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NITRIFICATION TREATMENT OF AMMONIUM POLLUTED HANOI GROUNDWATER USING A SWIM-BED TECHNOLOGY

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ABSTRACT

Ammonium removal by swim-bed attached immobilized nitrifier using a novel acryl-fiber carrier (commercial name is biofringe) material was carried out to investigate the effective treatment of Hanoi groundwater, which is contaminated by high level of ammonium. The ammonium removal efficiencies of 95-100% at volumetric loading rates up to 0.24 kg N/m³/d and hydraulic retention time (HRT) as short as 3 hours on the first period of 45 days were obtained in this study. The maximum biomass carrying capacity of biofringe and the effect of operation conditions such as temperature, pH, DO, alkalinity, etc. on the maximum acceptable ammonium loading of the reactor and ammonium removal efficiency were investigated. Ammonium was converted to nitrate in this process, effluent nitrite was closed to zero, pH in the reactor was changed between 6.9 and 7.5, the alkalinity consumption per unit of NH₄-N nitrified to NO₃-N ranged from 6.5 to 7.5 mg CaCO₃, the DO requirement was higher than 3 mg/l for the complete removal of applied ammonium at HRT of 3 hours, the effluent suspended solid was less than 20mg/L.

KEYWORDS

Ammonium removal, biofringe, groundwater, nitrification, swim-bed

INTRODUCTION

Groundwater, the main source for Hanoi water supply is presently contaminated by ammonium with concentration up to 30 mg-N/L. However the effectiveness of ammonium removal efficiencies are very low in the most of water supply treatment plants applying aeration, sedimentation, filtration and chloramine disinfections. Analytical results, that have done by the Center for Environmental Engineering of Towns and Industrial Areas (CEETIA) in 2000, showed that efficiencies of ammonium removal are very low at the water treatment plans where the groundwater sources have high concentrations of ammonium and iron, which are located mainly in the southern part of Hanoi (Nhue T. H. et al., 2001). Ammonium concentration in Hanoi tap water is commonly exceeded the limitation value of 1.5 mg/L set by the Vietnamese drinking water standard and WHO guide line for drinking water. (WHO, 2000)

Nitrification is the first step of nitrogen removal generally performed by autotrophic microorganisms and carried out by two different consecutive microbial processes. Ammonium is converted first to nitrite due to its oxidation by ammonia oxidizers such as *Nitrosomonas* spp., then nitrite oxidizers as *Nitrobacter* spp. converts nitrite to nitrate on second stage. Ammonia and nitrite oxidizers are aerobic and autotrophic bacteria and characterized by low specific growth rates (Watson et al., 1989).

This study focused on the potential of ammonium removal from Hanoi groundwater contaminated with high ammonium concentration of 30 mg NH₄-N/L by using a novel acryl resin fiber material as

biomass carrier called biofringe (BF) on continuous flow treatment. Newly developed swim-bed attached-growth process was applied on this study. There are some advantages of fixed-bed attached-growth processes over suspended-growth processes such as the longer retention time of biomass, thus making high hydraulic loadings possible, good effluent quality can be obtained without sludge recycle. Swim-bed attached-growth processes can also retain slow growing nitrifiers and control the clogging problem. These advantages enable for ammonium removal from groundwater containing high level of iron. The clogging problem due to iron hydroxide precipitation will be serious problem for water treatment.

The objectives of this research were:

- 1) To determine the maximum acceptable loading rate applicable to biological nitrification BF reactor.
- 2) To investigate optimal environmental conditions for sludge attachment and its retention capacity and,
- 3) To determine the maximum influent iron concentration affecting ammonium removal efficiency.

MATERIALS AND METHODS

Experimental set-up

The biomass carrier

The biomass carrier was a novel biofringe material. The material is composed of 3 mm diameter fringe yarns (NET Co. Ltd., BF-18) attached to a support filament as shown in Fig 1. The staple fiber of fringe yarns was a hydrophilic acrylic composite. Fringe yarns can move on the continuous flow, which flow through the reactor, so that biofringe material could retain nitrifiers with high growth rate.

