

Biological nitrogen removal from industrial wastewater discharged from metal recovery processes

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Abstract The wastewater generated from the processes of recovering precious metals from industrial wastes contains high concentrations of acids and alkalis such as nitric acid and aqueous ammonia, and of salts such as sodium chloride and sodium sulfate. Biological nitrogen removal from this wastewater was attempted by using a circulating bioreactor system equipped with an anaerobic packed bed and an aerobic three-phase fluidized bed. As a result of acclimating microorganisms with change of the hydraulic residence time, this system effectively removed nitrogen from diluted wastewater (T-N: from 2,000 to 4,000 g/m³), such that the total nitrogen concentration in the effluent met the sewage discharge control criteria in Japan (240 g/m³). The removal ratio of total nitrogen was 90% to 98% and that of ammonia was 80% to 92%. In addition, the characteristic equations for biological treatment were applied to this system on the assumption that both reactions of denitrification in the anaerobic reactor and nitrification in the aerobic reactor can be approximated to a first-order reaction. This simplified approach successfully led to a new analytical method for simulating the optimum volume ratio of anaerobic reactor to aerobic reactor for minimizing the total hydraulic residence time.

Keywords Biological nitrogen removal; denitrification; nitrification; metal recovery process

Introduction

Some industrial wastes such as printed circuit boards contain precious metals e.g. gold, silver, platinum and palladium. Recovery of the precious metals is necessary for best utilization of natural resources and the reduction of the amount of industrial wastes. However, large amounts of waste acid (aqua regia, nitric acid and hydrochloric acid) and alkali (aqueous ammonia) are generated from the metal recovery processes. In order to protect ponds and lakes from eutrophication, a discharge regulation of nitrogen compounds in wastewater has become stricter in many countries including Japan. Thus, it is necessary to develop and establish an appropriate method for removing nitrogen from the metal processing wastewater.

Recently, extensive studies on biological nitrogen removal from industrial wastewater were made. For example, Hirata *et al.* (1989) removed ammonia nitrogen from synthetic wastewater discharged from coke furnace; Fang *et al.* (1993) removed ammonia nitrogen from refinery wastewater. However, concentrations of ammonia nitrogen in those wastewaters were very low. Gupta and Sharma (1996) removed Kjeldahl nitrogen (KN) from diluted wastewater discharged from a urea plant using continuous flow stirred reactors, and obtained an ammonia nitrogen removal ratio of 96.6% (at NH₄-N: 250 g/m³/d) and a total KN removal ratio of 99.0% (at NH₄-N: 250 g/m³/d, urea-N: 250 g/m³/d). Bernet *et al.* (1996) carried out the denitrification of high-concentration synthetic wastewater (NO₃-N: 33.9 kg/m³) mixed with a wine distillery effluent as an example of industrial carbon source and obtained a denitrification rate of 21.9 kg/m³/d. Although they obtained high nitrification or denitrification rates, treatment of wastewater with high salinity has not yet been attempted by any of the above researchers.

Most of the wastewaters used in the previous studies described above were synthetic wastewaters. In contrast, the target wastewater in this study is actual wastewater exhausted

from the recovery process of precious metals from industrial wastes. This wastewater has high salinity and contains various base metals as well as high concentrations of nitrogen. Vredendregt *et al.* (1997) investigated the effect of salt concentration (up to 3.4 wt%) on the nitrification ability of microorganisms, and showed that the nitrification ability was greatly decreased when salt concentration exceeded 2.3 wt%. Yang *et al.* (1995) investigated the effect of salt concentration on the denitrification ability of microorganisms and demonstrated that over 2 wt% of sodium chloride greatly reduced denitrification rate. In view of previous reports regarding negative effects of high salinity on microorganism activities, biological treatment of the industrial wastewater used in this study is considered to be quite difficult. Nevertheless, we attempt a biological nitrogen removal on the assumption that microorganisms can be acclimated to a severe environment by exposure for long periods of time. In addition, since nitrifying and denitrifying bacteria have different sensitivity to salinity in wastewater, it is practically important to carry out analytical investigations on the volume ratio of anaerobic reactor to aerobic reactor for nitrogen removal from high-salinity industrial wastewater.

