Performance and mechanism of anaerobic biotrickling filter for removal of sulfite, sulfate, and hydrosulfite

Niantao Xue, Li Wang, Tianlong Zheng, Jianhua Wang and Qunhui Wang

ABSTRACT

A biotrickling filter (BTF) was designed for removal of sulfite (SO\textsubscript{3}\textsuperscript{2-}), sulfate (SO\textsubscript{4}\textsuperscript{2-}), and hydrosulfite (HSO\textsubscript{3}) produced from flue gas adsorbent during dual-alkali flue gas desulfurization. With an SO\textsubscript{3}\textsuperscript{2-} concentration of 0.89 g-S/(L packing), BTF could completely remove SO\textsubscript{3}\textsuperscript{2-} within 3 h with an elimination capacity (EC) of 296 g-S/(m\textsuperscript{3} h). With an SO\textsubscript{4}\textsuperscript{2-} concentration of 0.60 g-S/(L packing), the removal efficiency (RE) of SO\textsubscript{4}\textsuperscript{2-} reached 90.3% at 5.25 h and 95% at 24 h. With an HSO\textsubscript{3} concentration of 0.74 g-S/(L packing), HSO\textsubscript{3} could not be detected in the trickling liquid at 2 h with an EC of 370 g-S/(m\textsuperscript{3} h). The difference in desulfurization performance of the BTF was minor when sodium lactate and sodium acetate were used as carbon sources. Acetate was more superior when taking both the carbon/sulfur ratio (C/S) and RE into account. The total dissolved sulfide yield was over 70% with sodium acetate as the carbon source, which was 15–20% higher than that with sodium lactate. Sodium lactate was not completely degraded and acetic acid was produced. All oxidation–reduction potential values were lower than −370 mV, indicating a perfect anaerobic condition in the BTF. The BTF could efficiently treat sulfite, sulfate, and hydrosulfite and could replace the regeneration stage of the dual-alkali process.

Key words | biotrickling filter, carbon source, flue gas desulfurization, hydrosulfite (HSO\textsubscript{3}), sulfate (SO\textsubscript{4}\textsuperscript{2-}), sulfite (SO\textsubscript{3}\textsuperscript{2-})

INTRODUCTION

Sulfur dioxide (SO\textsubscript{2}) released from the burning of coal and fuel oil results in global environmental pollution and threatens industrial production and human life. Therefore, great efforts have been made to develop technologies for SO\textsubscript{2} control. Among many schemes, flue gas desulfurization (FGD) is the most reasonable one from both technological and economic perspectives (Gao et al. 2011). Based on the processes by which the desulfurization product is captured and the active ingredient is applied, they can be classified as dry, semidry, and wet processes, where wet processes have earned widespread use due to their lower operating cost, high desulfurization efficiency, and more stable operation (Gutiérrez Ortiz et al. 2006).

Removal of sulfur in wastewater, such as sulfite, sulfate, or hydrosulfite, is an important field of desalination. The popular desalination technology is membrane separation, including electrodialysis, reverse osmosis, or forward osmosis, etc. Bioprocess for wastewater treatment is a cost-effective and efficient technology. Biological treatment of sulfur will expand the scope of the study of desalination.

High sulfur-laden wastes are extensively produced from wet FGD. Depending on the coal source, scrubber type, quality of water makeup, additive use, and other operational conditions, FGD wastewater may carry total dissolved solids as high as 50,000 mg/L (US EPA 2009). The main treatment processes for FGD wastewater are the physico-chemical method (Lefers et al. 1987), fluidized bed method (Armstrong et al. 2013), membrane separation method (Bijmans et al. 2008; Yin et al. 2013), among others. However, these methods suffer from high operating costs.

