Bioresource Technology 182 (2015) 75–81

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Regeneration of elemental sulfur in a simultaneous sulfide and nitrate removal reactor under different dissolved oxygen conditions

Xiaowei Wang, Yu Zhang *, Jiti Zhou, Tingting Zhang, Mingxiang Chen

Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, PR China

HIGHLIGHTS

- 8.16 kg-S m^{-3} d^{-1} sulfide and 2.48 kg-N m^{-3} d^{-1} nitrate was simultaneously converted.
- S^0 regeneration efficiency reached 100% at 0.35–8.16 kg-S m^{-3} d^{-1} in appropriate DO.
- In 0.1–0.3 mg L^{-1} DO, TN removal efficiency was improved to 90% at high S^{2-} loading.

ARTICLE INFO

Article history:
Received 25 November 2014
Received in revised form 22 January 2015
Accepted 28 January 2015
Available online 4 February 2015

Keywords:
Sulfide removal
Nitrate-reducing
Dissolved oxygen
Elemental sulfur regeneration

ABSTRACT

A continuous reactor in microaerobic conditions was adopted for sulfide-oxidizing, nitrate-reducing and elemental sulfur (S^0) regenerating, simultaneously. The results showed that appropriate dissolved oxygen (DO) enhanced S^0 regeneration efficiency, sulfide oxidation efficiency, and nitrate reduction efficiency. When the DO concentration was 0.1–0.3 mg L^{-1}, the microaerobic bioreactor simultaneously converted 8.16 kg-S m^{-3} d^{-1} of sulfide to S^0 and 2.48 kg-N m^{-3} d^{-1} of nitrate to nitrogen with the sulfide and nitrate removal efficiency of 100% and 90% respectively. Compared with anaerobic sulfide and nitrate removal process previously reported, the loading sulfide was higher and more S^0 was generated during the operation in microaerobic reactor. Analysis using the 16S rDNA gene clone library revealed that *Azoarcus*, *Thauera*, *Paracoccus*, *Sulfurospirillum*, *Arcobacter* and *Clostridium* were the dominant microorganisms in the sulfide and nitrate removal system.

1. Introduction

Sulfur oxides (SO_2) and nitrogen oxides (NO_x), the major off-gases pollutants released from industrial, chemical, and petrochemical processes could result in serious environmental pollution, disturb ecosystem and threaten human health (Guo et al., 2014; Zhou et al., 2014). Considerable physico-chemical methods (e.g. Wet-FGD and SCR) have been proposed to reduce SO_2 and NO_x emissions (Guo et al., 2014). However, all these physico-chemical methods require complicated and expensive equipments and usually result in secondary pollutants production (Sohn and Kim, 2002). Therefore, more environment-friendly and more economical processes urgently need to be developed for SO_2 and NO_x treatment.

In biological flue gas desulfurization (BIO-FGD) process, scrubbed SO_2 (sulfite or sulfate) was reduced to sulfide by sulfate reducing bacteria (anaerobic stage); followed by oxidation of sulfide to S^0 via sulfide-oxidizing bacteria (aerobic stage) (Krishnakumar et al., 2005; Lohwacharin and Annachhatre, 2010). In the wet flue gas NO_x removal process, NO_x could be treated by oxidant, and then be scrubbed with alkaline solution in formation of nitrate (Mondal and Chelluboyana, 2013). However, the nitrate and nitrite needed to be treated before they were discharged to the environment (Zhou et al., 2014). Biological denitrification reaction could also occur efficiently under aerobic environment, as more and more novel species have been demonstrated (Kodama and Watanabe, 2004; Shi et al., 2013; Zhao et al., 2013). So both denitrification and sulfide oxidation to S^0 can occur in aerobic conditions.

