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Inhibition kinetics of nitritation and half-nitritation of old landfill leachate in a membrane bioreactor

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Nitritation can be used as a pretreatment for anaerobic ammonia oxidation (anammox). Various control strategies for nitritation and half-nitritation of old landfill leachate in a membrane bioreactor were investigated in this study and the inhibition kinetics of substrate, product and old landfill leachate on nitritation were analyzed via batch tests. The results demonstrated that old landfill leachate nitritation in the membrane bioreactor can be achieved by adjusting the influent loading and dissolved oxygen (DO). From days 105–126 of the observation period, the average effluent concentration was 871.3 mg/L and the accumulation rate of $NO_2^- - N$ was 97.2%. Half-nitritation was realized quickly by adjusting hydraulic retention time and DO. A low-DO control strategy appeared to best facilitate long-term and stable operation. Nitritation inhibition kinetic experiments showed that the inhibition of old landfill leachate was stronger than that of the substrate ($NH_4^+ - N$) or product ($NO_2^- - N$). The ammonia oxidation rate dropped by 22.2% when the concentration of old landfill leachate (calculated in chemical oxygen demand) was 1600.2 mg/L; further, when only free ammonia or free nitrous acid were used as a single inhibition factor, the ammonia oxidation rate dropped by 4.7–6.5% or 14.5–15.9%, respectively. Haldane, Aiba, and a revised inhibition kinetic model were adopted to separately fit the experimental data. The R^2 correlation coefficient values for these three models were 0.982, 0.996, and 0.992, respectively.

[**Key words:** Old landfill leachate; Membrane bioreactor; Nitritation; Half-nitritation; Inhibition kinetics]

Landfill leachate is a complex composition containing high levels of ammonia nitrogen in addition to toxic substances such as toxic organic matter and heavy metals (1,2). The organic matter of fresh landfill leachate shows good biodegradability and can be used in denitrification, which makes it well-suited to nitrogen removal. The biodegradability of organic matter in old landfill leachate is very poor, however, and may require expensive additional organic carbon sources for a conventional biological nitrogen removal process. In short: There is high demand for a cost-effective and energy-efficient nitrogen removal method.

Autotrophic nitrogen removal methods combining nitritation with anaerobic ammonia oxidation have garnered substantial research interest in high ammonia nitrogen and low carbon nitrogen ratio wastewater treatment (3,4). Existing combination methods can be split into two categories. In the first, $NO_2^- - N$ accumulation is performed before old landfill leachate as $C(NO_2^- - N)/C(NH_4^+ - N)$ is mixed in at 1:1.32 for anaerobic ammonia oxidation. In the second category, the control effluent $C(NO_2^- - N)/C(NH_4^+ - N)$ is about 1:1.32 in the nitritation stage for anaerobic ammonia oxidation. Both methods necessitate stable nitritation, which requires the interception of ammonia oxidizing bacteria (AOB) and the elimination of nitrite oxidizing bacteria (NOB). AOB are autotrophic and slow-growing (5). Membrane bioreactor (MBR) can efficiently intercept sludge and rapid concentrate AOB to truncate the amount of time necessary for nitritation. There have been several studies on MBR nitritation, but only in regards to treating wastewater with low concentrations of ammonia nitrogen (6,7), while the concentration of ammonia nitrogen is generally greater than 1000 mg/L in old landfill leachate. There have been few studies on the nitritation of old landfill leachate using MBR reactors.

Nitritation can be realized quickly if the appropriate temperature, pH, and dissolved oxygen (DO) are controlled (8,9). Half-nitritation can be controlled by hydraulic retention time (HRT), DO, or alkalinity if nitritation has been effectively realized (10,11). To achieve nitritation and allow stable operation of the MBR reactor, the operating conditions must be controlled and the influent loading gradually increased. HRT and DO should be separately adjusted to allow half-nitritation and stable operation.

Old landfill leachate exhibits high ammonia nitrogen and toxic effects on microbes. High $NH_4^+ - N$ and $NO_2^- - N$ accumulation causes a high concentration of free ammonia (FA) and free nitrous acid (FNA) that inhibits the activity of AOB and NOB (12,13). The organic matter and heavy metals in old landfill leachate also are toxic to AOB and NOB (14,15). There have been several studies on substrate inhibition kinetics (16), but few on product or old landfill leachate inhibition kinetics for nitritation. In an effort to fill this research gap, we determined the nitritation inhibition kinetics characteristics of substrates ($NH_4^+ - N$), product ($NO_2^- - N$), and old landfill leachate through batch experiments. Our primary goal is to provide guidance for the practical application of old landfill leachate nitritation in MBRs.