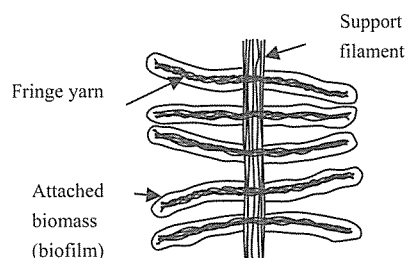


Fig. 1. Configuration for biomass carrier

The seed sludge

BF reactors were initially seeded with activated sludge that has been cultivated by fill and draw method under total oxidation conditions using a synthetic medium containing peptone and meat extract (Table 1) as the carbon, nitrogen and phosphorous sources.

Table 1. Synthetic medium composition for attached sludge culture

Composition	Influent concentration (mg/L)	Composition	Influent concentration (mg/L)
Peptone	240	CaCl ₂ .2H ₂ O	2.85
Meat extract	160	MgSO ₄ .7H ₂ O	3.0
NaCl	1.5	NaHCO ₃	63
KCl	2.1		

The synthetic groundwater

Table 2. Composition of synthetic ground water (mix in tap water)

Composition	Concentration (mg/L)	Source	Composition	Concentration (mg/L)	Source
NH ₄ -N	30	NH ₄ Cl	Ca	25	CaCl ₂ .2H ₂ O
NO ₃ -N	3.2	NaNO ₃	Mg	13	MgCl ₂ .H ₂ O
SO ₄ ²⁻	2.8	tap water	Na	35	tap water
SiO ₂	30.9	tap water	K	5.7	tap water
Fe (II)	0-18	FeCl ₂	Alkalinity	200 – 250 (as CaCO ₃)	NaHCO ₃

Synthetic groundwater used in this study was similar in composition with the polluted groundwater of Hanoi as shown in Table 2. This composition was based on the analytical results of groundwater in Hanoi area carried out by Hanoi Clean Water Business Company from 1994-2000.

Reactors description and operational conditions

Fig. 2 shows the schematic diagram of the experimental system. The two reactors used in this study were made from acrylic resin and have the same size, one for single biofinge layer (SBF), and the other for double biofinge layers (DBF) with higher finger yarn density. The reactors have downdraft and updraft sections in a parallel upright arrangement with cross-sectional area of downdraft and updraft sections of 100x100 mm and 100x25 mm, respectively. The height from bottom to outlet is 630 mm and then a total liquid volume is 7.7 liter. The reactors had the biofinge reaction zone of 530 mm and clear zone of 70 mm at the bottom and 30 mm at the top, approximately. Influent was fed within the downdraft section by using a peristaltic pump. Air was applied near the base of the updraft section for mixing and oxygenating the synthetic groundwater while circulating it through the reactor. The reactors were operated at room temperature of 25°C. The alkalinity and pH of influent were regulated by addition of NaHCO₃ solution. Bicarbonate was functioned as inorganic carbon source as well as the buffer.

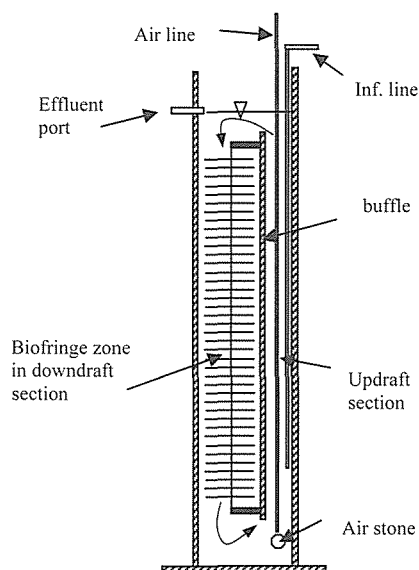


Fig. 2. Schematic diagram of the experimental system.

The SBF reactor was operated in the first period of study to determine maximum acceptable loading rate and optimal environmental conditions for sludge attachment and its retention capacity. Then the DBF reactor, which can encapsulate higher amount of organisms within biofinge was started up to investigate the stable operation at higher loading rate and the protective capacity from toxic shocks and adverse environmental condition such as temperature, etc. The experimental condition and average nitrification efficiency of SBF reactor in each phase are detailed in Table 3.

