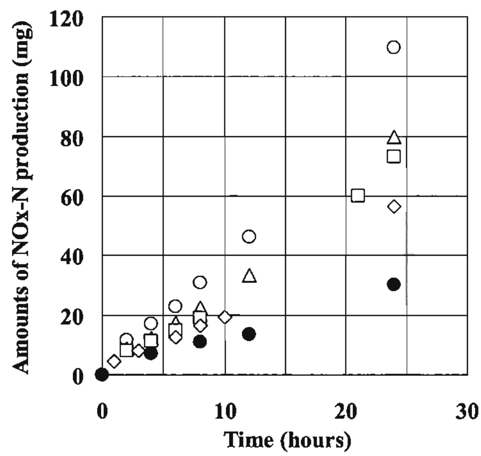

Fig. 7 Changes in amounts of NOx-N production during batch treatment of synthetic influents for nitrification studies using various density of pile fabrics with pile length 3.0 cm
Symbols: ○; Pile-H-36, △ ; Pile-H-18, □; Pile-H-9, ◇; Pile-H-6, ●; MB-T9-P

shown in these figures, the amount of NOx-N produced increased linearly with time. The specific NOx-N product rates were calculated from the slopes of the curves and are shown in Table 4. The specific NOx-N production rates of Pile-G samples were almost equal to that of MB-T9-P. On the other hand, the

Table 4 Amounts of attached sludge on biomass carrierand specific nitrification rates in batch nitrification experiments.

Biomass carriers	Amounts of attached sludge [g]	Specific nitrification rates [g-NOx-N/m²/day]
MB	0.252	5.9
G-60	0.284	8.7
G-30	0.275	4.9
G-15	0.243	5.4
G-10	0.160	5.0
H-36	0.845	20.1
H-18	0.610	13.5
H-9	0.526	12.6
H-6	0.594	11.6

MB: MB-T9-P, G: Pile length 1.0cm, H: Pile length 3.0cm

specific NOx-N production rates of Pile-H samples were over two times higher than that of MB-T9-P. In particular, the specific NOx-N production rate of Pile-H-36 was 3.4 times higher than that of MB-T9-P, reaching 20.1 g-NOx-N/m²/day. The masses of sludge attached to pile fabrics showed the same trends as those of the specific NOx-N production rates and the mass of sludge attached to Pile-H-36 was 3.4 times higher than that of MB-T9-P. From these results, we conclude that the specific NOx-N product rates depended on the mass of sludge attached to the pile fabric biomass carriers.

Continuous nitrification experiment using acrylic pile fabrics A continuous nitrification treatment using Pile-H-36, with the highest specific NOx-N product rate, was conducted. Fig. 8 shows the daily changes in nitrification efficiency. The T-N loading rates increased step by step with stepwise decreases in HRT of 24, 17 and 12 hours. T-N loading rates increased gradually with decreasing nitrification efficiencies. A nitrification efficiency of about 60% was obtained in the case of a T-N loading rate of 0.4 kg-N/m³/day. However, the NOx-N product rate recovered after increasing the HRT to 24 hours. Finally, a nitrification efficiency of about 75% was obtained under a T-N loading rate of 0.5 kg-N/m³/day and a HRT of 10 hours. These results confirmed the improvement of nitrification efficiencies using Pile-H-36 as a biomass carrier.

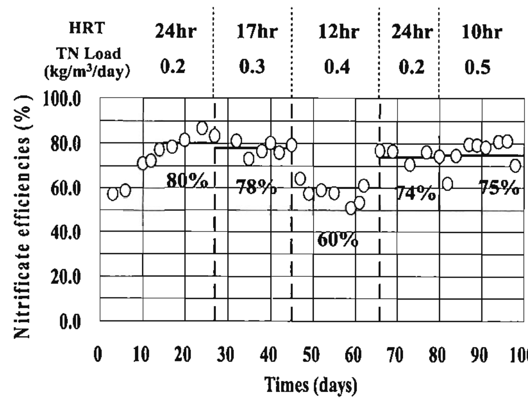

Fig. 8 Changes in nitrification efficiencies during continuous treatment of synthetic dye wastewater using acrylic pile fabrics (Pile-H-36) as biomass carrier

