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Free nitrous acid pretreatment of wasted activated sludge to exploit internal carbon source for enhanced denitrification

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HIGHLIGHTS

- Free nitrous acid (FNA) pretreatment of waste activated sludge (WAS) was studied.
- FNA pretreatment of WAS enhanced internal carbon source exploitation.
- Denitrification performance and sludge reduction improved after FNA pretreatment.
- FNA pretreatment also relieved greenhouse gas N_2O production in denitrification.

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ABSTRACT

Using internal carbon source contained in waste activated sludge (WAS) is beneficial for nitrogen removal from wastewater with low carbon/nitrogen ratio, but it is usually limited by sludge disintegration. This study presented a novel strategy based on free nitrous acid (FNA) pretreatment to intensify the release of organic matters from WAS for enhanced denitrification. During FNA pretreatment, soluble chemical oxygen demand (SCOD) production kept increasing when FNA increased from 0 to 2.04 mg HNO_2-N/L. Compared with untreated WAS, the internal carbon source production increased by 50% in a simultaneous fermentation and denitrification reactor fed with WAS pretreated by FNA for 24 h at 2.04 mg HNO_2-N/L. This also increased denitrification efficiency by 76% and sludge reduction by 87.5%. More importantly, greenhouse gas nitrous oxide production in denitrification was alleviated since more electrons could be provided by FNA pretreated WAS.

1. Introduction

Biological nitrogen removal (BNR) from wastewater is critical for reducing eutrophication. But the deficiency of organic carbon source usually affects denitrification. Adding external carbon sources (e.g. ethanol, methanol, acetate and glucose) can provide electron donors (Biradar et al., 2008; Kampas et al., 2009; Mokhayeri et al., 2008), but impose a financial burden for wastewater treatment plants (WWTPs). Meanwhile, large quantities of waste activated sludge (WAS) are produced from BNS processes, and the WAS treatment and disposal (i.e., sanitary landfill, incineration, composting) is costly (Weemaes et al., 2000) and takes up to approximately 60% of the overall WWTP costs (Saby et al., 2002). If the organic substances (like proteins and polysaccharides) contained in WAS can be effectively released, it can not only reduce the sludge amounts, but also serve as the internal carbon sources for BNR to save operational cost (Kampas et al., 2007). Fermentation-elutriation has been widely applied to produce volatile fatty acid (VFAs) from sludge, and the produced VFAs has been found as a suitable carbon source for denitrification (Kampas et al., 2009). Particularly, a simultaneous fermentation and denitrification reactor (SFDR) was proposed (Zhang et al., 2010), which enhanced the exploitation of internal carbon source contained in WAS by combining sludge fermentation and denitrification together. This system eventually achieved an efficient, *in situ* utilization of carbon source produced form WAS. Because the main components of WAS are mainly microbial cells and insoluble flocs, WAS reuse has been hindered by sludge breakdown and bacterial decay (Ge et al., 2011; Pijuan et al., 2012). Therefore, finding a

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feasible way of exploiting internal carbon source contained in WAS and saving BNR and sludge treatment costs bears a profound significant for sustainable, stable and efficient operation of WWTPs.

Sludge pretreatment could improve the VFA production from WAS. The pretreatment technologies are mechanical (using high pressure or high speed homogenizer; hydrodynamic cavitation, and ultrasound) (Biradar et al., 2010; Onyeche, 2007; Zhang et al., 2007), chemical (with the addition of acid, base, ozone, and chlorine oxidant) (Heinz, 2007; Saby et al., 2002; Tong and Chen, 2009), thermal (thermophilic pretreatment at 50–60 °C) (Ge et al., 2011), and electrical (Neis et al., 2008) approaches. All of these pretreatment methods aim at enhancing sludge floc disintegration and disrupting microbial cells, and thus the extracellular and/or intracellular constituents can be released to bulk aqueous phase. These soluble biopolymers are further hydrolyzed and acidized to organic acids. Ultrasonic pretreatment at 0.5 W/mL for 30 min effectively destroyed sludge floc and lyse biological cells, with sludge mass decreasing by 23.9% (Zhang et al., 2007). Hydrodynamic cavitation (HC) accelerated SCOD production from excess cell mass (Biradar et al., 2010). High-pressure thermal hydrolysis (HPTH) pretreatment (130–180 °C at 6–12 bar) considerably improved WAS fermentation yield, and the volumetric VFAs generation rate of the pretreated WAS was 4–6 times of raw WAS (Morgan-Sagastume et al., 2011). Fermentation liquids have been used as an effective carbon source to improve total nitrogen removal efficience in a two-step sludge alkaline fermentation and A_2O system (Gao et al., 2011). Particle ozonation pretreatment for sludge in anoxic/aerobic reactor reduced the sludge biomass of 25 with a dosage of 0.05 g O_3/g total suspended solids (TSS) (Dytczak et al., 2007). However, most of those technologies required intensive cost (high energy inputs) and large consumption of chemicals, and are not environmentally friendly.