Therefore, the objective of the present study is to propose a novel method for simultaneous flue gas desulfurization and denitrification. This novel method consists of three serial processes: (1) SO_2 can be washed by alkaline solution in an absorption tower, scrubbed SO_2 (sulfite or sulfate) was commonly reduced to sulfide by sulfate reducing bacteria (Jiang et al., 2013); (2) NO_x can be treated by alkaline solution containing oxidant, and then NO_x could be converted to nitrate (Mondal and Chelluboyana, 2013); (3)

* Corresponding author. Tel.: +86 411 84706240; fax: +86 411 84706252.
E-mail address: zhangyu@dlut.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.biortech.2015.01.123
0960-8524/

Harmless treatment of sulfide ($S^{2-} \rightarrow S^0$) and nitrate ($NO_3^- \rightarrow N_2$) with high S^0 regeneration efficiency could be achieved simultaneously in an aerobic or microaerobic bioreactor. The advantages of this proposed process is that on the basis of biological desulfurization, simply adding a NO_x absorption tower can achieve the goal of simultaneous desulfurization and denitrification using aerobic oxidation of sulfide and aerobic denitrification characteristics, and at the same time, regenerate S^0 and make nitrogen oxide emissions innocuous.

The key step of this novel method is biological transformation process of sulfide and nitrate in aerobic conditions. A lot of researches on separate sulfide and nitrate bio-removal under aerobic conditions have been published (de Graaff et al., 2012; Krishnakumar et al., 2005; Kodama and Watanabe, 2004; Lohwacharin and Annachhatre, 2010; Shi et al., 2013; Zhao et al., 2013). Studies on simultaneous sulfide and nitrate removal in anaerobic conditions were also reported extensively (Table 1). Yet, few researches focused on simultaneous sulfide and nitrate removal under aerobic conditions. It was hard to obtain stable nitrate removal efficiency in the presence of high sulfide concentration, because excess sulfide inhibited the activity of denitrifers in anaerobic conditions (Beristain-Cardoso et al., 2009; Manconi et al., 2007). It was demonstrated that the sulfide and nitrate removal performance was enhanced by the presence of a limited quantity of oxygen in bioreactor (Chen et al., 2010a). The activity of sulfide oxidase was stimulated by microaerobic conditions leading to increased sulfide removal efficiency. Thus the overall sulfide and nitrate removal performance could be improved through reduced inhibition of sulfide on denitrifiers (Chen et al., 2010c). So the DO is a key factor simultaneously influencing sulfide oxidation, nitrate reduction, and S^0 regeneration.

However, the effects of DO on the regeneration of S^0 and its potential contributions to the removal of enriched sulfide and nitrate have not been investigated in the literature. Therefore, the objective of the present study is to propose a novel method for treating enriched sulfide and nitrate with high S^0 regeneration efficiency and short processing time under different DO conditions. The coupling effects among sulfide-oxidizing bacteria, and nitrate-reducing bacteria on sulfide and nitrate removal were explored. The symbiotic relationship among these bacteria was evaluated by polymerase chain reaction -16S rDNA gene cloning, sequencing, and phylogenetic analysis.

2. Methods

2.1. Bioreactor design

A microaerobic bioreactor, a 100 mm × 800 mm (diameter × height) polymethyl methacrylate cylinder with 3.7 L active volume and covered with a water jacket to keep the operational temperature at 30.0 ± 0.5 °C, was used for this research (Fig. S1). Seed sludge was collected from the secondary clarifier of Chunliu wastewater treatment plant (Dalian, China). Suspended solids (SS) and volatile suspended solids (VSS) in seed granules were 6.1 g L^{-1} and 4.0 g L^{-1} respectively. The influent synthetic wastewater of 1000 ml consisted of $Na_2S{\cdot}9H_2O$ 0.75–5.8 g, $NaNO_3$ 0.5–6.0 g, yeast extract 0.5 g, KH_2PO_4 0.2 g, $CaCl_2$ 0.1 g, glucose 1.0∼2.0 g, and other trace metals. The pH of the influent was maintained at 8.0 ± 0.2 by bicarbonate and hydrochloric acid addition. DO was adjusted by changing gas flow rate.

2.2. The bioreactor start-up period and degradation period

In the start-up period (day 0–100), we mainly enhanced the sulfide loading from 110 to 430 mg L^{-1} and nitrate loading from 50 to 220 mg L^{-1} by gradually increasing their influent concentrations with COD/S/N ratio maintained constant at 10:2:1.

