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Study of Autotrophic Denitrification Process with Different Electron Acceptor on Sulfide Control in An Anoxic CSTR

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Abstract: Sulfide autotrophic denitrification (SADN) is a biological process performed by sulfur-oxidizing nitrogen-reducing (SO-NR) cultures in an anoxic environment. This process can effectively remove both sulfide ($S\text{-}S^{2-}$), nitrate ($N\text{-}NO_3^-$) and nitrite ($N\text{-}NO_2^-$), which is an alternative technology in mainstream biological sulfide and nitrogen removal. The study aim is to determine the optimal operating condition of a SADN-Continuous Stirred Tank Reactor (CSTR) that can effectively eliminate $S\text{-}S^{2-}$ while also generating elemental sulfur ($S\text{-}S^0$) and nitrogen gas (N_2) as products of partial SADN. To investigate the performance and biological sulfur and nitrogen conversion processes, a laboratory-scale SADN-CSTR was employed to treat high $S\text{-}S^{2-}$ wastewater and vary nitrate and nitrite per sulfide molar ratios ($[N\text{-}NO_3^-]+[N\text{-}NO_2^-]/[S\text{-}S^{2-}]$ ratios) ranging from 0.6+0.0 to 0.0+0.6.

The results illustrated that the $[N\text{-}NO_3^-]+[N\text{-}NO_2^-]/[S\text{-}S^{2-}]$ ratios between 0.6+0.0 achieved the $S\text{-}S^{2-}$ removal rate (SRR) around 7.74±0.10 mmole-S/L·d (sulfide removal efficiency (SRE) was 99.8%). When feeding the bioreactor with wastewater at the ratio of 0.3+0.3 and 0.0+0.6, the SRR declined to 7.32±0.11 and 6.79±0.17 mmole-S/L·d (SRE were 93.42±2.98 % and 86.93±2.52 %). The $S\text{-}S^0$ production rate was found maximum, as 6.47±0.12 mmole-S/L·d at the ratio of 0.4+0.2. However, when the bioreactor was run at the ratios of 0.3+0.3, the $S\text{-}S^{2-}$remained increased, and detected $N\text{-}NO_2^-$ in the effluent. The results obtained in this work can be used as a practical reference for the development for controlling of $S\text{-}S^{2-}$ and $S\text{-}S^0$ production by SADN.

Keywords: Sulfide autotrophic denitrification; Electron acceptor; Molar ratio

1. INTRODUCTION

Although increased demand of concentrated latex would improve Thailand's economy, the concentrated latex processes generate the waste that has a high negative impact on the environment. Especially, the wastewater discharge of this factory is composed of COD 33.02 - 43.11 g/L, TKN 1.55 - 1.59 gN/L, and sulfate (SO_4^{2-}) 4.93 - 7.50 gSO_4^{2-}/L (Raketh et al., 2021). Currently, concentrated latex processing wastewater is treated in an anaerobic digester, and an aerobic treatment system. However, under anaerobic conditions, SO_4^{2-} is reduced to hydrogen sulfide (H_2S), resulting in H_2S in biogas (Lin et al., 2018). However, TKN is converted to nitrate ($N\text{-}NO_3^-$) by nitrification in aerobic conditions (Rahimi et al., 2020).

Sulfide autotrophic denitrification (SADN) is a combination of anoxic sulfur-oxidation and denitrification processes and is driven by sulfur-oxidizing nitrogen-reducing (SO-NR) cultures. It employs sulfide ($S\text{-}S^{2-}$) as an electron donor and oxidizes $S\text{-}S^{2-}$ to $S\text{-}S^0$ and to $S\text{-}SO_4^{2-}$ as a final product, in order ($S\text{-}S^{2-} \rightarrow S\text{-}S^0 \rightarrow S\text{-}SO_4^{2-}$), whereas nitrate ($N\text{-}NO_3^-$) is utilized as an electron acceptor and reduces $N\text{-}NO_3^-$ to $N\text{-}NO_2^-$ and N_2, respectively ($N\text{-}NO_3^- \rightarrow N\text{-}NO_2^- \rightarrow N_2$) to obtain energy (Di Capua et al., 2019). The advantage of the SADN process is economical, and no air addition requirement in biogas cleanup, maintains CH_4 content in biogas while simultaneously removing H_2S in the biogas and $N\text{-}NO_3^-$ in wastewater (Di Capua et al., 2019).

SADN bioreactors usually receive the effluent from nitrification bioreactor because autotrophic denitrifiers require NO_3^- as electron acceptor to obtain energy. However, nitrate production trough nitrification needs of a high oxygen demand, thus leading to high operating cost. To alleviate this problem, nitrite from a partial nitrification bioreactor can be used as electron acceptor in SADN, instead of nitrate. Most of the previous works focusing on SADN performance use a single electron acceptor (only NO_3^- and only NO_2^-) according to Eq. (1)-(9) rather than mixed electron acceptors (NO_3^-+NO_2^-). This gap needs more research to explain the effect of mixed electron acceptors.

