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Elemental sulfur as an electron acceptor for organic matter removal in a new high-rate anaerobic biological wastewater treatment process

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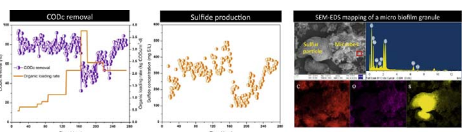
GRAPHICAL ABSTRACT



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ABSTRACT

Elemental sulfur can serve as an economical external sulfur source replacing sulfate as an electron acceptor in sulfidogenic processes for wastewater treatment with sludge minimization. However, the biological sulfur reduction has not yet been considered in wastewater treatment due to the insolubility of sulfur. In this study, a laboratory-scale sulfur-reducing anaerobic fluidized bed (SRAFB) reactor was built to investigate the feasibility of the high-rate sulfur-reducing anaerobic wastewater treatment process. After 273 d of operation, the organics removal and sulfide production rates were determined as 1.71 kg CODc/m^3-d (CODc: carbonaceous COD) and 2.71 kg S/m^3-d, respectively, at a high organic loading rate of 2.14 kg CODc/m^3-d with a hydraulic retention time of only 3 h. Biofilm growth on sulfur particles resulted in high sludge settleability (23 ± 3 mL/g of SVI_{30}) (SVI_{30}: sludge volume index in 30 min) and thus high sludge concentration. As expected, a low sludge yield of 0.16 kg VSS/kg CODc (VSS: volatile suspended solids) was also obtained. Although sulfur reducers could not be identified in this study, *Geobacter* and *Desulfomicrobium* were the most likely sulfur reducers. This work suggests that elemental sulfur can serve as an electron acceptor in the new high-rate anaerobic sulfidogenic process for sludge-minimized wastewater treatment.

1. Introduction

The treatment and disposal of waste activated sludge have always been a challenge in the operation of biological wastewater treatment plants (WWTPs) both in public and private sectors [1]. The cost of sludge treatment generally accounts for up to 60% of total operational costs of WWTPs [2,3]. The cost is particularly high in China, which produced approximately 33 million tons of waste activated sludge in 2013 alone [4]. The production of excessive sewage sludge has been rapidly increasing due to the rapid urbanization and industrial development [2,4].

A biological sulfate reduction (BSR)-driven process known as the "sulfate reduction, autotrophic denitrification, and nitrification integrated (SANI) process" has recently been developed [5,6] because of the occurrence of sulfate in sewage originating from the seawater toilet flushing in Hong Kong [7]. This novel biological nutrient removal (BNR) process has been successfully applied in the treatment of sulfate-laden sewage with at least 70% biological sludge reduction [5,6,8]. Further benefits of the SANI process have also been confirmed, including heavy metal and/or pathogen removal [9,10].

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Sulfate content in municipal wastewater is insufficient for a BSR process in most cases. Previous studies used sulfite from flue gas desulfurization to facilitate the BSR process [11–13], but the cost of storing and transporting an external sulfur source is significantly high. Alternatively, elemental sulfur could be an ideal sulfur source for sulfidogenic processes [14] and can be recovered through a sulfide oxidation process under oxygen-limited conditions [15]. Therefore, if such an elemental sulfur reduction process can be developed and integrated with existing techniques of sulfide oxidation and sulfur recovery [15,16], an internal sulfur cycling (ISC) process including sulfur reduction and sulfide oxidation can further be developed to minimize the cost of external sulfur sourcing for BSR processes. Although sulfide oxidation and recovery techniques have been studied extensively [15–17], the elemental sulfur reduction process has not been reported in the literature.

Several technical issues should be addressed in developing this novel BSR process. The first issue is whether sulfur can be effectively reduced or not. Many microorganisms, such as *Wolinella succinogenes, Pseudomonas, Geobacter*, *Desulfuromonas*, *Desulfuromusa*, *Desulfovibrio,* and *Desulfomicrobium*, can biologically reduce elemental sulfur to sulfide using a wide range of organic substrates, including sugars, lactate, peptone, ethanol, propionate, and acetate, as electron donors through dissimilatory sulfur reduction [18,19]. For instance, acetate can be utilized as described by Eq. (1) [20]. However, no information on elemental sulfur reduction by such microorganisms for engineering purposes has been reported in the literature.

$$Acetate^{-} + 4S^{0} + H^{+} + 2H_2O \rightarrow 2CO_2 + 4H_2S \quad \Delta G^{0} = -39\ kJ/mol \tag{1}$$

The second issue is how the bioavailability of elemental sulfur can be enhanced while its water solubility is only 5 μg/L at 25 °C and a neutral pH value [21]. Strengthening the direct contact between sulfur particles and sulfur reducers would likely achieve the high-rate sulfur reduction, but no such method has yet been developed.

This study uses elemental sulfur particles to serve as electron acceptors in BSR and provide micro-carriers for the self-immobilization of sulfidogenic biomass to form a biofilm, thus increasing the biomass capacity and sulfur reduction rate. A laboratory-scale sulfur-reducing anaerobic fluidized bed (SRAFB) reactor was constructed and continuously operated for 273 days to (a) extensively evaluate its performance in elemental sulfur-driven organics removal and sulfide generation by determining the critical operating parameters to achieve high BSR efficiency and (b) assess the sludge yield of this reactor. The properties of the reactor sludge and its microbial community were also analyzed to characterize the biofilm in the reactor.