The objectives of this study are to establish a biological treatment system capable of removing nitrogen from industrial wastewater discharged from metal recovery processes in order to meet the sewage discharge control criteria in Japan (T-N: 240 g/m³) and to establish a practical estimation method for optimization of reactor design and operational conditions.

Material and methods

Experimental system

In this study, two series of anaerobic-aerobic circulating bioreactor systems (System A and System B) were used. Figure 1 shows the schematic diagram of this experimental system. This system consisted of four tanks: an anaerobic reactor (System A: 2 L, System B: 3 L), the first sedimentation tank (1 L), an aerobic reactor (1 L) and the second sedimentation tank (1 L). Effluent wastewater of the second sedimentation tank was circulated into the anaerobic reactor using a tubing pump. The volume of the circulated wastewater was adjusted such that it was fourfold that of the influent. The anaerobic reactor was packed with sponge cubic medium (56 vol%, cubic sides: 12 mm). The aerobic reactor was a completely mixing three-phase fluidized bed reactor where poly(vinylalcohol) particles coated with activated carbon (22 vol%, 1–2 mm diameter) were used as fluidizing media. The hydraulic residence time (HRT) was changed according to the treatment ability of this system.

Characteristics of wastewater

The wastewater used in this study was exhausted from a factory that recovers precious metals from industrial wastes. This wastewater will hereafter be referred to as “metallurgic wastewater”. This wastewater commonly contains high concentrations of ions such as Na⁺, K⁺, Ca²⁺ and Cl⁻ as well as several kinds of metal ions such as Cu²⁺, Zn²⁺, Pb²⁺ and Fe²⁺. However, the wastewater properties such as components and concentrations changed from time to time. In this study, from two- to fivefold diluted metallurgic wastewater was supplied to the reactor to control inlet T-N. Sodium acetate or acetic acid was added to the inlet solution as a carbon source for denitrification. The properties of the inlet solution were T-N: 3,100±1,300 g/m³, NO_x-N: 2200±1200 g/m³, NH₄-N: 800±500 g/m³, DOC: 1900±1200 g/m³ (C/N=1–1.5).

Seeding sludge

A seeding sludge for the anaerobic reactor was collected from the ditches in a factory treating photographic processing wastewater and metallurgic wastewater, and was acclimated

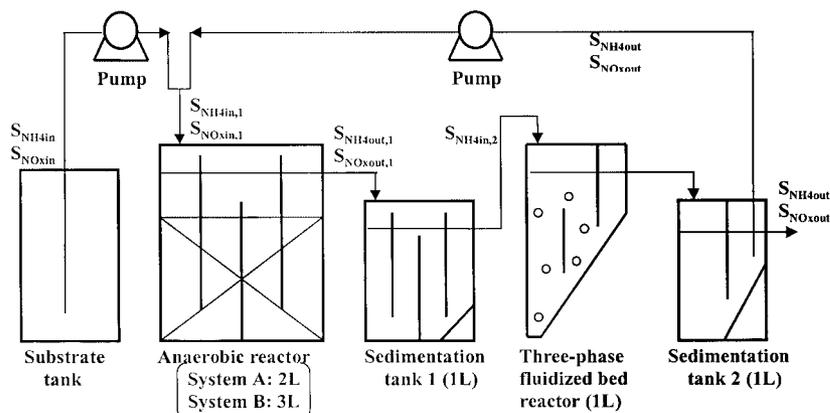


Figure 1 Schematic diagram of experimental system

in diluted metallurgic wastewater for five months. To obtain seeding sludge for the aerobic reactor, a mixture of microorganisms was acclimated in metallurgic wastewater while its concentration increased gradually.

Analytical method

All samples were filtered before water quality measurements. All measurements were carried out according to the Standard Methods for Examination of Wastewater published by the Japan Sewage Works Association. Total nitrogen concentration was measured by the ultraviolet absorbance method (spectrophotometer: HITACHI 150–20 at 220 nm) after oxidation with potassium peroxodisulfate. Concentrations of nitrate and nitrite ions were measured with HPLC (column: TOSOH IC-Anion-PW, detector: TOSOH UV-8011 at 230 nm). Ammonia concentration was measured with an ammonium electrode (DKK 7161). DOC was measured with a TOC meter (Shimadzu TOC-500).

