

Industrial flue gas desulfurization waste may offer an opportunity to facilitate SANI[®] application for significant sludge minimization in freshwater wastewater treatment

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ABSTRACT

This paper reports an exploratory study on the use of a sulfite-rich industrial effluent to enable the integration of a sulfite–sulfide–sulfate cycle to the conventional carbon and nitrogen cycles in wastewater treatment to achieve sludge minimization through the non-sludge-producing Sulfate reduction, Autotrophic denitrification and Nitrification Integrated (SANI) process. A laboratory-scale sulfite reduction reactor was set up for treating sulfite-rich synthetic wastewater simulating the wastewater from industrial flue gas desulfurization (FGD) units. The results indicated that the sulfite reduction reactor can be started up within 11 d, which was much faster than that using sulfate. Thiosulfate was found to be the major sulfite reduction intermediate, accounting for about 30% of the total reduced sulfur in the reactor effluent, which may enable additional footprint reduction of the autotrophic denitrification reactor in the SANI process. This study indicated that it was possible to make use of the FGD effluent for applying the FGD–SANI process in treating freshwater-based sewage.

Key words | flue gas desulfurization, SANI, sulfite reduction

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INTRODUCTION

A novel Sulfate reduction, Autotrophic denitrification and Nitrification Integrated (SANI[®]) process for wastewater treatment, was developed as a sludge-minimized sewage treatment process, and has been proven to have no excessive biological sludge production by both laboratory and pilot studies (Lau *et al.* 2006; Wang *et al.* 2009; Lu *et al.* 2011). This sulfur cycle-based biological nitrogen removal (BNR) process saves at least 36% energy compared with conventional BNR processes (Lu *et al.* 2011). This is mainly because sulfate acts as an electron carrier for facilitating efficient anaerobic organic conversion as well as efficient autotrophic denitrification (Lu *et al.* 2009), as shown in Figure 1.

In coastal cities like Hong Kong, seawater toilet flushing saves more than 20% freshwater while providing sufficient sulfate (>500 mg/L) for application of the SANI process. In continental areas, various low-cost sulfate sources are available to offer the opportunity to realize this significant sludge-minimized sewage treatment process

for freshwater wastewater. Industrial flue gas desulfurization wastes could provide such a sulfur source since fossil energy-based heating facilities and power stations are popular in developing countries. A SO₂-absorbing flue gas desulfurization (FGD) system alone can provide sufficient sulfite-rich waste for application of SANI in a near by freshwater-based wastewater treatment works. Hence, sulfite reduction in an integrated system of FGD and SANI, named FGD–SANI process, may offer an opportunity to optimize the original sulfate reduction SANI process. Since reduction of sulfate to sulfite by sulfate-reducing bacteria (SRB) is the rate-limited step (Ren *et al.* 2009), sulfite reduction could be more efficient than sulfate reduction, potentially making SANI more compact. On the other hand, sulfite reduction may produce some thiosulfates (Suh & Akagi 1969), which may accumulate to limit sulfite reduction and thus carbon oxidation rate. As an exploratory study, specific focuses will be placed on sulfite reduction in FGD–SANI.

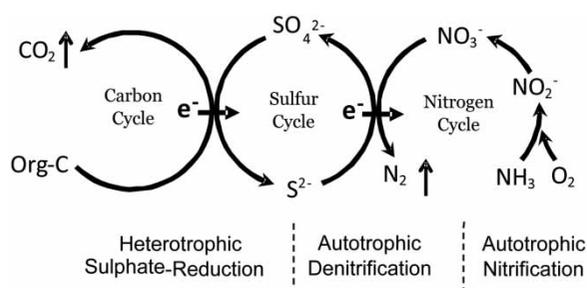


Figure 1 | Schematic diagram of SANI[®] process.