Table 3. Experimental condition and nitrification efficiency of the SBF reactor

Phase (day)	HRT (hours)	VLR* (kg NH ₄ -N/m ₃ .d)	Air flow rate (L/min)	Ammonium removal rate (%)	Nitrification efficiency (%)
A (0-40)	18-4	0.04-0.18	2	95.23±6.00	93.51 ± 6.34
B (40-54)	3	0.24	2	95.56±4.46	92.63 ± 7.40
C (54-71)	3	0.24	1	89.34±8.61	79.54 ± 8.43
D (71-81)	6	0.12	2	72.64±6.84	52.62 ± 8.18
E (81-101)	4	0.12	2	85.37±4.69	41.56 ± 4.98

VLR*: Volumetric loading rate

Batch experiment

For the determination of kinetic parameters as well as evaluation nitrification capacity of sludge from swim-bed attached-growth process, batch nitrification experiment was conducted at 25°C in 1 liter flasks equipped with initial VSS of 475 mg/L. Excess amount of oxygen was supplied for complete mixing and oxygenating using air pump. Sludge used for batch experiments were detached from biomass after long operation in swim-bed nitrification process using biofinge.

The medium used for batch experiments contained 190.8 mg NH_4Cl (50 mg $\text{NH}_4\text{-N/L}$). Tap water was used for influent dilution water and a source of mineral substrate. 500 mg of NaHCO_3 was added to the influent. Mixed liquor samples taken every hour were analyzed for water quality. Biomass were rejected by using centrifugation with 3,000 rounds per minute for 10 min before analyzing.

Analytical methods

Sludge retention capacity of BF and biomass concentration were estimated by SS, MLSS and MLVSS, respectively.

According to Standard methods for examination of water and wastewater, nitrate was determined by using the UV spectrophotometer screening method, nitrite by the colorimetric method, alkalinity by the titration method. NH_4^+ was determined by OPP method (Jota Kanda, 1995), the pH level was measured using a pH meter (320 TOLEDO). Dissolved oxygen (DO) was measured using DO meter (HORIBA).

RESULTS AND DISCUSSION

The attachment of sludge

The SBF reactor was started on the first stage of our study. In the start up period, 15.4 g of activated sludge was placed in the reactors, then tap water was added to get an initial total sludge concentration of 2.0 g/L. Air flow was set at 2 L/min to circulate the solution through the reaction zone, at a velocity of 11.0 cm/sec.. Attachment of sludge on the biofringe material, which was determined by the decrease in MLSS concentration has proceeded as shown in Fig. 3. The attachment of sludge during a 32 hours period was 8.9 g. This corresponds 17.8 g/m of biofringe support filament in SBF reactors, corresponding to 1.14 g $\text{MLSS/L}_{\text{reactor}}$

Ammonium removal capacity

Following the sludge attachment period, influent was introduced with an initial $\text{NH}_4\text{-N}$ concentration of approximately 30 mg/L. Previous study on nitrification of Hanoi groundwater contaminated $\text{NH}_4\text{-N}$ using fixed-bed attached-growth process (Furukawa K. et al., 2003) reported that nitrification process was inhibited completely by existence of iron at concentration of 18 mg/L. So that, synthetic groundwater

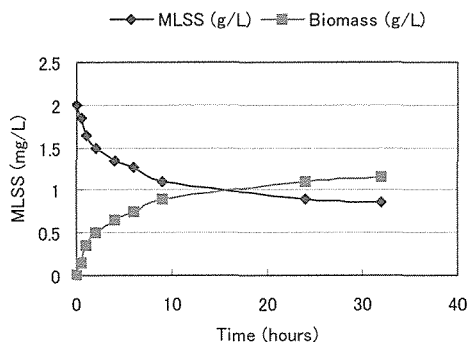


Fig. 3. Attaching profiles of activated

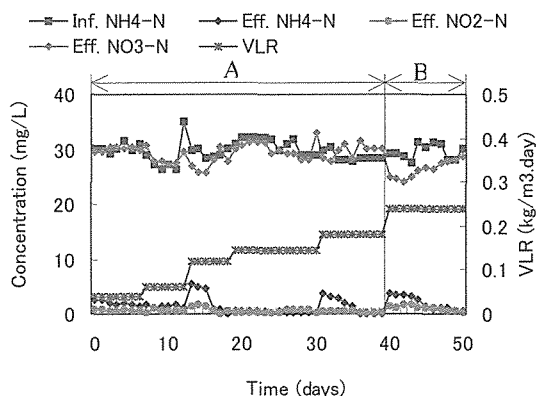


Fig. 4. Changes in influent $\text{NH}_4\text{-N}$, loading rate and effluent $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ in phase A and B