Biocides, including alcohols, phenolic compounds, glutaraldehyde, magnesium hydroxide and hydrogen peroxide have been employed to deactive microorganisms (Block, 2001). When bacteria were exposed to hydrogen peroxide at 30–1000 mg/L for 10–360 min, strong biocidal effect on bacteria were produced (Block, 2001). Although some of antimicrobial agents were effective to sludge disintegration, their applications may be limited by their inherent toxicity and persistence. Recently, free nitrite acid (FNA) has been found to be extraordinarily biocidal to some microbial groups. Viable cells of anaerobic sewer biofilms decreased by approximately 80% after 6–24 h treatment at FNA of 0.2 mg HNO_2-N/L (Jiang et al., 2011b), and the relationship between the biocidal effect and FNA concentrations was exponential. The intermittent FNA dosage was optimal to control sulfide and methane production in sewers (Jiang et al., 2011a). Moreover, the viable fraction of WAS decreased 80% when FNA concentration was up to 2.02 mg HNO_2-N/L, and the biodegradability of the FNA pretreated sludge increased by 50% (Pijuan et al., 2012).

However, the effect of FNA pretreatment on exploiting internal carbon source contained in WAS for enhanced denitrification has not been well understood yet. Compared with pretreatment methods, FNA pretreatment has two key advantages. Firstly, it is environmentally friendly since nitrite as biocides could be reduced into nitrogen gas in subsequent denitrification process. Secondly, the cost of adding nitrite is low since it could be produced in a sludge reject water treatment system (Law et al., 2015). The feasibility of FNA pretreatment to increase internal carbon source exploitation for enhanced denitrification was investigated in this study. There were three tasks. First, the biocidal of FNA on the sludge disintegration was elucidated by measuring the loss of viable cells and the released SCOD, proteins and polysaccharides. Second, the role of FNA treatment on exploiting internal carbon source contained in WAS was determined by comparing denitrification and sludge reduction of WAS with and without FNA treatment in a simultaneous fermentation and denitrification reactor. Finally, FNA pretreatment for reducing nitrous oxide (N_2O) production was studied.

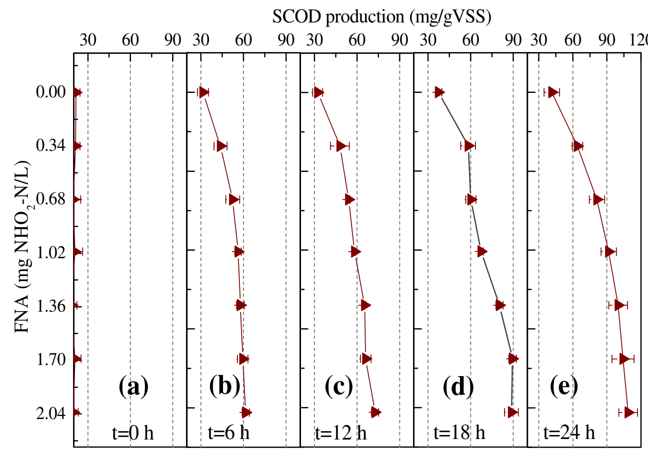

Fig. 1. Organic matter release from the FND pretreated WAS at different FNA concentrations (0–2.04 mg/L) and different pretreatment times (0–24 h).

2. Methods

2.1. Sludge source

WAS was taken from a pilot scale BNR sequence batch reactor (SBR) fed with domestic wastewater. The sludge retention time (SRT) was 25 d. Average SCOD and total chemical oxygen demand (TCOD) of WAS were 53.3 mg/L and 19.6 g/L, respectively. pH varied in the range of 7.0–7.4. The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were 15.7 g/L and 11.4 g/L.

The sludge for simultaneous fermentation and denitrification (SFD) was obtained from a 10 L lab-scale SBR operated at room temperature with the SRT of 50 d, SCOD of 350 mg/L, MLSS of 12.5 g/L, MLVSS of 7.8 g/L, and pH of 7.6–7.8.

2.2. Batch tests to determine FNA biocidal effect

In order to evaluate the effect of FNA pretreatment on sludge disintegration or destroying microbial cells, seven sets of batch tests were conducted using WAS (hereafter called Test 1). The working volume of a sealed batch reactor was 0.5 L. After withdrawn from the pilot scale SBR, WAS was washed for three times by centrifugation at 4000 rpm for 5 min to remove any remaining external carbon. The concentrated WAS was diluted by adding Milli-Q water in batch reactor, and MLSS and MLVSS were adjusted to 15 g/L and 11 g/L, respectively. Different volumes of a nitrite stock solution (147.9 g/L $NaNO_2$) were added to batch reactors to obtain the initial nitrite concentrations of 0, 50, 100, 150, 200, 250, and 300 mgN/L, respectively. All the experiments were conducted for 24 h under strict anoxic condition by sparging high-purity N_2 into the batch reactors for 10 min before tests. pH was controlled at 5.5 ± 0.1 by manually adding 1.0 M HCl or 1.0 M NaOH. pH was measured online using a pH meter (pH/oxi340i, WTW Company, Germany). FNA concentration was calculated using the formula: $S_{NO_2^- \text{-N}}/(K_a \times 10^{pH})$ with the K_a value determined by $K_a = e^{-2300/(273+T)}$ (Anthonisen et al., 1976), and T was the measured temperature (26 ± 1 °C). Thus, the corresponding FNA concentrations were determined to be 0, 0.34, 0.68, 1.02,