MATERIAL AND METHODS

Two laboratory-scale column reactors (Reactor 1 (R1) and Reactor 2 (R2)) were set up to investigate the performance of a Sulfite Reduction Up-flow Sludge Bed (SRUSB). The reactors were fed with sodium lactate and synthetic wastewater as carbon source, respectively. As lactate was regarded as an organic substrate for enrichment of SRB (Widdel 1988) and many species of SRB can live on lactate as an electron donor and carbon source (Liamleam & Annachhatre 2007), it was selected as the electron donor for R1 to establish a suitable condition for SRB cultivation. In parallel, in order to simulate the treatment of real freshwater-based wastewater, synthetic wastewater was fed into R2 to determine the activity of sulfite-reducing SRB in using different carbon source. These reactors were seeded with anaerobic sludge taken from a local sewage treatment plant. The reactors' configurations and operation conditions

are summarized in Table 1, while stock and mineral solutions were used for preparation of synthetic wastewater (Wang *et al.* 2009). The stock solution and trace solution were diluted with deionized water to 8 L to prepare the influent chemical oxygen demand (COD) at three levels (see Table 1). R1 was then operated for 36 d under a constant condition while that in R2 was operated under three different conditions (that in Phases 1–3) in order to determine the optimal operation conditions for the FGD–SANI process, including pH, ratio of COD to $\text{SO}_3^{2-}\text{-S}$ in the influent and the organic loading.

Sodium sulfite solution was used as sulfite source for both reactors. It was prepared once a day and stored at 4 °C in an oxygen-free container prior to being pumped into the reactors directly. As sodium sulfite is alkaline, some drops of 6 mol/L HCl solution were used to adjust the influent pH to 7.3 ± 0.1 for both reactors except during the first phase of R2. The sodium sulfite solution, lactate feed or synthetic wastewater are both stored separately, each of which was pumped continuously to R1 or R2 by using two different peristaltic pumps at a hydraulic retention time (HRT) of 6 h and an up-flow velocity at 0.5 m/h, with an internal recycle ratio of 4:1 for R1 and 2:1 for R2. Figure 2 shows the set-up of both reactors.

ANALYTICAL METHODS

Regular sample analyses included pH, COD, total organic carbon (TOC), volatile fatty acids (VFA), alkalinity, SO_3^{2-} ,

Table 1 | Reactor description and operating conditions of SRUSB in each stage

Reactor	R1	R2		
Inner diameter (cm)	5.4	5.4		
Height (cm)	60	100		
Effective volume (L)	1.37	2.49		
Up-flow velocity (m/h)	0.5	0.5		
Carbon source	Sodium lactate	Synthetic wastewater		
Flow rate (L/d)	5.48	9.96		
HRT (h)	6	6		
		Phase 1	Phase 2	Phase 3
Inf. pH	7.3 ± 0.1	8.2 ± 0.1	7.3 ± 0.1	7.3 ± 0.1
Average Inf. COD (mg/L)	291	469	513	261
Average Inf. $\text{SO}_3^{2-}\text{-S}$ (mg/L)	224	461	405	467
Average ratio of Inf. COD to Inf. $\text{SO}_3^{2-}\text{-S}$	1.3	1.02	1.27	0.56
Operating period (d)	0–36	0–26	27–62	63–102

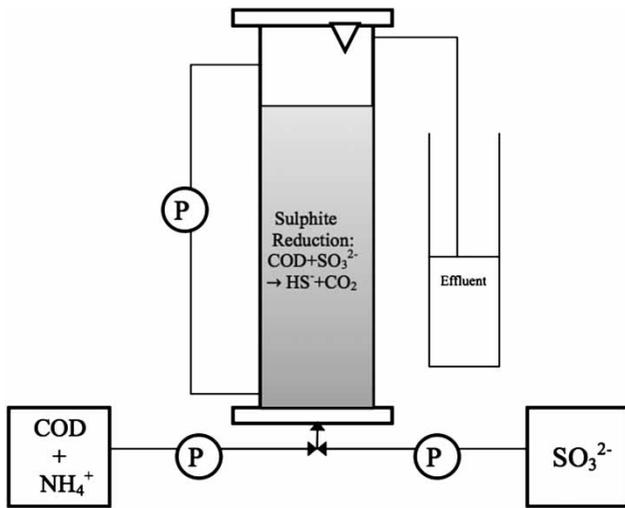


Figure 2 | Schematic of the reactor.