Continuous nitrification/denitrification using acrylic pile fabrics The results of continuous nitrification/denitrification using acrylic pile fabrics are shown in Fig. 9. First, synthetic dyeing wastewater was added at location A in Fig. 4. T-N removal efficiencies reached about 40% one week later and decreased gradually to about 20%. During this period, the effluent pH was between 8 and 9. Therefore, nitrogen removal by ammonium stripping occurred prior to the nitrification reaction. Next, the influent feed position was changed to location B in Fig. 4. T-N removal efficiencies reached about 40% and decreased gradually to less than 20%. The influent feed position was then changed to locations B and C simultaneously in Fig. 4. T-N removal efficiencies reached over 50% but then decreased gradually to less than 20%. The sludge attached on the surface of these pile fabrics was observed at the end of this experiment as shown in Fig. 10. The left side of the photos shows the biomass carrier ② with influent feeding to the inside of biomass carrier and the right side of the photos shows the biomass carrier ③ without influent feeding to the inside of biomass carrier. Both photos show sludge attachment on the aerobic side of the biomass carrier. However, no clogging occurred and a clear surface was maintained in the biomass carrier ③ installed in the anaerobic zone in the absence of influent feeding to the anaerobic zone. On the other hand, clogging and consequent poor diffusion conditions were observed inside biomass carrier ② in the case of influent feeding to the anaerobic zone.

Hence, the elimination of clogging was essential for stable nitrogen removal in this treatment process. Therefore, we obtained the acrylic pile fabrics of Pile–I (manufactured by Ohyapile Co., Ltd.) in a base cloth with a mesh structure for improving the diffusion rate, as shown in Fig.11. The same continuous nitrification/denitrification experiment was then carried out. Table 5 shows a summary of this experiment. From Runs I to III, under a constant influent T-N concentration of 200 mg/l, HRTs were gradually decreased to 23, 15 and 12 hours. High nitrification efficiencies of about 80% was obtained but T-N removal efficiencies were at a low level of about 24%, with no relationship to HRT. On the other hand, the TOC removal efficiencies averaged 82 to 93%. From these results, we concluded that the lack of an H-donor was the main reason for failure of denitrification. Influent TOC concentrations (Inf.TOC) contained in the synthetic dye wastewater were then increased stepwise under an HRT of 12 hours in Runs IV and V. As a result, we were able to achieve averages of 35% and 56% denitrification efficiencies under Inf.TOCs of 270 mg/l and 450mg/l, respectively, at an HRT of 12 hours. Moreover, an average denitrification efficiency of about 77% was obtained with decreasing influent loading rate by increasing the HRT to 19 hours and the Inf.TOC to 450 mg/l (Run VI). In this experiment, T-N removal rates were obtained 0.22 and 0.20 kg/m^3/day at HRT of 12 hours and 19 hours, respectively. These T-N

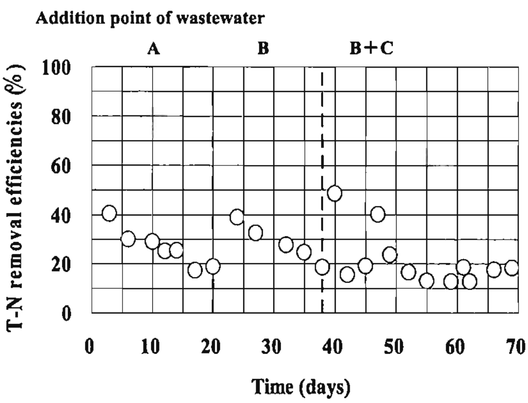

Fig. 9 Time courses of TN removal efficiencies during continuous treatment of synthetic dye wastewater using acrylic pile fabrics (Pile-H-36) as biomass carriers