Results and discussion

Figure 2 shows concentration changes of T-N, $\text{NO}_x\text{-N}$ and $\text{NH}_4\text{-N}$ in the influent and effluent of each reactor with time. The concentration of $\text{NH}_4\text{-N}$ in the anaerobic reactor was lower than that at the inlet, not because of nitrification in the anaerobic reactor but because of dilution caused by the circulation. After 180 days, the T-N value of the effluent became stable. Nevertheless, it was much higher than the level stipulated by sewage discharge control criteria in Japan (240 g/m^3). In order to meet the sewage discharge control criteria, the hydraulic residence time (HRT) of both systems (System A and System B) was extended by ten times (10 days in aerobic reactor). About 10 days after this operation, the T-N values of the effluent of both systems met the sewage discharge control criteria. From day 331, inlet wastewater whose T-N concentration was $4,000 \pm 400 \text{ g/m}^3$ ($\text{NO}_x\text{-N}$: $2900 \pm 300 \text{ g/m}^3$, $\text{NH}_x\text{-N}$: $900 \pm 80 \text{ g/m}^3$) was supplied. The effluent was nevertheless kept below the sewage discharge control level. From day 423, HRT was reduced to 6.7 days (in the aerobic reactor). After that, the concentration of T-N in the effluent increased to about 100 g/m^3 , and then stabilized at about 50 g/m^3 , where T-N consisted mainly of $\text{NH}_4\text{-N}$ (see Figures 2 (b) and (c)). HRT was further reduced to 5 days (in the aerobic reactor) at day 593. The concentration of $\text{NO}_x\text{-N}$ in the effluent remained at zero (Figure 2 (b)), while that of $\text{NH}_4\text{-N}$ gradually increased within 50 days to reach about 200 g/m^3 at day 654 (Figure 2 (c)). However, in the same manner as before, it began to decrease and became stable. Maximum T-N volumetric removal rate in the anaerobic reactor was $0.24 \text{ kg/m}^3/\text{d}$ and nitrification