$\text{S}_2\text{O}_3^{2-}$ and sulfide. SO_3^{2-} was measured by titration (APHA 1998). TOC was measured by using a TOC analyzer (Shimadzu TOC-5000A); thiosulfate was determined by using an Ion Chromatograph (DIONEX, ICS-900); while sulfide ($\text{H}_2\text{S} + \text{HS}^-$) was analysed by Methylene Blue method (APHA 1998). MLSS, TSS and COD were measured respectively according to *Standard Methods* (APHA 1998). VFA and alkalinity were measured by using a five-point titration method (Moosbrugger et al. 1993) with a pH meter (Orion Model 0420A1).

RESULTS AND DISCUSSION

Sulfite reduction

Figure 3(a) shows that R1 was successfully started-up within 11 d because sulfite removal efficiency reached >95%. This start-up period is shorter than that of a sulfate reduction SRUSB (Wang et al. 2009). This fast start-up period may be explained from the two-step sulfate reduction process: (1) SO_4^{2-} reduced to SO_3^{2-} and (2) SO_3^{2-} to HS^- , of which the first step needs more energy and hence limits the whole sulfate reduction rate (Ren et al. 2009).

By far there have been two biological sulfite reduction metabolism pathways proposed: direct pathway and indirect pathway. Direct pathway means that 1 mole sulfite can accept six mole electrons from electron donors and directly reduces to sulfide, while in indirect pathway, sulfite reduction should be a multi-step process with intermediate generation before the formation of final product sulfide

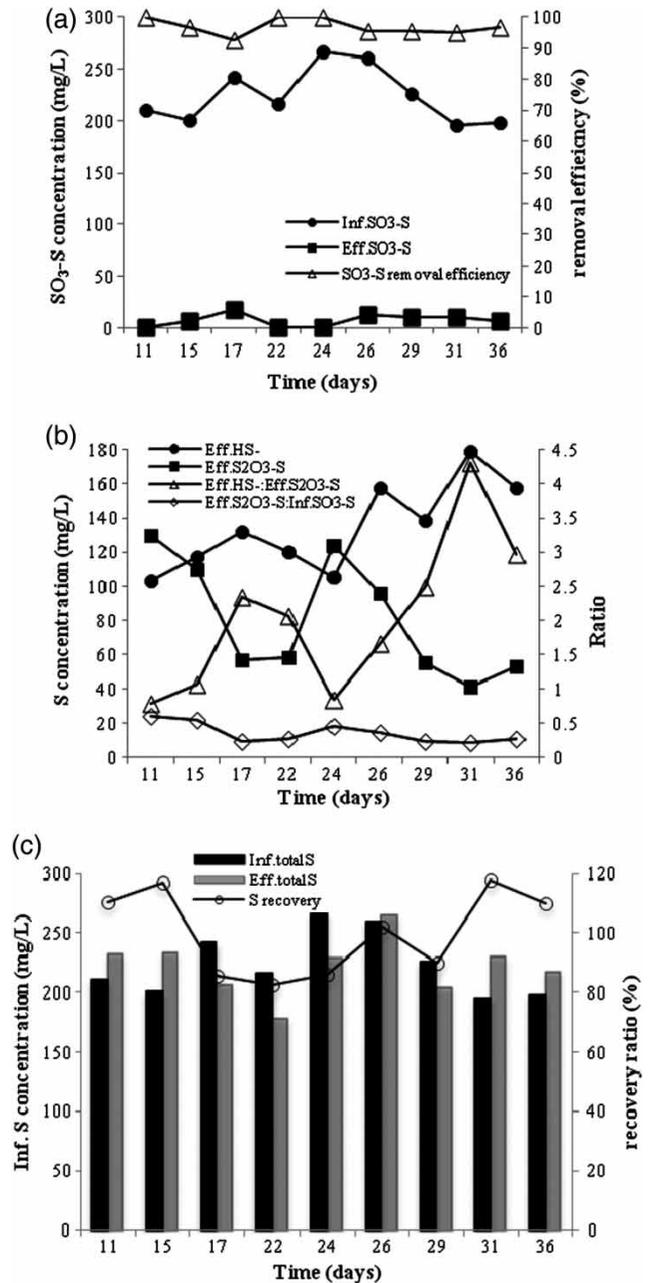
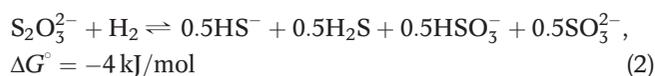
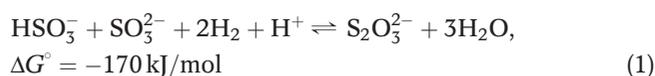