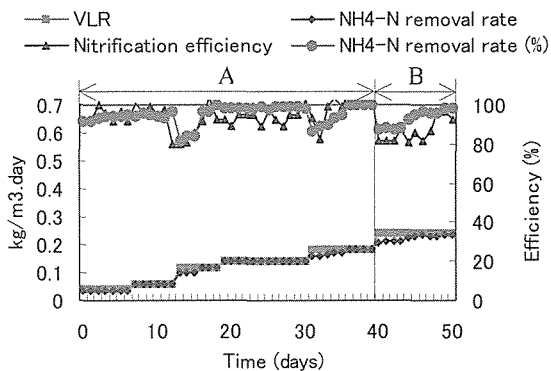


Fig. 5. Changes in VLR, ammonia removal rate and nitrification efficiency in phase A and B

without iron was used in this study. By stepwise reduction of the hydraulic retention time (HRT), the ammonium removal rate of SBF reactor reached to 0.24 kg N/m³/day and a stable treatment from day 45 was achieved. DO and water flow velocity were 5-6 mg/L and 11-12 cm/s through the reactor, respectively. Nitrification efficiencies ranged from 95-100% were obtained at HRT of 3 hours.

Fig. 4 and 5 show the results obtained from the first 50 days. NH₄-N was converted to NO₃-N in this process, effluent NO₂-N concentration was closed to zero and effluent suspended solid (SS) concentrations were less than 20/L. The color of biomass was changed from light brown of initial seeding sludge to brown orange. Ammonium removal rate as high as 0.24 kg-N/m³/day was maintained after short period of 45 days, with specific nitrification rate, which estimated from the continuous experiment of 10 mg-N/mg MLSS/hour. These experimental results means that biofringe as biomass carrier could retain active nitrifiers.

Variation in pH and alkalinity

Stoichiometry of nitrification process shows that the oxidation of ammonium produces hydrogen ions in a ratio 2 moles per 1 mole of NH₄⁺, i.e. pH decrease is inevitable for ammonium oxidation. Alkalinity presents in solution as inorganic source and buffer. The results are shown in Fig. 6. In this experiment the alkalinity consumption per mg of NH₄-N nitrified to NO₃-N ranging from 6.5 to 7.5 mg CaCO₃ (7.1±0.6) was measured. This was in accordance with values being reported from previous studies (Villaverde S. et al., 1996). pH values were 6.9 to 7.5 through the reactor. Previous studies have been reported that the range of pH of 7-8 is optimum pH for nitrification (Painter at al., 1983, Antonious at al. 1990). It was clear that with the Hanoi groundwater alkalinity of 200-230 mgCaCO₃/L is enough for nitrification process.

DO influence

In order to study the DO influence over swim-bed nitrification process, air flow was reduced to 1 L/min from day 54. DO reduced to 3.0 mg/L and water flow velocity through the biofringe zone reduced to 9.0 cm/s. Ammonium removal rates and nitrification efficiencies were decreased from day 59 and reduced sharply to 66 and 62% at day 71 with effluent NH₄-N and NO₃-N were 9.5 and 17.42 mg/L, respectively. Effluent SS was increased to 80 mg/L in this period and alkalinity consumptions were decreased, pH in reactor was increased to 7.8 to 8. Results are shown in Fig. 7, 8. It should be pointed out that swim-bed immobilized attached nitrification process was inhibited at DO concentration of 3.0 mg/L, which was in accordance with the reports by other authors (Hem et al., 1994 and Rasten, 2000). However, our obtained results was slightly different with another reports, in which optimum minimum DO concentrations for nitrification process were experimentally determined to 2.0~2.5 mg/L (Bitton G., 1999, Yoo K. at al., 1999), and 1.7 mg/L (Ruiz G., at al., 2002). This means that DO concentration lower than 3.0 mg/L and low flow velocity in the biofringe zone may cause substrate diffusion limitation. That is the thick biomass layers attached on biofringe caused the low oxygen environment in the inner part of biomass, so that nitrifiers were inhibited, then were detached from biofringe. It was supported by the fact of

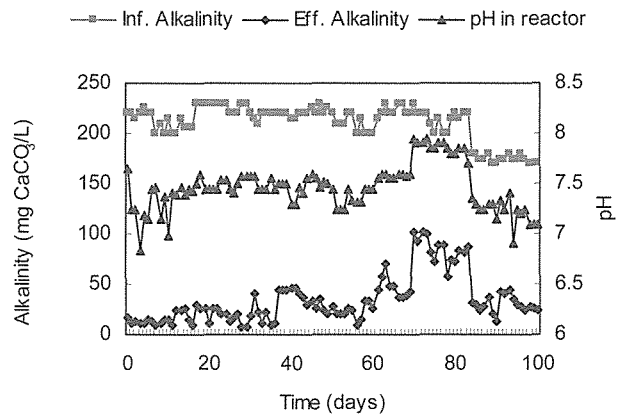


Fig 6. Changes in influent, effluent alkalinity and pH through the reactor

higher effluent SS and insufficient biomass to cope with the high loading rate resulted in the decrease of nitrification efficiencies and ammonium removal rates.