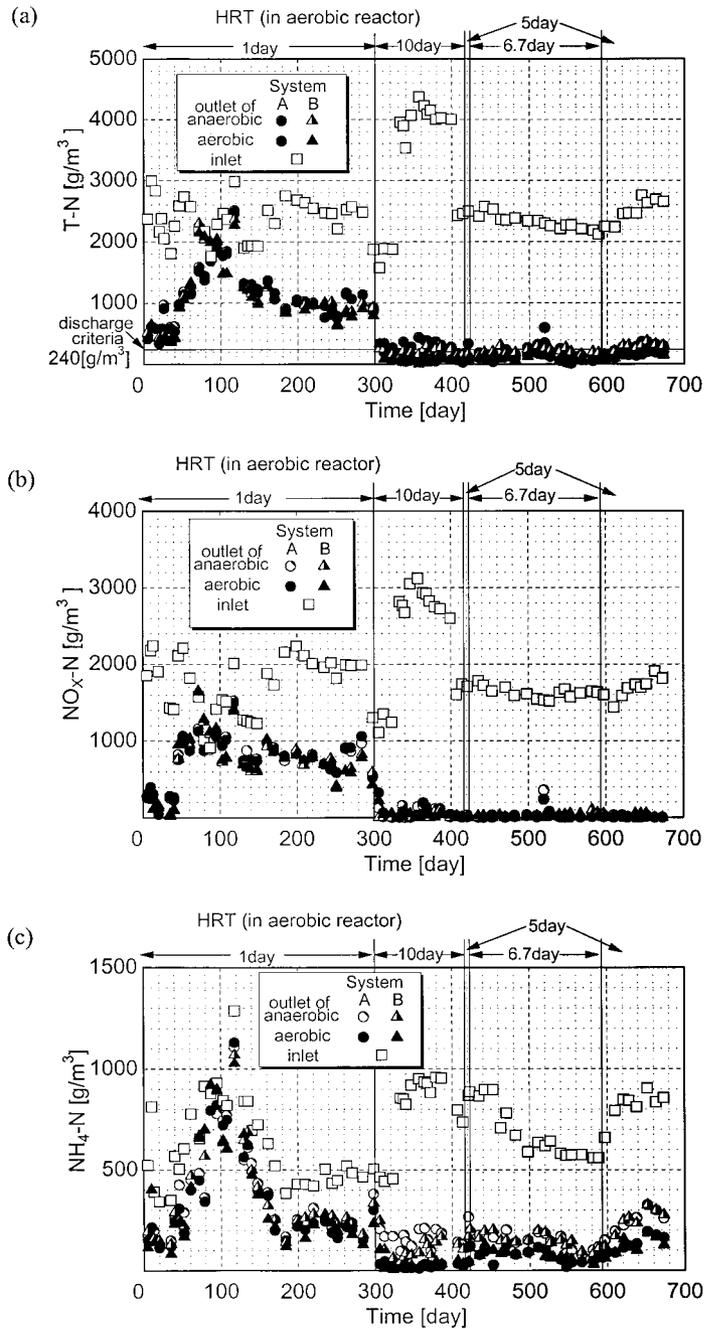


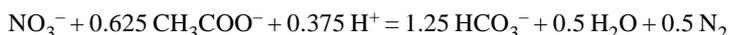
Figure 2 Nitrogen concentration changes with time. (a) T-N; (b) NO_x-N; (c) NH₄-N

rate in the aerobic reactor was 0.14 kg/m³/d. The removal ratio of total nitrogen was 90% to 98% and that of ammonia was 80% to 92%.

On the whole, when HRT was reduced, the concentration of NH₄-N in the effluent increased for a while and after that, it gradually decreased. This means that nitrification efficiency in the aerobic reactor was lower until microorganisms became acclimated to the loading changes (HRT and wastewater quality). In contrast, the concentration of NO_x-N in the effluent hardly changed. This means that denitrification ability in the anaerobic reactor

did not reach a maximum in this range of loading rate. As a result, the main component of T-N in the final effluent was $\text{NH}_4\text{-N}$, which indicated that overall nitrogen removal rate in this system greatly depended on the nitrification ability.

Figure 3 shows concentration changes of dissolved total organic carbon (DOC) in the influent and effluent of each reactor with time. While HRT was set at 1 day, denitrification was so unstable due to higher loading rate that the amount of DOC consumption largely fluctuated. However, after extending HRT to 10 days, denitrification was stabilised, which resulted in maintaining lower DOC concentration in the effluent of anaerobic reactors. In the stable period (day 300–day 676), the average stoichiometric ratio of $\text{NO}_x\text{-N}$ reduction to DOC consumption, i.e. C/N molar ratio in a denitrification step, was calculated as 1.35 and 1.32 for the systems A and B, respectively. A simplified stoichiometry for the energy-producing part of the denitrification reaction using acetate as electron donor can be expressed as follows.



From the above stoichiometric formula, the theoretical C/N molar ratio in the denitrification step can be calculated as 1.25. The difference between experimental and theoretical value of carbon source consumed during denitrification corresponded to the apparent sludge increase, which was relatively low probably due to lysis and hydrolysis during long retention in the anaerobic reactor.

Mathematical analysis

To estimate the performances of each reactor, the following mathematical analysis was made. The characteristic equations for biological treatment in the aerobic and anaerobic reactors are as follows (Hirata *et al.* (1988), Hirata and Noguchi (1994), Hirata and Meutia (1996)).