Figure 3 | (a) Performance of sulfite reduction in Reactor 1 for 36 d; (b) effluent sulfide-S and thiosulfate-S and the ratio of effluent thiosulfate to influent sulfite and the ratio of effluent sulfide to effluent thiosulfate; and (c) sulfur balance.

(Ren et al. 2009). During the sulfite reduction step, a significant amount of thiosulfate was produced, concurring with the findings of Suh & Akagi (1969) that thiosulfate was an intermediate during the reduction of sulfite, as shown in Figure 3(b). This intermediate accounts for 62% of influent SO_3^{2-} -S on day 8, and decreased to around 25% after one month. Similar to R1, thiosulfate was also detected in R2 throughout the operation, as shown in Figure 3(b). It is

interestingly noticed that the ratio of thiosulfate over influent SO_3^{2-} -S remains rather constant (Table 2) despite the fact that the ratio of COD: SO_3^{2-} -S in the influent varied between 0.56 and 1.27 (Table 2). This phenomenon may be due to difference in thermodynamics involved in the two-step bio-reduction of sulfite from thiosulfate to sulfide, possibly described by Equations (1) and (2).



Apparently, reduction of thiosulfate to sulfide requires much more energy than that in reduction of sulfite to thiosulfate, explaining why thiosulfate tends to accumulate in sulfite reduction.

Organic removal efficiency

The performance of Reactor R2 is shown in Figure 4. During phase 1 (Day 1–26) when no influent pH control was employed, the organic removal efficiency was low. When the influent pH was adjusted to 7.3, organic removal started to increase, even though the ratio of COD to SO_3^{2-} -S increased from 1.02 to 1.27 during phase 2 operation (Day 27–62) when a maximum of 65% was reached. During phase 3 operation (Day 63–102) when the COD to SO_3^{2-} -S ratio reduced to 0.56, organic removal increased to 80%. The lower organic removal efficiency as compared with that of sulfate reduction in SANI (Wang et al. 2009) is thought to be due to thiosulfate accumulation (Figure 4(b)), as 1 g sulfate-S reduced to 1 g sulfide oxidizes 2 g COD while 1 g sulfite-S to thiosulfate-S consumes only 0.5 g COD. Nevertheless, despite a lower rate of COD removal in sulfite reduction, organic removal efficiency increased to 80% when a high COD-to-sulfite ratio was applied. This indicated that a higher COD-to-sulfite ratio may be needed for FGD-SANI, which can be achieved through adjusting the mixing ratio of FGD waste to municipal wastewater. On the other hand, thiosulfate may favour autotrophic

Table 2 | Average percentage of S_2O_3 accounted for total S in each phase of R2

	Phase 1	Phase 2	Phase 3
COD/ SO_3 -S ratio	1.02	1.27	0.56
S_2O_3 -S percentage (%)	32.92	34.66	35.91