2. Materials and methods

2.1. Reactor setup and operation

The SRAFB reactor was made of plexiglass with an effective volume of 3.02 L (Fig. 1). A lamella sedimentation tank with an effective volume of 2.64 L was used to separate sludge from the SRAFB effluent. All the sludge in the sedimentation tank was recycled back to the SRAFB reactor using a peristaltic pump.

Seeding sludge was collected from the Sha Tin Sewage Treatment Works (STW) in Hong Kong, China because it contains a high abundance of sulfate-reducing bacteria (SRB) [22,23]. Analytical-grade sublimated elemental sulfur (Damao, China, purity > 99.5%, size in 20–40 μm) was used as a biofilm carrier and an electron acceptor in the SRAFB reactor. Ten grams of the sublimated sulfur particles were mixed with the seeding sludge at the start of the SRAFB reactor operation and sulfur was supplemented on a daily basis depending on the daily sulfur consumption during the operation.

The bioreactor was continuously fed with synthetic domestic wastewater and magnetically stirred in a temperature-controlled chamber (~25 °C) for 273 d. To avoid fluctuations in the sulfide production rate due to different organic matter concentrations in the influent wastewater, synthetic domestic wastewater was prepared according to our previous research [11] (Table S1) by adding 840 mg/L sodium bicarbonate ($NaHCO_3$) (as a buffer solution).

A stepwise decrease in the hydraulic retention time (HRT) from 13.5 h to 1.7 h was performed to determine the operational parameters for the high-rate sulfur-reducing anaerobic wastewater treatment. HRT was thereafter increased back to 3.0 h by adjusting the flow rate to investigate critical organic loading rates (OLRs) and HRTs. The detailed information on OLRs and HRTs is presented in Table 1. The aforementioned HRT is the total HRT of the entire system, including that of the sedimentation tank. The HRT of the SRAFB reactor was approximately half the total HRT (Table 1). At the end of the sixth period, the SRAFB reactor was disconnected for three days to study the mechanisms of high-rate sulfur reduction [24].

Daily measurements of organic matter and dissolved sulfide in the influent and effluent of the SRAFB reactor were conducted to determine the removal of organics and generation of sulfide.

2.2. Sampling and analytical methods

The influent and effluent of the SRAFB reactor were collected and immediately filtered through disposable Millipore filters (0.45 μm pore size). The samples were then analyzed for various water quality parameters such as dissolved sulfide (H_2S, HS^-, and S^{2-}), pH, alkalinity, and volatile fatty acids (VFAs). Total organic carbon (TOC) was measured instead of CODc in this study to eliminate the effect of dissolved sulfide on carbonaceous COD (hereafter referred to as CODc) measurement [25]. TOC was analyzed with a TOC analyzer (Shimadzu TOC-5000A), followed by the conversion to CODc based on a theoretical ratio of 2.67 g COD/1.00 g TOC [25]. Dissolved sulfide was determined by the methylene blue method [26]. Sulfate and thiosulfate concentrations in water samples were quantified using an ion chromatograph (DIONEX-900). Sulfur in the sludge samples was extracted based on the method of McGuire and Hamers [27] using high-performance liquid chromatography (HPLC, Shimadzu LC-10AT, Japan) and a Kromasil column (C_{18}, 5μ, 100 Å) equipped with a UV detector at 254 nm. VFAs and alkalinity were analyzed using the five-point titration method [28]. pH was measured with a pH meter (HQ40D). Sludge volume index in 30 min (SVI_{30}), mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS) were measured following the standard methods [26].

2.3. Sludge yield evaluation

The sludge yield of the SRAFB reactor was determined from the CODc removal and net total biomass growth (Eqs. (2) and (3)). The amount of daily removed CODc was determined by multiplying the CODc removal efficiency by volumetric OLR (kg CODc/m^3-d). The observed biomass growth (kg VSS/m^3-d) was obtained by periodically measuring the biomass amount in the reactor. The sludge loss during sampling was considered when evaluating the sludge yield. No other sludge withdrawals were conducted. Stable system performance was achieved with minimum HRT (3.0 h) and maximum OLR (2.14 kg CODc/m^3-d) at the final stage (Day 218 to 273). Accordingly, the sludge yields in the SRAFB reactor were assessed in this time period to determine the bioreactor's sludge production.

$$Sludge\ yield_{obsered} = \frac{X_{t_2} - X_{t_1}}{\sum_{t_1}^{t_2} CODc_{removed}} \tag{2}$$

$$Sludge\ yield_{actual} = \frac{X_{t_2} - X_{t_1} + \sum_{t_1}^{t_2} X_{effluent} + X_{\mathrm{sampling}}}{\sum_{t_1}^{t_2} CODc_{removed}} \tag{3}$$

where *Sludge yield*$_{obsered}$ and *Sludge yield*$_{actual}$ represent the actual and