Anaerobic, plug flow, Monod type:

$$\frac{X_b V}{Q_l(S_{in} - S_{out})} = \frac{1}{Ku} + \frac{K_m}{K_u} \cdot \frac{\ln(S_{in} / S_{out})}{S_{in} - S_{out}} \quad (1)$$

Aerobic, completely mixing flow, Monod type:

$$\frac{X_b V}{Q_l(S_{in} - S_{out})} = \frac{1}{K} + \frac{K_m}{K_u} \cdot \frac{1}{S_{out}} \quad (2)$$

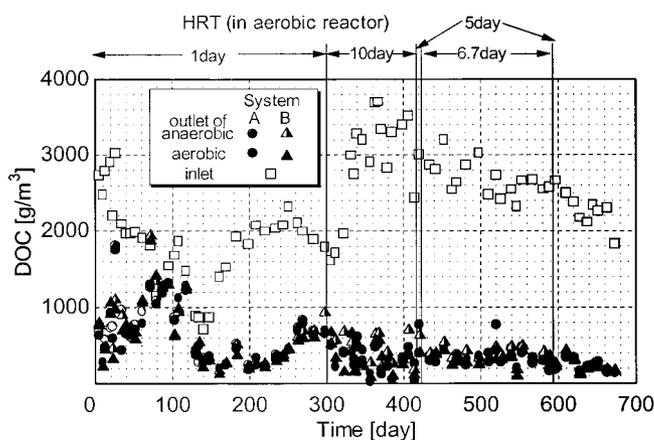


Figure 3 DOC concentration changes with time

S_{in} and S_{out} are inlet and outlet concentrations, Q_l is volumetric liquid flow rate, X_b is total density of microorganisms, V is volume of reactor, and K_u , K_m and K are characteristic coefficients. When Eqs. (1) and (2) are applied to nitrification and denitrification processes, respectively, Eqs. (3) and (4) are derived taking circulation into consideration.

$$\frac{\tau_1}{S_{NO_{Xin,1}} - S_{NO_{Xout,1}}} = \frac{1}{X_b K_u} + \frac{K_m}{X_b K_u} \cdot \frac{\ln(S_{NO_{Xin,1}} / S_{NO_{Xout,1}})}{S_{NO_{Xin,1}} - S_{NO_{Xout,1}}} \quad (3)$$

$$\frac{\tau_2}{S_{NH_{4in,2}} - S_{NH_{4out}}} = \frac{1}{X_b K} + \frac{K_m}{X_b K} \cdot \frac{1}{S_{NH_{4out}}} \quad (4)$$

τ_1 and τ_2 are the HRTs of anaerobic and aerobic reactors with consideration of circulation (against volumetric flow rate: $(1+R)Q_l$ where R is circulation ratio), $S_{NO_{Xin,1}}$ and $S_{NO_{Xout,1}}$ are inlet and outlet concentrations of NO_X -N in the anaerobic reactor, and $S_{NH_{4in,2}}$ and $S_{NH_{4out}}$ are inlet and outlet concentrations of NH_4 -N in the aerobic reactor. When characteristic coefficients: $K_A = K_m / (X_b K_u)$, $K_B = K_m / (X_b K)$, $K_C = 1 / (X_b K_u)$, $K_D = 1 / (X_b K)$ are defined, Eqs. (3) and (4) are transformed to Eqs. (5) and (6), respectively.

$$\frac{\tau_1}{S_{NO_{Xin,1}} - S_{NO_{Xout,1}}} = K_A \cdot \frac{\ln(S_{NO_{Xin,1}} / S_{NO_{Xout,1}})}{S_{NO_{Xin,1}} - S_{NO_{Xout,1}}} + K_C \quad (5)$$

$$\frac{\tau_2}{S_{NH_{4in,2}} - S_{NH_{4out}}} = K_B \cdot \frac{1}{S_{NH_{4out}}} + K_D \quad (6)$$

As plotted in Figures 4(a) and (b), K_A and K_B can be determined from the slope of the lines, and K_C and K_D can be determined from the intercept.

Figure 4(a) suggests that denitrification is approximated to a first-order reaction, and the slope decreases with decreasing HRT. The treatment ability improves as the slope decreases. In this present study, the slope of double-circular and double-triangular plots, K_A , is 0.6 d. Figure 4(b) shows that the major part of the plot except that at HRT=10 days follows a straight line. It is considered that 10 days was such a long HRT in the aerobic reactor that part of water was vaporized with aeration. Thus, if this experimental data was neglected, the first-order reaction can be also applied to nitrification, where the slope, K_B , is 1.0 d.