Explanation for nitrite accumulation

In order to recover nitrification efficiency, air flow rate was increased again to 2 l/min from day 72. Ammonium loading rate was reduced to 0.12 kg-N/m³/day by increasing HRT to 6 hours. DO reached 6 mg/L through the whole reactor. Ammonia removal rates increased gradually up to 83% but nitrification efficiency was still 34.8% at day 81. Nitrite accumulation was occurred and effluent SS concentration were at high level of 20-40 mg/L. The reason of this result might be caused by the low growth rate of nitrite oxidizing bacteria under high pH of 7.5-8.0. This observation also might be caused by nitrite oxidizers inhibition by free ammonia. According to Ford's equation, free ammonia concentrations from 71 was calculated to 0.21-0.36 mg/L. Previous researches have reported that at free ammonia whose concentration greater than 0.1-1.0 mg/L could inhibit nitrite oxidizers (Athonisen et al.,1976, W. Bae et al., 2001). To clarify whether inhibition of nitrite oxidizers by free ammonia or lack of nitrite oxidizers caused nitrite accumulation in reactor, alkalinity was reduced to 180 mg CaCO₃/L from day 81. Reactor pHs were decreased to 7~7.4 and the free ammonia were decreased to less than 0.1 mg/L. Nitrification efficiencies were still at low level of 34-40%. These results were shown in Fig. 7 and Fig. 8. It could be explained that nitrite accumulated in reactor was caused by low population of nitrite oxidizers remaining within reactor, indicated by high concentration of effluent SS in phase D and continuous low nitrification efficiency and nitrite accumulation trend in phase E.

Batch experiment

The Monod type model was applied for the analysis of our obtained nitrification treatment results to determine the specific ammonium removal rate or nitrification rate. Data from batch experiments are shown in Fig. 9 and linear Monod plots from these data as shown in Fig. 10 and 11. Specific maximum ammonium removal rate V_m and saturation constants K_N were determined to:

$$V_m = 1.19 \text{ mg-N/mg VSS/day and } K_N = 2.19 \text{ mg NH}_4\text{-N/L}$$

The obtained V_m of sludge taken from swim-bed attached-growth nitrification process by using biofringe was at high value compare with results founded from previous studies of 0.28 to 1.44

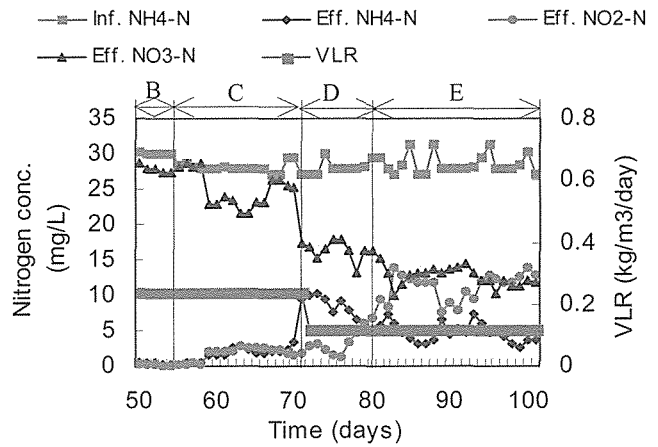


Fig. 7. Changes in influent NH₄-N, loading rate and effluent NH₄-N, NO₂-N, NO₃-N in phase C, D and E