$S^{2-} + 1.6NO_3^- + 1.6H^+ \rightarrow SO_4^{2-} + 0.8N_2 + 0.8H_2O$	ΔG^o = -743.9 kJ/reaction	(1)
$S^{2-} + 2.67NO_2^- + 2.67H^+ \rightarrow SO_4^{2-} + 1.33N_2 + 1.33H_2O$	ΔG^o = -920.3 kJ/reaction	(2)
$S^0 + 1.2NO_3^- + 0.4H_2O \rightarrow SO_4^{2-} + 0.6N_2 + 0.8H^+$	ΔG^o = -547.6 kJ/reaction	(3)
$S^0 + 2.0NO_2^- \rightarrow SO_4^{2-} + 0.6N_2 + 0.8H^+$	ΔG^o = -675.6 kJ/reaction	(4)
$S^{2-} + 4NO_3^- \rightarrow SO_4^{2-} + 4NO_2^-$	ΔG^o = -501.4 kJ/reaction	(5)
$S^{2-} + NO_3^- + 2H^+ \rightarrow S^0 + NO_2^- + H_2O$	ΔG^o = -130.4 kJ/reaction	(6)
$S^{2-} + 0.4NO_3^- + 2.4H^+ \rightarrow S^0 + 0.2N_2 + 1.2H_2O$	ΔG^o = -191.0 kJ/reaction	(7)
$S^{2-} + 0.25NO_3^- + 2.5H^+ \rightarrow S^0 + 2.5NH_4^+ + 0.75H_2O$	ΔG^o = -98.0 kJ/reaction	(8)
$S^{2-} + 0.67NO_2^- + 2.67H^+ \rightarrow S^0 + 0.33N_2 + 1.33H_2O$	ΔG^o = -240.3 kJ/reaction	(9)

Therefore, the present study aimed to investigate the dynamic of a SADN-CSTR for the removal of $S\text{-}S^{2-}$ and production of $S\text{-}S^0$ and N_2 under partial SADN. The study involved the characterization of bioreactor performance and functional microbial activity, with a focus on identifying the optimal operating conditions. Specifically, the study examined the impact of varying the $[NO_3^-]+[NO_2^-]/[S^{2-}]$ molar ratio in the feed from 0.6+0.0 to 0.0+0.6.

2. MATERIALS AND METHODS

The SADN-CSTR was made of transparent PVC, with a total volume and effective volume of 5.5 and 5.0 L, respectively. The SADN-CSTR was fed with two enriching mediums: (1) sulfide wastewater; and (2) nitrate and nitrite wastewater and mineral and micronutrient elements. The mineral and micronutrient element solutions were adapted from Polizzi et al. (2022). The final pH of all feeds was controlled at 7.7 - 7.8 by adding 1 N HCl or 1 N NaOH and flushed with N_2 to maintain the anoxic conditions.

At the startup of this experiment, the inoculated sludge from the laboratory was introduced into the bioreactor at a concentration of 1.0 gMLSS/L and added wastewater to make up the final effective volume. The bioreactor was fed with wastewater containing $S\text{-}S^{2-}$ but varying $N\text{-}NO_3^-$ and $N\text{-}NO_2^-$ at four different $[NO_3^-]+[NO_2^-]/[S^{2-}]$ ratio levels, including 0.6+0.0, 0.3+0.3, 0.4+0.2, and 0.0+0.6 in the feed.

3. RESULTS AND DISCUSSION

Figure 1 shows the s-sulfur compounds and n-nitrogen compounds profiles in the SADN-CSTR over a period of 112 days. Figure 1(a) shows the $S\text{-}S^{2-}$ loading rate (SLR) in the feed was maintained at a value of 7.76±0.20 mmole-S/L·d. The bioreactor was operated at $[N\text{-}NO_3^-]+[N\text{-}NO_2^-]/[S\text{-}S^{2-}]$ ratios of 0.6+0.0, the $S\text{-}S^{2-}$ removal rate (SRR) and $S\text{-}S^{2-}$ removal efficiency (SRE) equaled 7.74±0.10 mmole-S/L·d and 99.88±0.05%, respectively. At a ratio of 0.3+0.3, both the SRR and SRE exhibited a slightly decline, but at the ratio of 0.0+0.6 resulted in a dramatic decrease in both the SRR and SRE with values dropping to 6.47±0.12 mmole-S/L·d and 86.93±2.98 %, respectively. This result confirms the significance of the electron acceptor in the $S\text{-}S^{2-}$ oxidation. When $N\text{-}NO_3^-$ was the main fraction, the microbial activity could

effectively eliminate all S-S^{2-} in the bioreactor, whereas in nitrite over nitrate case, the microbial activity was stopped by no electron acceptor to receive electrons from S-S^{2-} (Chung et al., 2014).