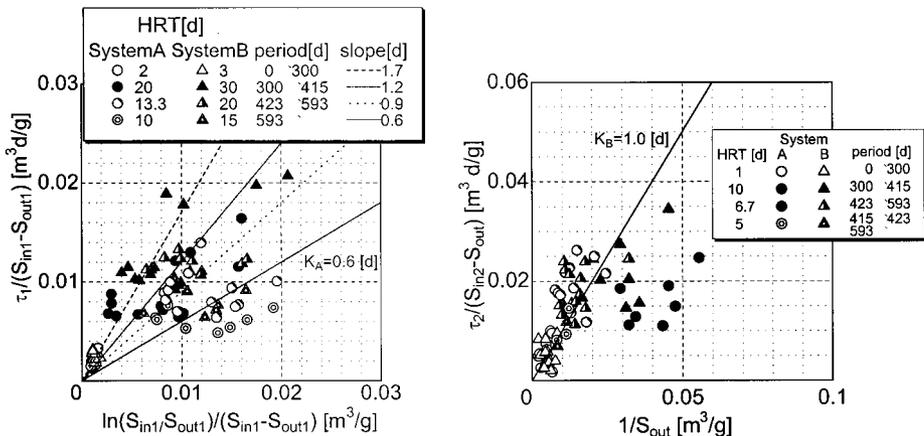


Figure 4 Evaluation of the characteristic coefficients of biological reaction rate (K_A and K_B). (a) anaerobic reactor; (b) aerobic reactor

To obtain the optimum volume ratio of anaerobic reactor to aerobic reactor, the following analysis was examined. The total HRT of this system is obtained using the following Eq. (7)

$$\tau_{total} = (1+R)(\tau_1 + \tau_2) = (1+R) \left(K_A \cdot \ln \frac{S_{NOXin,1}}{S_{NOXout,1}} + K_B \cdot \frac{S_{NH4in,2} - S_{NH4out}}{S_{NH4out}} \right) \quad (7)$$

Assuming that (i) T-N consists of only NO_X -N and NH_4 -N; (ii) denitrification occurs only in the anaerobic reactor; and (iii) nitrification occurs only in the aerobic reactor, $S_{NOXin,1}$, $S_{NOXout,1}$ and $S_{NH4in,2}$ are expressed as follows.

$$S_{NH4in,2} = S_{NH4out,1} = S_{NH4in,1} = \frac{S_{NH4in} + RS_{NH4out}}{1+R} \quad (8)$$

$$S_{NOXin,1} = \frac{S_{NOXin} + RS_{NOXout}}{1+R} = \frac{S_{NOXin} + R(S_d - S_{NH4out})}{1+R} \quad (9)$$

$$S_{NOXout,1} = S_d - S_{NH4out,1} = \frac{S_d(1+R) - S_{NH4in} - RS_{NH4out}}{1+R} \quad (10)$$

Here, S_d is T-N discharge control criteria. When Eqs. (8), (9) and (10) are substituted into Eq. (7), then, Eq. (11) is obtained.

$$\begin{aligned} \tau_{total} &= (1+R)(\tau_1 - \tau_2) \\ &= (1+R) \left(K_A \cdot \ln \frac{S_{NOXin} + R(S_d - S_{NH4out})}{S_d(1+R) - S_{NH4in} - RS_{NH4out}} + K_B \cdot \frac{S_{NH4in} - S_{NH4out}}{(1+R)S_{NH4out}} \right) \end{aligned} \quad (11)$$

Here, the HRT of each reactor is as follows.