During the degradation period (I–III), the influent concentrations of sulfide and nitrate were remained at 430 mg L^{-1} and 220 mg L^{-1} respectively, corresponding to 2200 mg L^{-1} COD and COD/S/N ratio remaining constant at 10:2:1. In the degradation period (IV), the influent concentration of sulfide and nitrate were kept at 750 mg L^{-1} and 220 mg L^{-1} respectively, corresponding to 2200 mg L^{-1} COD and COD/S/N ratio remaining constant at 10:3:1. The changing of hydraulic retention time (HRT) was performed to change the loading of influent. The variation of loaded substrates and DO were shown in Table 2. During each changing period, effluents were collected every day to measure concentrations of sulfide, sulfate, thiosulfate, nitrate, nitrite and COD. The concentrations of sulfide, sulfate, thiosulfate, nitrate, nitrite and COD in influents were also measured every day.

2.3. Effects of DO on S^0 generation efficiency and sulfide and nitrate removal efficiencies in the degradation period

The DO was stepwise changed in order to investigate the effects of DO on S^0 regeneration efficiency and sulfide and nitrate removal efficiencies. The degradation period consisted of four stages, I (2.16 kg-S m^{-3} d^{-1} and 1.27 kg-N m^{-3} d^{-1}), II (3.28 kg-S m^{-3} d^{-1} and 1.88 kg-N m^{-3} d^{-1}), III (4.60 kg-S m^{-3} d^{-1} and 2.42 kg-N m^{-3} d^{-1}), IV (8.16 kg-S m^{-3} d^{-1} and 2.48 kg-N m^{-3} d^{-1}). Stages I–III were divided into three different DO concentrations, A (DO < 0.1 mg L^{-1}), B (0.1 < DO < 0.3 mg L^{-1}), C (0.3 < DO < 0.5 mg L^{-1}) whereas stage IV was divided into another three different DO concentrations, B (0.1 < DO < 0.3 mg L^{-1}), C (0.3 < DO < 0.5 mg L^{-1}), D (0.5 < DO < 0.7 mg L^{-1}).

Table 1
Recent continuous tests on oxidation of sulfide-containing substrate in sulfide and nitrate.

Reference	Reactor	Sulfur	S loading[f] (removal)	S^0 regeneration loading[f]	Nitrogen	*N* loading[f] (removal)	Remarks
Reyes-Avila et al. (2004)	CSTR[a]	$S^{2-} \rightarrow S^0$	0.294 (100%)	Partial	$NO_3^- \rightarrow N_2$	0.209 (100%)	Anaerobic
Chen et al. (2008)	EGSB[b]	$S^{2-} \rightarrow S^0$	3.1 (>90%)	3.3	$NO_3^- \rightarrow N_2$	1.45 (54–66%)	Anaerobic
Chen et al. (2009)	EGSB[b]	$S^{2-} \rightarrow S^0$	4.8 (99.1%)	5.3	$NO_3^- \rightarrow N_2$	2.6 (93%)	Anaerobic
Chen et al. (2010b)	EGSB[b]	$S^{2-} \rightarrow S^0$	3.0 (90%)	2.7	$NO_3^- \rightarrow N_2$	1.78 (90%)	Anaerobic
Li et al. (2009)	AAGBR[c]	$S^{2-} \rightarrow S^0$	1.8 (100%)	1.58	$NO_3^- \rightarrow N_2$	0.472 (99.9%)	Anaerobic
Zhou et al. (2011)	EGSB[b]	$S^{2-} \rightarrow S^0$	5.2 (62.5%)	3.22	$NO_3^- \rightarrow N_2$	2.07 (80%)	Anaerobic
Beristain-Cardoso et al. (2011)	UASB[d]	$S^{2-} \rightarrow S^0$	0.29 (100%)	0.21	$NO_3^- \rightarrow N_2$	0.62 (70%)	Anaerobic
This work	ASR[e]	$S^{2-} \rightarrow S^0$	8.16 (100%)	8.16	$NO_3^- \rightarrow N_2$	2.48 (90%)	Microaerobic

[a] CSTR: continuous stirred tank reactor.
[b] EGSB: expanded granular sludge bed reactor.
[c] AAGBR: anaerobic attache d-growth bioreactor.
[d] UASB: upflow anaerobic sludge blanket.
[e] ASR: activated sludge reactor.
[f] Loading: kg m^{-3} d^{-1}.