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Stable nitrification under sulfide supply in a sequencing batch reactor with a long fill period

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ABSTRACT

Ammonia-containing wastewater often also contains sulfide, which severely inhibits biological nitrification. In this study, the applicability of a sequencing batch reactor (SBR) with a long fill period to achieve stable nitrification of sulfide-containing anaerobic digestion effluent was evaluated. During the start-up period, in which no sulfide was supplied to the reactor (Phase I, experimental days 0–18), ammonium was oxidized to nitrate stably after day 6. During the period in which sulfide was supplied at 32 mg-S L^{-1} d^{-1} (Phase II, experimental days 18–30), the nitrification efficiency temporarily decreased to 79%, but recovered rapidly to 100% within two days. The sulfide tolerance of the sludge in the SBR was evaluated by batch bioassays at the end of the start-up period. The results showed that the half-maximum inhibitory concentration (IC_{50}) for the sludge was 0.73 mg-S L^{-1}, which was a typical value. Therefore, pre-existing sulfide tolerance of the sludge was not the main factor enabling stable nitrification during the sulfide supply period. Throughout the experimental period, the reactor was operated using a long sludge retention time of 139 days. The effective sludge retention in the SBR with a long fill period probably promoted the acclimatization of the microbes to sulfide, allowing the nitrification performance to remain stable even under sulfide supply.

1. Introduction

Appropriate management of wastewater discharged from human activities is essential for establishing a sustainable society. Human-derived wastewater often contains a high concentration of nitrogen compounds, and sequential nitrification-denitrification processes have been used for effective nitrogen treatment [1]. The role of nitrification is to oxidize the ammonium to nitrate via the following two steps (Eqs. (1)-(2), [2]) before denitrification, in which the nitrate is converted to nitrogen gas.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

Thus, a successful nitrification process is a key factor for the complete removal of nitrogen from wastewater. However, the nitrification process is sensitive to some inhibitors in wastewater, such as organic compounds, heavy metals, and sulfide [3–5]. Sulfide is a strong inhibitor, and exists in many types of nitrogen-containing wastewater, such as those from petroleum refineries [6], tanneries [7], and food processing plants [8]. In addition, the effluent from anaerobic digesters (ADEs) often contain soluble sulfide along with ammonium; sometimes the sulfide concentration is greater than 10 mg-S L^{-1} [9].

Previous studies have demonstrated that low sulfide concentrations severely inhibit nitrification performance. Table 1 summarizes some previous reports related to the inhibition of nitrification by sulfide in the treatment of waste gas and wastewater. Kim et al. [11] attempted to treat synthetic waste gas containing NH_3 and H_2S, and indicated that NH_3 treatment efficiency decreased approximately 70% under high concentration of H_2S supply over 200 ppm. The mechanism by which sulfide inhibits nitrifying bacteria has also been studied by batch bioassays using a synthetic medium. For instance, Bejarano-Ortiz et al. [12] observed a greater than 50% decrease in the nitrification rate at a sulfide concentration of 3.1 mg-S L^{-1}. In synthetic wastewater treatment, Æsøy et al. [13] indicated that supplying sulfide at a loading rate of approximately 10 mg-S L^{-1} d^{-1} lowered the nitrification efficiency by approximately 70% in a continuous moving-bed reactor with a hydraulic retention time (HRT) of 1–2 h. Beristain-Cardoso et al. [14] evaluated the nitrification performance of a continuous stirred tank reactor (CSTR) with an HRT of 1.8 days at sulfide loading rates of 32 and 76 mg-S L^{-1} d^{-1}. They reported that significant inhibition of nitrification was observed during the first two weeks at each sulfide loading rate, but the nitrification process then recovered due to

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Table 1
Previous reports of the effect of sulfide inhibition on nitrification.

Substrate form	Sulfide concentration of substrate	Inoculum	Process	Reactor	Remark	Reference
Synthetic waste gas	60, 120 ppmv	*Arthrobacter oxydans* CH8 and *Pseudomonas putida* CH11	Continuous	Biofilter	H_2S concentration increased from 60 to 120 ppmv, reduced NH_3 removal efficiency from 98 to 94%.	[10]
Synthetic waste gas	30–450 ppmv	Activated sludge and *Thiobacillus thioparus*	Continuous	Biofilter	At H_2S concentrations above 200 ppm, the bacterial nitrification activity was inhibited, and NH_3 removal efficiency decreased from 90 to 30%.	[11]
Synthetic medium	0, 3.1, 6.4, 13.5, 52.0, 112 mg L^{-1}	Nitrifying sludge	Batch	Flask	At an H_2S concentration of 3.1–112 mg-S L^{-1}, NH_4^+ consumptions rate decreased 51–92% compared to the 0 mg-S L^{-1} condition, and NO_2^- was accumulated.	[12]
Synthetic medium	0, 15 mg L^{-1}	Nitrifying sludge	Batch	Flask	The net maximum specific growth rate of nitrifying bacteria decreased 75.9% after 0.5 h anaerobic exposure, compared to the under aerated conditions.	[9]
Synthetic wastewater	0, 0.5–2.6 mg L^{-1}	N. D.	Continuous	Moving bed biofilm reactor	Nitrification rate decreased 30–70% compared to at 0 mg-S L^{-1} conditions.	[13]
Synthetic wastewater	0, 65, 137 mg L^{-1}	Nitrifying sludge	Continuous	Continuous stirred-tank reactor	Nitrification was inhibited for approximately the first two weeks of each sulfide loading phase.	[14]