Anaerobic reactor:

$$(1+R)\tau_1 = (1+R)K_A \cdot \ln \frac{S_{NOXin} + R(S_d - S_{NH4out})}{S_d(1+R) - S_{NH4in} - RS_{NH4out}} \quad (12)$$

Aerobic reactor:

$$(1+R)\tau_2 = (1+R)K_B \cdot \ln \frac{S_{NH4in} + -S_{NH4out}}{(1+R)S_{NH4out}} \quad (13)$$

Here, $K_A=0.6$ d (the slope of the line in Figure 4 (a)), $K_B=1.0$ d (the slope of the line in Figure 4 (b)), $R=4$, $S_d=240$ g/m³ (discharge control criteria), $S_{NOXin}=3,200$ g/m³ and $S_{NH4in}=900$ g/m³ (at the highest inlet concentration in our experiment) give the total HRT of this system as a function of S_{NH4out} as shown in Figure 5. The minimum total HRT was 26.4 d (anaerobic: 13.0 d from Eq. (12), aerobic: 13.4 d from Eq. (13)) at $S_{NH4out}=62.3$ g/m³. As a result, the optimum volume ratio of anaerobic reactor to aerobic reactor could be estimated at 1:1 with consideration of the loading rate fluctuation.

It seems, as shown in Figure 2, that nitrification is a rate-limiting step in the nitrogen removal process and thus the HRT in the aerobic reactor is a critical factor to reduce the nitrogen concentration in the effluent. However, a careful determination of HRT balance between anaerobic and aerobic reactors is needed when both NH_4 -N and NO_X -N is contained in the influent, because the sewage discharge control criteria is established on the basis of T-N value. The analytical result demonstrates that almost the same HRT for anaerobic and aerobic reactors is suitable when this type of nitrate-rich wastewater is treated to attain the T-N criteria with minimization of the total HRT in the system.

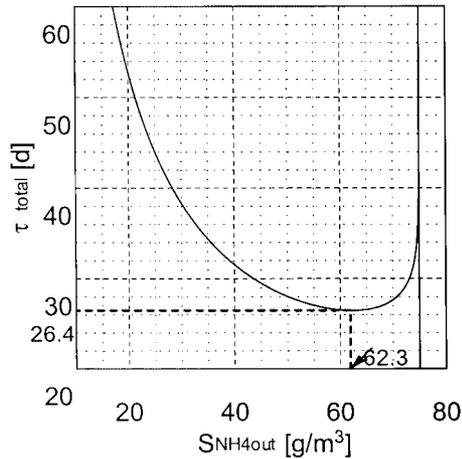


Figure 5 Evaluation of minimum HRT

Conclusion

Biological nitrogen removal from metallurgic wastewater, which had been discharged from the processes of recovering precious metals, was attempted by using an anaerobic-aerobic circulating bioreactor system, and the following results were obtained.

1. By acclimating nitrifying and denitrifying bacteria with gradual reduction of hydraulic residence time (HRT), the concentration of T-N in effluent met the sewage discharge control criteria in Japan (240 g/m³) where the removal ratio of nitrogen was 90% to 98%. As a result, maximum T-N volumetric removal rate was 0.24 kg/m³/d.
2. In order to minimize total HRT through the system with maintenance of effluent T-N concentration below discharge control criteria, a simple method for the determination of the optimum volume ratio of anaerobic reactor to aerobic reactor was established and successfully applied to the nitrogen removal process of high-salinity industrial wastewater.

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Nomenclature

K = characteristic coefficient in Eq. (2) (1/d)

K_A = characteristic coefficient in Eq. (5) (d) $K_A/K_m/(X_b K_u)$

K_B = characteristic coefficient in Eq. (6) (d) $K_B/K_m/(X_b K)$

K_C = characteristic coefficient in Eq. (5) (g d/m³) $K_C/1/(X_b K_u)$

K_D = characteristic coefficient in Eq. (6) (g d/m³) $K_D/1/(X_b K)$

K_m = saturation constant for substrate (g/m³)

K_u = characteristic coefficient in Eq. (1) (1/d)

Q_l = volumetric liquid flow rate (m³/d)

R = circulation ratio (-)

S = concentration of substrate (g/m³)

S_d = discharge control criteria (g/m³)

V = volume of reactor (m³)

X_b = concentration of microorganism (g/m³)

t = hydraulic residence time (d)

subscript

in = inlet

out = outlet

$NO_x = NO_x\text{-N} = NO_2\text{-N} + NO_3\text{-N}$

$NH_4 = NH_4\text{-N}$

total = anaerobic and aerobic reactors

₁ = anaerobic reactor

₂ = aerobic reactor

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