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Effective carbon and nitrogen removal with reduced sulfur oxidation in an anaerobic baffled reactor for fresh leachate treatment

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The application of an anaerobic baffled reactor (ABR) with four compartments was investigated for the simultaneous removal of carbon and nitrogen from leachate. The nitrified effluent was recycled to compartment 3 of the ABR, thereby avoiding the adverse influence of nitrogen oxides on anaerobic methanogenesis in compartment 1. Nitrified effluent recirculation not only enhanced chemical oxygen demand removal (>95.6%) but also improved the total nitrogen removal efficiency from 12.7% to 67.4% with increasing recirculation ratio from 0.25 to 2. The challenge of insufficient carbon sources for heterotrophic denitrification in compartment 3 with a high recirculation ratio could be overcome by step feeding of leachate. Moreover, various reduced sulfurs (e.g., sulfide, elemental sulfur, and organic sulfur) were involved in nitrate reduction via sulfur-based autotrophic denitrification. The addition of sulfide to compartment 3 further confirmed nitrate reduction using reduced sulfur as an electron donor. The interaction of organic carbon, reduced sulfur, and nitrate in leachate treatment needs further study.

[**Key words:** Anaerobic–aerobic system; Recirculation ratio; Leachate; Simultaneous denitrification and methanogenesis; Sulfur-based autotrophic denitrification]

In China, fermentation of food wastes in refuse pits of municipal solid waste incineration (MSWI) plants results in a large volume of fresh leachate. Such leachate contains high levels of contaminants, including organic compounds, ammonia, suspended solid (SS), and various sulfur species (e.g., sulfide, sulfate, elemental sulfur, and organic sulfur) (1), which should be treated before being discharged. Conventionally, anaerobic digestion is usually applied in leachate treatment for treating high-strength organic compounds, with methane production and utilization as an alternative energy resource (1,2). Since the last two decades, considerable effort has been dedicated to integrate denitrification and methanogenesis in a single anaerobic bioreactor (3–7). However, one of the challenges is that denitrification in a methanogenic system can channel the electron equivalents from methanogenesis, inhibiting methane production until the completion of nitrate reduction (8,9). Therefore, to reduce nitrate inhibition to methanogenesis, different configurations were investigated to realize simultaneous denitrification and methanogenesis in a single anaerobic reactor, including completely stirred anaerobic reactor, anaerobic upflow filter, upflow anaerobic sludge blanket, and anaerobic baffled reactor (ABR) (6–13). Among these studies, ABR with nitrified effluent from a downstream nitrification unit recycling to the feed point of ABR shows efficient simultaneous carbon and nitrate removal (97% and 100%, respectively) from brewery wastewater (13). However, this configuration results in biogas with methane composition decreasing from 50% to 25% during nitrate recirculation, which is less useful as an energy source compared with the normal biogas produced in a single anaerobic reactor. Thus, considering the plug flow multi-stage characteristics of a bioreactor, this study proposed to recycle nitrified effluent to the middle compartment of ABR to separate methanogenesis and denitrification in different compartments. This method may recover biogas with high purity of methane from the front methanogenic dominant compartments and further consume subsequent organic carbon by nitrate reduction in the subsequent compartment.

In an anaerobic environment, sulfate and/or elemental sulfur reduction to sulfide can also occur with methane production from leachate. The reduced sulfur might be involved in nitrate reduction as an electron donor. The interactions and electron flow in the matrix of sulfide and nitrate under anaerobic conditions have been recently examined (14–17), but most of these studies were conducted in batch assays using synthetic media, such as acetate, butyrate, or dextrin/peptone. The effect of reduced sulfur on nitrate reduction in real scenarios needs further investigation. Given the complex characteristics of leachate with various forms of reduced sulfur, nitrogen, and organic carbon compounds, investigating the role of reduced sulfur compounds in nitrate reduction pathways is quite challenging.

Therefore, in this study, to explore a feasible process for the simultaneous removal of carbon and nitrogen from leachate, a modified ABR followed by an aerobic reactor was designed and established. In this ABR, nitrified effluent was recycled to compartment 3 under different recirculation ratios. In addition,

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more attention was given on the role of reduced sulfur during nitrogen removal in the ABR for fresh leachate treatment.