ppmv: parts per million volume fraction

acclimatization. Their use of a relatively long HRT compared to that of Æsøy et al. [13] probably retained the microbes effectively in the reactor, resulting in the recovery of nitrification ability. However, during an actual treatment process, prolonged instability in the nitrification performance leads to a large amount of ammonium entering the denitrification process, from which ammonia cannot be removed. The remaining ammonia is discharged directly into the aquatic environment, causing eutrophication. Therefore, typical continuous CSTR operation is likely inappropriate for maintaining stable nitrification efficiency when HS^- is supplied. Instead, a reactor operation method that can shorten the sulfide inhibition period during the nitrification process should be applied.

SBR is one of the reactors to be known to retain sludge more effectively than continuous reactors, because the supernatant is discharged only after the sludge has settled. A higher sludge retention time (SRT) has several advantages, such as preventing the wash-out of slow-growing microbes, including nitrifying bacteria, from the system and increasing the biodiversity of the microbes. Therefore, SBRs with higher SRTs are used for the treatment of inhibitory wastewater [15,16], because of the low microbe growth rate under inhibitory conditions [17]. The basic operation cycle of a SBR is divided into five periods: the fill, reaction, settling, draw, and idle periods [18]. Generally, pulse substrate feeding is used for filling, and the fill and reaction periods are separated. However, a high concentration of inhibitory substrates such as sulfide can strongly affect the process of nitrification. In contrast, SBR operation in which a long fill period is combined with the reaction period might be beneficial for treating high-strength inhibitory wastewater, because the substrate concentration will not vary significantly throughout the cycle [19,20]. Thus, SBR operation with a long fill period is preferable for inhibitory wastewater treatment. However, to our knowledge, no study has directly reported the reduction of inhibition by using an SBR with a long fill period. The aim of this study was to evaluate the nitrification performance of ammonium from anaerobic digestion effluent (ADE) containing sulfide using an SBR with a long fill period.

2. Materials and methods

2.1. Reactor operation

An SBR with a working volume of 2.1 L was used. Nitrifying sludge obtained from an A_2O (anaerobic/anoxic/aerobic) wastewater treatment plant at the Hokubu Second Water Regeneration Center (Yokohama, Japan) was used as the inoculum. The pH, ionic compound concentrations, and volatile suspended solid (VSS) concentrations of the nitrifying sludge were 6.4, 0.0 mg-NH_4^+-N L^{-1}, 37.6 mg-NO_3^--N L^{-1}, 66.4 mg-PO_4^{3-}-P L^{-1}, 32.7 mg-SO_4^{2-}-S L^{-1} and 3.6 mg-VSS L^{-1}, respectively. This sludge was washed repeatedly with distilled water to remove ionic compounds from the liquid phase, and then added to the reactor at a sludge concentration of 2.7 mg-VSS L^{-1}. Centrifuged ADE from the Hokubu Sludge Treatment Center (Yokohama, Japan) was used as the substrate after filtration through a glass fiber filter with a pore size of 0.45 μm (Advantec, GC-50). The reactor was operated using a 12 h cycle consisting of three periods: the combined filling and reaction for avoiding a high load for a short period (11.5 h; with feeding, stirrer agitation at 200 rpm, aeration, and pH control); the settling period (20 min); and the drawing period (10 min). The ADE was supplied with an HRT of 3 days. The volume exchange ratio (VER, the ratio of the volume added during an operation cycle to the maximum reactor volume ratio) was 0.17. The temperature was controlled at 30 ± 1 °C using a water bath. The dissolved oxygen (DO) concentration was maintained between 2.0 and 5.0 mg-O_2 L^{-1} by regulating the airflow rate. The pH was automatically maintained above 7.5 through the addition of 2 N NaOH by a process controller. The SBR was operated for 30 days. During the first 18 days of operation, only ADE was supplied to obtain stable nitrification ability for ADE treatment (Phase I, day 0–17).