Figure 2 shows nitrate, nitrite, and nitrogen oxide removal rates (NO_3^--RR, NO_2^--RR, and NO_x^--RR) of all ratios related to the nitrate and nitrite fractions. The NO_x^--RR and nitrogen oxide removal rate (NO_x^--RE) of 0.6+0.0, 0.4+0.2, and 0.6+0.0 equaled 4.50 - 4.60 mmole-N/L·d and 99.0%, respectively, and they were higher than 0.3+0.3. Although both NO_x^--RE and NO_x^--RR of 0.6+0.0, 0.4+0.2, and 0.6+0.0 were not different, the N/S molar ratio could control the S-S^0 and S-SO_4^{2-} production rates of the microbial (Fig. 1(a)). The results indicate the highest rate of S-SO_4^{2-} production rate (6.47±0.12 mmole-N/L·d) when using single nitrate, which was higher than the combination acceptor (N-NO_3^-+N-NO_2^-) and single nitrite (0.0+0.6). Moreover, when using single nitrite showed the lowest S-SO_4^{2-}, which was 0.69±0.05 mmole-S/L·d), but S-S^0 production rate higher than single nitrate.

But SO_4^{2-} production rate followed the nitrate fraction, whereas at the ratio of 0.4+0.2 provided the highest S-S^0 production rate. Moreover, at higher nitrite molar ratios (0.3+0.3 and 0.0+0.6) were found residue S-S^{2-} in effluent, and dropping of S-S^{2-} oxidation process. However, when the bioreactor was run at ratios of 0.3+0.3, the NO_3^--RR, NO_2^--RR and NO_x^--RR equaled 2.34±0.05, 2.03±0.03, and 4.35 mmole-N/L·d, respectively, and found the remained N-NO_2^- in the effluent because SO-NR culture favors N-NO_3^- than N-NO_2^-, which provides more energy than N-NO_2^- (Chung et al., 2014).

The highest production rate of S-S^0, reaching 6.47±0.12 mmole-S/L·d, was observed at the ratio of 0.4+0.2. However, this condition was found the highest accumulation of S-S^0 because almost electron acceptor was extensively utilized in the S-S^{2-} oxidation to S-S^0 process. This phenomenon results in an insufficient supply of electron acceptors to facilitate the conversion of the produced S-S^0 to S-SO_4^{2-} (Lin et al., 2018). This result is correlated with the concentration of the present S-SO_4^{2-} in the effluent.

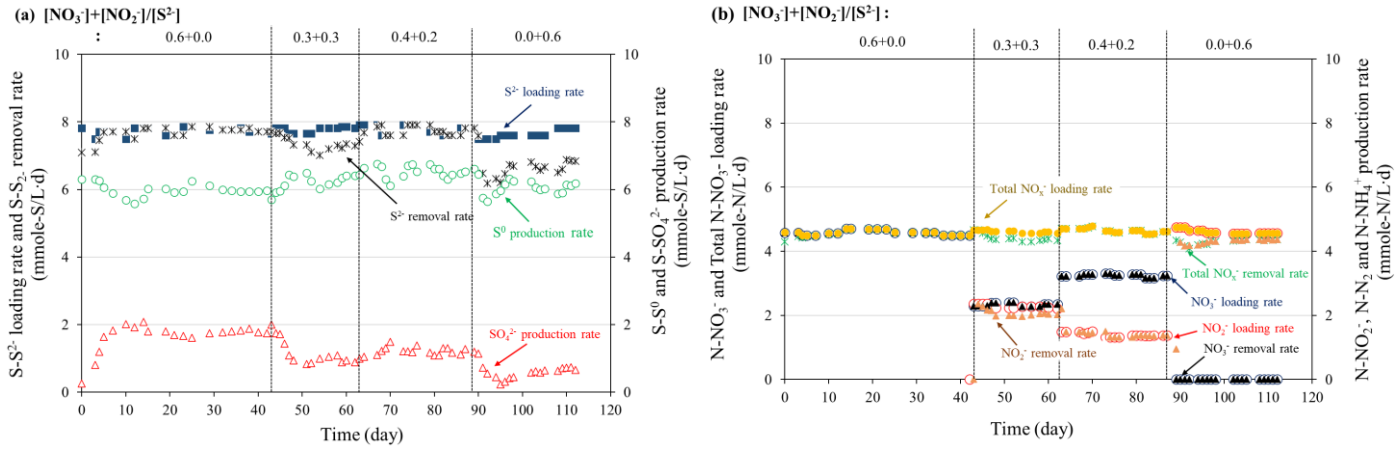


Figure 1. Long-term performance of SADN-CSTR; (a) S-Sulfur compounds variation profile, and (b) N-Nitrogen compounds variation profile.

CONCLUSIONS

The results illustrated that the [N-NO_3^-]+[N-NO_2^-]/[S-S^{2-}] ratios between 0.6+0.0 achieved the S-S^{2-} removal rate (SRR) around 7.74±0.10 mmole-S/L·d (sulfide removal efficiency (SRE) was 99.8%). When feeding the bioreactor with wastewater at the ratio of 0.3+0.3 and 0.0+0.6, the SRR declined to 7.32±0.11 and 6.79±0.17 mmole-S/L·d (SRE were 93.42±2.98 % and 86.93±2.52 %). The S-S^0 production rate was found maximum, as

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