Dual-alkali, a widely used process in the industry, is a regenerative (cyclic) process: after reaction with sulfur...
dioxide, an active ingredient is regenerated and returned back to the process, which lowers absorbent consumption. In the absorption stage, NaOH, Na₂SO₃, or NaCO₃ function as the first alkali to absorb SO₂ from the flue gas stream. In the regeneration stage, the absorbent is sent to the lime reactor, lime slurry or limestone, and the second alkali is used to regenerate the spent absorbent, which is recirculated to remove SO₂ (Guan et al. 2009). The obtained semi-hydrated calcium sulfite can be oxidized to produce gypsum. However, the gypsum is of poor quality due to the presence of ash and Na₂SO₄ (a byproduct of desulfurization). Therefore it is generally discarded, resulting in a bulk of industrial solid wastes that trigger environmental concerns (Wang et al. 2013). Transportation costs, low purity, and regulations regarding ash constituents in the building material do not allow FGD gypsum to compete with natural gypsum (Kaufman et al. 1997). Thus it is necessary to develop new processes to replace the regeneration stage of the dual-alkali process.

A bioprocess for the treatment of desulfurized wastewater provides an attractive alternative to conventional processes of physico-chemical desulfurization (Wang et al. 2010). During the biosulfurization process, microbes reduce contaminants at the oxidized states, such as sulfur dioxide (SO₂), sulfate (SO₄²⁻), sulfite (SO₃²⁻), and thiosulfate (HSO₄⁻), to sulfur in a reduction state without secondary pollution. The highlight of biological treatment of wastewater, which is presently the most popular technology, is its low operating cost. Therefore, biosulfurization is a good prospect for FGD wastewater treatment.

Anaerobic biological sulfate reduction (BSR) is a promising technology for FGD wastewater treatment. At an anaerobic condition, anaerobic reduction microbes such as sulfate reduction bacteria (SRB), can reduce SO₄²⁻, SO₃²⁻, or HSO₄⁻ to S²⁻. Aerobic or anaerobic microbes can then oxidize S²⁻ to elemental S⁰. However, it has been seldom used for the treatment of FGD wastewater. The main reaction formulae of the different SRB with different carbon sources at the reduction stage are listed as follows:

\[
\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} = \text{HS}^- + 2\text{HCO}_3^- \quad (3)
\]

\[
4\text{H}_2 + \text{SO}_4^{2-} + \text{CO}_2 = \text{HS}^- + 2\text{HCO}_3^- + 3\text{H}_2\text{O} \quad (4)
\]

\[
3\text{CH}_3\text{CHOHCOO}^- + 2\text{SO}_4^{2-} = 2\text{HS}^- + \text{H}^+ + 3\text{HCO}_3^- + 3\text{CH}_3\text{COO}^- \quad (5)
\]

\[
3\text{CH}_3\text{COO}^- + 4\text{HSO}_4^- = 4\text{HS}^- + 3\text{HCO}_3^- + 3\text{H}_2\text{O} + 3\text{CO}_2 \quad (6)
\]

The main reaction formulae at the oxidation stage are listed as follows:

\[
2\text{HS}^- + \text{O}_2 = 2\text{S}^0 + 2\text{OH}^- \quad (7)
\]

\[
2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (8)
\]

A crucial factor for obtaining high efficiency in the sulfate-reducing process is the selection of an appropriate carbon source as electron donor (Márquez-Reyes et al. 2015). At anaerobic condition, sulfate (the terminal electron acceptor) is reduced to sulfides and coupled with suitable organic carbon source (electron donor) oxidation by SRB. SRB prefers simple-structured molecules for direct oxidation. H₂, lactate, ethanol, methanol, formate, propionate, acetate, butyrate, glucose, sucrose, and other substances were reported to have been used in batch or continuous modes (Liamleam & Annachhatre 2007; Neculita et al. 2007). Butanol could be used as a carbon source, and very good results have been obtained (Sarti & Zaiat 2011). The reaction equations for sulfate reduction with different carbon sources have been found. However, their mechanisms, such as total sulfur yield, changes in pH, and oxidation–reduction potential (ORP), have not been reported so far. As such, looking for a cheap and abundantly available alternative organic carbon source for SRB is a logical step (Das et al. 2015). A study on this mechanism will benefit the search for a suitable carbon source.