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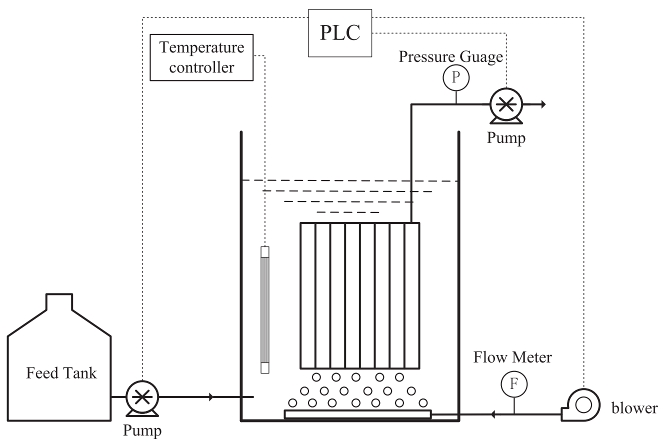

FIG. 1. Schematic diagram of MBR reactor.

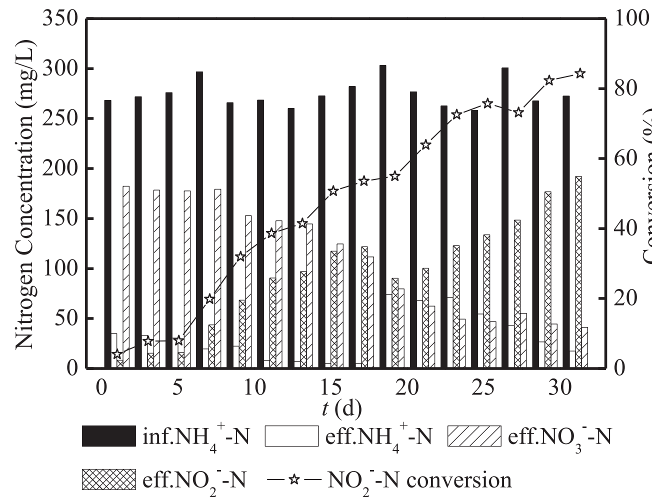

FIG. 2. Performance of nitritation during start-up.

MATERIALS AND METHODS

Experimental set-up and operational conditions An MBR reactor made from organic glass with an effective volume of 25 L was used for these experiments (as shown in Fig. 1). The membrane component is a hollow fiber membrane made from polyvinylidene fluoride with a pore size and area of 0.1 μm and 0.5 m^2, respectively. The influent and effluent pumps were controlled using a programmable logic controller. The membrane was operated at a flux of 2.28 L/($m^2 \cdot h$) with intermittent suction (8 min suction, 2 min relaxation). The aeration rates were 40–160 L/h and controlled via rotor flowmeter throughout the experiment. The transmembrane pressure (TMP) was measured with a vacuum gauge (JZ 00000578, Tianjin Ji Xing Company, China). The temperature was controlled at $(30 \pm 1)^\circ$C using a heater. The HRT was 22 h, and there was no sludge discharge during the experiment.

Characteristics of old landfill leachate and seed sludge The seed sludge (nitrification sludge) was taken from Gao Bei Dian wastewater treatment plant in Beijing, which employs a typical anoxic-aerobic process for treating municipal wastewater and achieves satisfactory biological nitrogen removal. Initial inoculation sludge concentration mixed liquor suspended solids (MLSS) was 3104 mg/L and mixed liquor volatile suspended solids (MLVSS) was 2540 mg/L.

The old (over 5 years) landfill leachate was taken from Gao An Tun municipal landfill, stored in sealed in plastic drums, and renewed once per month during the experiment. The specific water quality is as follows: NH_4^+-N, 900–1500 mg/L; NO_2^--N, 0–2 mg/L; NO_3^--N, 0–8 mg/L; chemical oxygen demand (COD), 2000–4000 mg/L; pH, 7.5–8.5; alkalinity, 6000–10,000 mg/L.