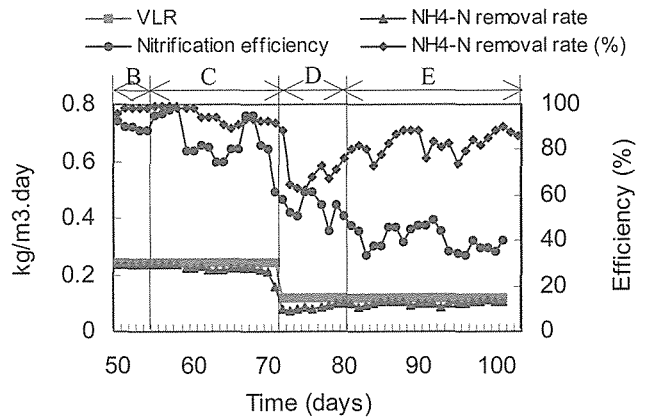


Fig. 8. Changes in nitrification efficiency and ammonia removal rate in phase C, D and E

(day⁻¹) for nitrite oxidizers. Nitrite concentrations from all samples were as small as 0.05-0.1 mg N/L, which indicated that nitrite oxidizers have a high activity and sufficient amount. It was also pointed out that nitrite oxidizers in this experiment was not inhibited by free ammonia at concentration of 6.43 to 3.56 mg/L during the first hour of batch experiment, corresponded with ammonium concentration of 50 to 27.8 mg/L.

CONCLUSIONS

NH₄-N removal by swim-bed attached immobilized nitrifiers using a novel biofringe material was studied to investigate the effective treatment of Hanoi groundwater, which is contaminated by high level of ammonia. Nitrification efficiencies of 95-100% were obtained at volumetric loading rate up to 0.24 kg NH₄-N/m³.d and HRT as shorts as 3 hours.

Alkalinity consumption of 7.1 mg as CaCO₃ per mg of NH₄-N oxidized to NO₃-N and pH from 7-7.5 were observed. This means that there is no requirement of adding inorganic carbon source and buffer to the Hanoi groundwater (200-230 mg/L of alkalinity).

Nitrification efficiency was decreased at low DO concentration of 3.0 mg/L.

The sludge from BF reactor showed a high nitrification activity. Maximum ammonium removal rate and saturation constant were determined to be 1.19 mg-N/mg VSS/day and 2.19 mg NH₄-N/L, respectively.

Further studies are going on now with DBF reactors to continue to determine the maximum loading rate and maximum influent iron concentration affecting ammonium removal efficiency as well as investigate the protection capacity of reactors from toxic shocks and adverse environmental condition.

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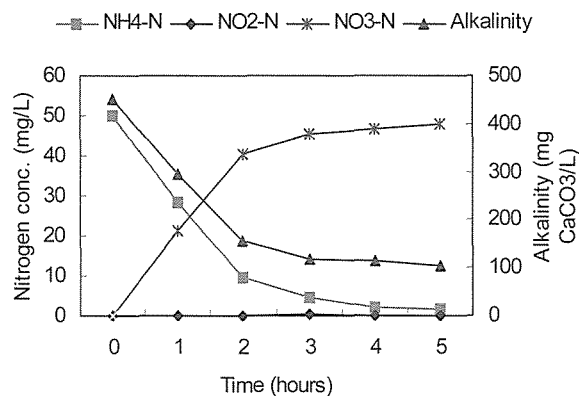


Fig. 9. Change in NH₄-N, NO₂-N, NO₃-N and alkalinity in batch experiment.

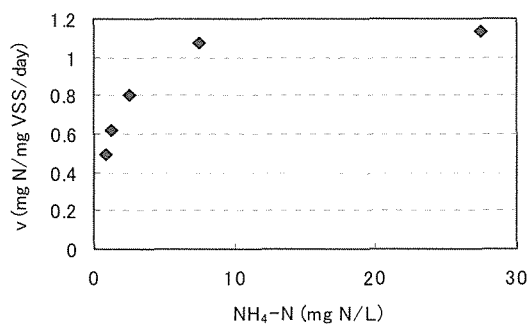


Fig. 10. Specific ammonium removal rate as function of NH₄-N

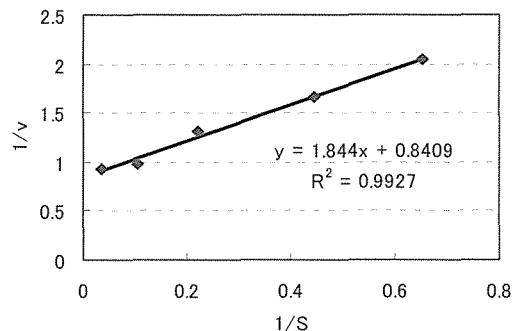


Fig. 11. Linear curve of Monod kinetics.

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