This study aims to: (1) explore the performance of a bio-trickling filter (BTF) for the simultaneous treatment of sulfite, sulfate, and hydrosulfite in FGD wastewater to
replace the regeneration stage of the dual-alkali process; and (2) identify the effects of different carbon sources on the desulfurization performance of BTF. BTF has been widely used in treatment of exhaust air (Melse et al. 2012), and is a potential technology for wastewater treatment. Thus, it was chosen for the present work.

MATERIALS AND METHODS

Operation of the BTF

The BTF system for desulfurization is shown in Figure 1. The sealed BTF was composed of two segments, with each being 80 mm in inner diameter, 500 mm in height, 300 mm in packing height and 1.5 L in effective volume. The ball-shaped fiber packaging materials were spheroidal or ellipsoidal shapes (Xue et al. 2010). An air vent on the top of the BTF collected the H₂S gas in gas sampling bags (polyvinylidene fluoride). Effluent from the BTF flowed to the trickling liquid tank, which was automatically controlled by a temperature-controller and heating tape. The trickling liquid in the tank was pumped to the top of the BTF and then trickled down to packaging materials. Flow of the trickling liquid was adjusted by a voltage- and current-steady power supply.

Performance of BTF for removal of sulfite, sulfate, and hydrosulfite

The BTF was operated in a batch mode. At 35 °C, exactly 3.5 L simulated desulfurization wastewater, with an Na₂SO₃ concentration of 3.0 g/L and an Na₂SO₄ concentration of 2.3 g/L respectively, was prepared. It is known that the pK₁ of H₂SO₃ is 1.81, pK₂ is 6.91. As the pH of the desulfurization wastewater often remains between 4 and 6, SO₃²⁻ is mainly in the form of HSO₃⁻. Simulated desulfurization wastewater was prepared with an NaHSO₃ concentration of 2,060 mg/L, 4,000 mg/L, 4,000 mg/L, and 6,500 mg/L, and pH regulated by HCl of 6.38, 5.51, 4.99, and 4.99, respectively.

As the simulated desulfurization wastewater was being prepared, ultrasonic deoxygenated water was used, ascorbic acid was added, and the wastewater was aerated with N₂ for 10 min to get rid of dissolved oxygen. The BTF was flushed with N₂ and the wastewater was added to the BTF.

RESULTS AND DISCUSSION

Performance of BTF for removal of sulfite, sulfate, and hydrosulfite

At anaerobic conditions, SO₃²⁻ was reduced to sulfide, including S²⁻, HS⁻, and H₂S, called the total dissolved sulfide (TDS). TDS yield is an index for the reduction degree of SO₅²⁻ and the performance of the BTF. The SO₅²⁻ concentration was 2.22 g-SO₃²⁻/(L packing), i.e., 0.89 g-S/(L packing). Changes in sulfite concentration and the TDS yield are shown in Figure 2. SO₅²⁻ in the wastewater was completely removed within 3 h, with an elimination capacity (EC) of 296 g-S/(m³ h). The achievable EC of sulfite was 300 g-S/(m³ h) at a removal efficiency (RE) of 100% in a laboratory-scale expanded granular sludge bed reactor (Weijma et al. 2000), perhaps indicating that BTF was as suitable as an expanded granular sludge bed reactor for SO₅²⁻ removal. It was 16.5 mmol-S/(L h), i.e., 528 g-S/(m³ h) in an immobilized cell recycle reactor (Selvaraj et al. 1997a, b), which achieved a higher EC. However, the operation of immobilized cells was more complex than that of free cells.
The produced TDS reached the highest concentration at 3 h, and then it decreased slowly, being still 200 mg/L at 30 h. Sulfur-oxidizing bacteria are mostly aerobic. Only the Thiothrix denitrificans at anaerobic condition could oxidize $S^{2-}$ to elemental sulfur with $S^{2-}$ itself as the electron donor. However, the dominant bacteria in BTF were SRB, rather than $T$ denitrificans, because SRB were inoculated in advance. Further oxidation of $S^{2-}$ and $HS^{-}$ to $S^{0}$ is necessary for the complete removal of sulfur from the effluent.