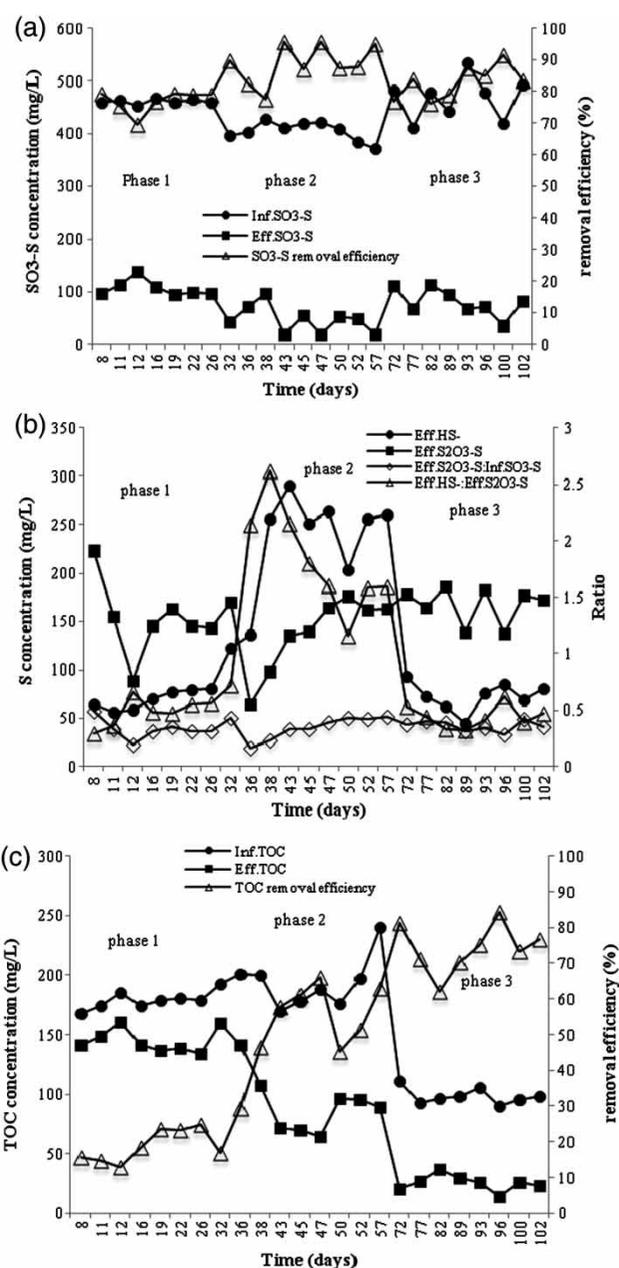


Figure 4 | (a) Performance of sulfite reduction in Reactor 2 for 102 d; (b) effluent sulfide-S and thiosulfate-S and the ratio of effluent thiosulfate to influent sulfite and ratio of effluent sulfide to effluent thiosulfate; (c) TOC removal for R2.

denitrification because the denitrification rate with thiosulfate could be 4.6 times higher as compared to the sulfide-based rate due to less toxicity on denitrifiers from thiosulfate (Cardoso et al. 2006). Further studies on the optimization of the FGD-SANI process is therefore required.

Sulfur balance based on SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, HS^- and S^{2-} of the reactors showed average 100.2% recovery (Figure 4(c)), indicating that neither elemental sulfur accumulation in the

reactors nor volatile hydrogen sulfide escaping to atmosphere (reactor pH 7.8) had occurred during the experiment.

CONCLUSION

SRUSB started up very fast in the laboratory-scale tests using lactate and a synthetic wastewater as the electron donor. As sodium sulfite is rather alkaline, pH control by addition of HCl to the influent is required. Thiosulfate was detected to be a major intermediate in the sulfite reduction process. Moreover, it was noted that the amount of thiosulfate remains rather constant despite the relatively large changes in ratio of COD to SO₃-S (1.02, 1.27 and 0.56). While thiosulfate formation could possibly ease the autotrophic denitrification for BNR, the lower organic removal efficiency appeared to be a constraint affecting the overall performance of the reactor. Overall, the study indicated that sulfite reduction as the first step of FGD-SANI is possible and further study on process optimization is necessary.

ACKNOWLEDGEMENTS

The study is supported by the National Natural Science Foundation of China (51178194), Science and Technology Planning Project of Guangdong Province, China (2012A030600005).

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First received 10 November 2012; accepted in revised form 13 February 2013