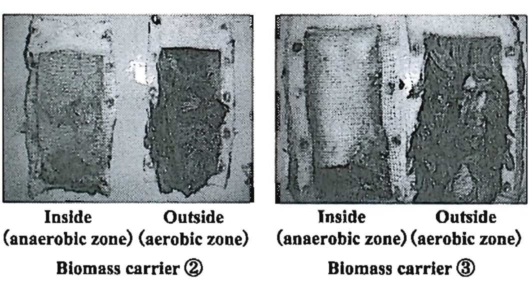

Fig. 10 Photographs of biomass carriers at the end of experiment

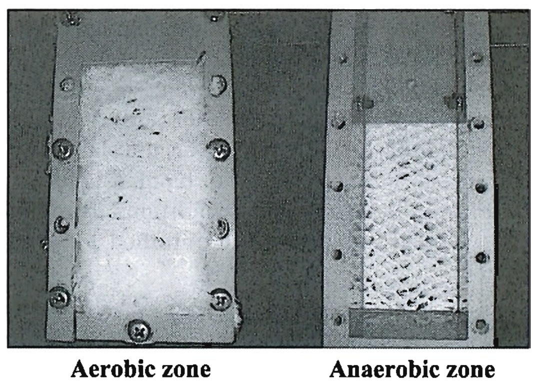

Fig. 11 Photographs of biomass carriers (Pile–I) for continuous nitrification and denitrification treatment

Table 5 Results of continuous nitrification and T-N removal efficiencies using acrylic pile fabrics (Pile–I) as biomass carrier

RUN	HRT (hrs)	Influent TOC (mg/l)	Nitrification efficiencies (%)	T-N removal efficiencies (%)	TOC removal efficiencies (%)
I	23	210	84	24	93
II	15	210	82	23	93
III	12	210	77	24	82
IV	12	270	81	35	93
V	12	450	82	56	96
VI	19	450	99	77	95

Average Influent T-N = 200 mg/l

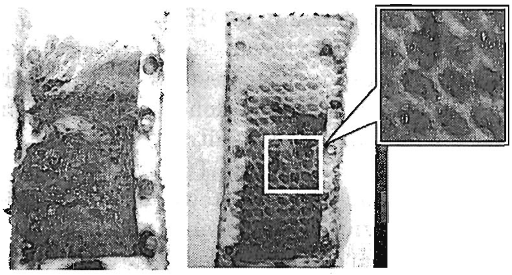

Fig. 12 Photographs of biomass carriers (Pile-I) at the end of continuous nitrification and denitrification treatment

removal rates were higher than that of 0.11 kg/m^3/day at HRT of 1.3 days using nonwoven biomass carriers in our previous studies[9]. At the end of this experiment, the sludge attached on the surface of Pile-I was observed. Fig. 12 shows photos of the biomass carriers on which activated sludge was attached. We observed that the sludge was attached on the surface of aerobic pile fabrics outside of the biomass carrier unit. On the other hand, little biomass accumulated on the mesh base inside the biomass carrier unit and high diffusion conditions through the pile were able to be maintained for long periods.

CONCLUSIONS

The following conclusions were obtained from the study:

(1) Biomass carriers containing acrylic fiber retained slow growing nitrifying bacteria. The length of the pile should be as long as possible to obtain a large height corrugation.

(2) The specific NOx–N production rate using the acrylic pile fabric Pile–H–36 was 3.4 times higher than that of MB–T9–P and reached 20.1 g–NOx–N/m^2/day. About 75% nitrification efficiencies were obtained under a T–N loading rate of 0.5 kg–N/m^3/day and a HRT of 10 hours during continuous nitrification using acrylic pile fabrics.

(3) During nitrification/denitrification treatment using acrylic pile fabrics, clogging and consequent poor diffusion were observed inside the biomass carrier. The elimination of clogging is essential to achieve stable nitrogen removal in this treatment process.

(4) Continuous nitrification/denitrification experiments were carried out using acrylic pile fabrics in a base cloth with a mesh structure to improve the diffusion rate. There was little biomass accumulation on the pile fabric surfaces, so a high diffusion rate through the pile was maintained for long periods. Denitrification efficiencies of 56 and 77% were achieved with an Inf. TOC of 450 mg/*l* and HRTs of 12 and 19 hours, respectively.

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