MATERIALS AND METHODS

Characteristics of leachate from MSWI plant The leachate was collected from a refuse storage pit in Lucheng MSWI plant (Jiangsu Province, China). The main composition of the leachate used in this study is shown in Table 1. The characteristics of the leachate varied because of the different sampling times depending on various conditions, such as the degree of compaction, waste composition, climate, and moisture contents in wastes. Food wastes with high moisture content comprised the largest fraction (60%–70% by weight) of municipal solid waste. Fermentation of the organic fraction in food wastes resulted in a large volume of fresh leachate containing high levels of contaminants, including organic compounds, ammonia, SS, and various sulfur species (e.g., sulfide, sulfate, elemental sulfur, and organic sulfur). The leachate was transported to the laboratory in sealed plastic barrels and stored at 4 °C in a refrigerator before use.

Experimental setup Fig. 1 shows a schematic of the lab-scale experimental setup, which consisted of an ABR with a working volume of 10 L and an aerobic reactor with a working volume of 3 L. A peristaltic pump was used to feed leachate into the ABR continuously.

The ABR was constructed with internal dimensions of 500 mm × 100 mm × 300 mm (length × width × height) using 10 mm-thick transparent plexiglass. The ABR was divided into four compartments (with volume ratio of 3:2:2:3). Vertical high/low baffles (5 mm-thick) were inserted to subdivide each compartment width into upflow and downflow chambers at a 4:1 ratio. The lower portions of the baffles were bent 2 cm above the reactor bottom at a 45° angle to the flow at the center of the upflow chamber to achieve effective mixing and contact between the feed and solids. The baffles forced the overflow and underflow of the wastewater as it progressed through the reactor. The ABR was enclosed within a water jacket to maintain a constant temperature of 35 ± 1 °C throughout the study. Samples were collected from sampling ports located about 50 mm from the top of each compartment. The sludge sampling sites were located 30 mm from the bottom of each compartment.

The aerobic reactor was a plexiglass-made cylindrical reactor with a diameter of 15 cm and height of 20 cm, which was operated at room temperature (20 °C–30 °C). Aeration was provided using an air module pump device with an aeration range of 0.3–0.5 L/min, which was controlled through a knob on the aeration equipment. The dissolved oxygen content was maintained at 0.5–3.0 mg/L. Continuous mixing was provided with a stirrer in the aerobic reactor.

TABLE 1. Characteristics of leachate from refuse storage pit in MSWI plant.

Item	Range (mg/L)	Average (mg/L)
SCOD	21000–32500	26300
NH_4^+–N	760–2100	1200
TN	950–2670	1500
VFAs	11200–14600	12900
SO_4^{2-}–S	0.8–27.1	7.8
S^{2-}–S	2–11.4	6.7
SS	1500–3000	2100
pH	6.9–7.7	7.3

Reactor inoculation and operation The ABR used in this study has been operated under continuous operation mode for more than 170 days to treat leachate without any nitrogen oxide acclimatization. The ABR was initially seeded with anaerobic granular sludge (VSS of 37.6 g/L) collected from a full-scale upflow anaerobic sludge bioreactor treating leachate. The reactor was sealed after inoculation, and the headspace above the four compartments was flushed with oxygen-free argon gas to displace residual air from the system. Prior to recirculation experiments, the ABR was operated at a hydraulic retention time (HRT) of 10 days. Once the COD removal efficiency and gas production in the ABR reached a steady state, the ABR effluent was fed into the aerobic reactor that was seeded with sludge (MLVSS of 4.5 g/L) obtained from the secondary sedimentation tank of the Quyang sewage treatment plant (Shanghai, China). The nitrified effluent from the aerobic reactor was then recirculated to the top of the downflow chamber of compartment 3 of the ABR with recirculation ratios of 0.25, 0.5, and 2 for denitrification purposes by a peristaltic pump, with timers used to change the flow rate. The influent leachate was step fed into compartments 1 and 2 with equal flux when the carbon source was insufficient for denitrification, as shown in Fig. 1 (dashed line). After studying the effect of the recirculation ratio, sulfide was supplemented as sodium sulfide (227 mg S/L) to compartment 3 with a recirculation ratio of 0.5 to further examine the role of reduced sulfur in nitrogen reduction.

During the experiments at each stage, the supernatant liquor samples were collected separately from six points for analysis: the inlet of ABR, the four compartments (the fourth compartment as the outlet of ABR), and the outlet of the aerobic reactor.