Inhibition kinetics experiments The nitritation-activated sludge samples were separately cleaned 3–5 times with deionized water and phosphate buffered saline (PBS) after removal from the MBR at 71 d. The level of MLSS was about 5.04 g/L after concentration. For each batch experiment, 150 mL of concentrated sludge was transferred to a beaker and diluted to 1 L. The concentration of NH_4^+-N was 60–1000 mg/L when NH_4^+-N was the single inhibition factor, and the concentration of NO_2^--N was 50–700 mg/L but the NH_4^+-N concentration was adjusted to about 180 mg/L when NO_2^--N was the single inhibition factor. In order to eliminate the influence of substrate inhibition, ammonium chloride was used to adjust the NH_4^+-N concentration to match the concentration during the old landfill leachate inhibition experiments. Sodium bicarbonate and hydrochloric acid were used to adjust the alkalinity and keep the pH constant. All experiments were conducted in a constant temperature incubator which was controlled at $(30 \pm 1)^\circ$C temperature. Sampling intervals were 30 min. Ammonia oxidation rate, NO_2^--N generation rate, and NO_3^--N generation rate were measured and calculated in triplicate.

Inhibition kinetics models The inhibition kinetics of the substrate is described by the Haldane model as follows (17):

$$v = \frac{v_{max} S}{k_s + S + \frac{S^2}{k_h}} \quad (1)$$

where v is the substrate conversion rate, g/(g·d); v_{max} is the maximum conversion rate, g/(g·d); S is the substrate concentration, mg/L; k_S is half-saturation constant, mg/L; k_h is Haldane inhibiting kinetics constant, mg/L.

The inhibition kinetics of the product is described by the Aiba model (18), which was originally used to describe ethanol fermentation product inhibition. The equation as the follows:

$$v = \frac{v_{max} S}{k_s + S} \exp\left(-\frac{S}{k_a}\right) \quad (2)$$

where v is the substrate conversion rate, g/(g·d); v_{max} is the maximum conversion rate, g/(g·d); S is the substrate concentration, mg/L; k_S is half-saturation constant, mg/L; k_a is Aiba inhibiting kinetics constant, mg/L.

The inhibition kinetics of old landfill leachate is described by chlorophenol inhibition kinetics model when acetic acid was degraded (19). The equation as the follows:

$$v = \frac{v_{max}[k_0] S x}{k_s[k_1] + S} \quad (3)$$

where v is the substrate conversion rate, g/(g·d); v_{max} is the maximum conversion rate, g/(g·d); S is the substrate concentration, mg/L; k_S is half-saturation constant, mg/L; k_0 and k_1 are inhibiting constant.

k_0 and k_1 are calculated according to the following formula:

$$k_0 = [1 - \alpha/\beta]^m \quad (4)$$

$$k_1 = [1 - \alpha/\beta]^n \quad (5)$$

where α is toxic substance concentration, mg/L; β is toxic substance fully inhibition concentration, mg/L; m and n are constant.

The above formula was revised by introducing the speed ratio (λ) as follows:

$$\lambda = \frac{1 - [\alpha/\beta]^n}{1 + [\alpha/\beta]^m} \quad (6)$$

where $\lambda = v/v_0$, λ is speed ratio, v is the conversion rate under different old landfill leachate concentration, g/(g·d); v_0 is the conversion rate of no old landfill leachate, g/(g·d).

Chemical analysis and calculation procedures NH_4^+-N, NO_2^--N, NO_3^--N, chemical oxygen demand (COD), MLSS and MLVSS were analyzed according to standard methods (20). pH and temperature were determined by WTW/Multi3420 tester.

NO_2^--N accumulation rate (R), free ammonia (FA) and free nitrous acid (FNA) were calculated according to the following equations:

$$R = \frac{C_{[NO_2^--N]}}{C_{[NO_2^--N]} + C_{[NO_3^--N]}} \times 100\% \quad (7)$$

$$FA = \frac{17}{14} \times \frac{C_{[NH_4^+-N]} \times 10^{pH}}{e^{[6344/(273+T)]} + 10^{pH}} \quad (8)$$

$$FNA = \frac{47}{14} \times \frac{C_{[NO_2^--N]}}{e^{[-2300/(273+T)]} \times 10^{pH}} \quad (9)$$

where $C[NH_4^+-N]$, $C[NO_2^--N]$ and $C[NO_3^--N]$ are the effluent concentration of NH_4^+-N, NO_2^--N and NO_3^--N, respectively, mg/L; T is temperature, °C.

RESULTS AND DISCUSSION

Nitritation start-up under low DO conditions It is generally accepted that NOB are inhibited and AOB are concentrated when the appropriate temperature, pH, and DO are controlled to realize