Analytical methods Sulfide analysis was performed using the methylene blue method (18) immediately after filtering through a 0.45 μm filter to minimize oxidation loss. In brief, the samples were diluted with 6.9 mL of deionized water and reacted with 2 mL of zinc acetate, 1 mL of *N,N*-dimethyl-*p*-phenylenediamine dihydrochloride, and 0.1 mL of ammonium ferric sulfate [$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$]. Absorbance was then measured spectrophotometrically at 665 nm (Unico 2100, Unico, USA). The liquid samples for the analysis of other parameters were treated with 0.2 mL of 2 M zinc chloride to precipitate the remaining sulfide and then centrifuged at 11,000 ×g for 10 min (Thermal Multifuge X1R, Thermo Fisher Scientific, USA). The resulting supernatants were filtered through 0.22 μm filters, and the filtrate was stored at 4 °C before analysis. Ammonium, nitrate, nitrite and sulfate ion concentrations were determined using ion chromatography (Dionex ICS-3000, Dionex, Sunnyvale, CA, USA) as described by Xie at al. (19). Soluble chemical oxygen demand (SCOD) was determined by placing 2 mL of COD reagent into a series of vials (Hach, Loveland, CO, USA). The vials were heated in a COD reactor (Hach DRB200) for 120 min after which the absorbance was measured using a spectrophotometer (Hach DR3900). The concentration of soluble total nitrogen (TN) was determined by a total organic carbon (TOC)/TN analyzer (TOC-L CPN CN200, Shimadzu, Japan) equipped with a platinum catalyst quartz tube. Volatile fatty acids (VFAs) were measured using gas chromatography (GC) with a flame ionization detector (Agilent 6890N, Agilent, USA). Elemental and organic sulfurs were examined by GC-mass spectrometry (GC–MS) (Shimadzu QP 2010) after liquid–liquid extraction with carbon disulfide (CS_2) as an extraction agent. All the other conventional parameters, such as and solid concentrations (TSS and VSS), were analyzed according to standard methods (20).

The biogas was collected separately from the upper part of each compartment daily. Biogas composition, including N_2, CH_4, and CO_2, was measured using GC (Agilent 6890N) with a thermal conductivity detector and an analytical column (Supelco Hayesep Q, 80/100 mesh). The temperatures of the column, injector, and detector were 50 °C, 120 °C, and 80 °C, respectively.

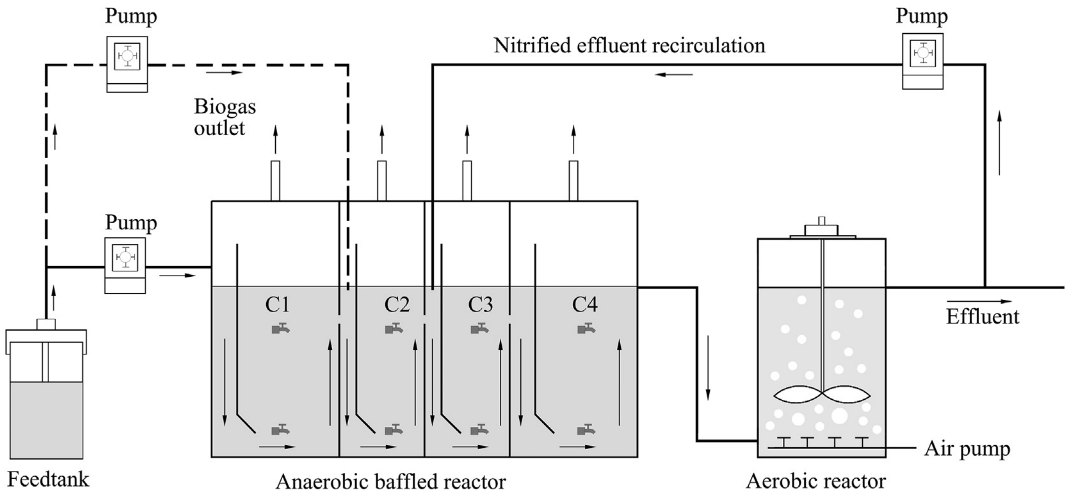

FIG. 1. Schematic of anaerobic baffled reactor (ABR) with aerobic reactor.