**Performance of BTF for sulfate removal**

The $SO_{4}^{2-}$ concentration was 1.81 g-SO$_{4}^{2-}$/L packing, i.e., 0.60 g-S/L packing. Changes in the sulfate and its RE in the trickling liquid were continuously detected and are demonstrated in Figure 3. The sulfate concentration at 8 h remained stable at around 115 mg/L, and decreased to 78 mg/L at 24 h. The RE of sulfate reached 79% at 2 h, 90.3% at 5.25 h, and slowly rose to 95% at 24 h, indicating that the screened SRB in our previous work could reduce $SO_{4}^{2-}$ effectively. The best efficiency for sulfate removal (71%) was accomplished in an anaerobic sequencing batch reactor that was mechanically stirred during the assay with a chemical oxygen demand (COD)/$SO_{4}^{2-}$ ratio of 1.34 (Friedl et al. 2009). The up-flow anaerobic sludge blanket reactor, inverse fluidized bed reactor, and gas lift anaerobic membrane bioreactor can all be applied for the treatment of leachate through the construction and demolition of debris sand with the highest sulfate RE of 75–85% (Kijjanapanich et al. 2014). The BTF could achieve a high RE of sulfate.

**Performance of BTF for hydrosulfite removal**

The $HSO_{3}^{-}$ concentration was 1.87 g-SO$_{3}^{2-}$/L packing, i.e., 0.74 g-S/L packing. The removal rate of HSO$_{3}^{-}$ in the BTF was quick. The RE was above 95% at 0.5 h, and HSO$_{3}^{-}$ could not be detected in the trickling liquid at 2 h with an EC of 370 g-S/(m$^3$ h). The value of the pH rapidly rose and stabilized at 7.0–7.5 at 0.5 h. The initial pH rise was due to the neutralization of the alkaline biofilm. However, the pH did not fluctuate. Overall, the pH exhibited similar changes in the four tests as reported in our previous work (Zheng et al. 2014). In summary, sulfite, sulfate, and hydrosulfite in desulfurization absorbent could be effectively removed in an anaerobic BTF.

**Mechanism for SRB using different carbon sources**

Lactate is a potential carbon source and energy donor, offering advantages in the BSR process. It supports the growth of a wide spectrum of SRB, encouraging microbial diversity and the consequent resilience of treatment systems (Kaksonen et al. 2006). Sodium lactate was used as carbon source in our previous test, and the BTF performed well. The following experiment was conducted to understand whether sodium lactate was either completely degraded into H$_2$O and CO$_2$ or stayed at the acetic acid stage. The

**Figure 2** | Changes in sulfite concentration and TDS yield.

**Figure 3** | Changes in sulfate and its RE in BTF.
concentration of sodium lactate (analytically pure) was 5 mL/L with a carbon/sulfur ratio (C/S, carbon is expressed with COD in this paper) of 1.5. By contrast, sodium acetate, CH₃COONa·3H₂O (analytically pure) of 5.0 g/L, equivalent to COD of 2,049 mg/L with C/S of 0.92, was also used as carbon source in the study to determine whether SRB could be used to degrade acetate.

The difference in the effect of the two carbon sources on the desulfurization performance of BTF was minor (see Figure 4). At 0.5 h, the RE of SO₂⁻ with sodium lactate and sodium acetate as carbon sources, respectively. Afterward, the RE of SO₂⁻ with sodium acetate as a carbon source was higher than the RE with sodium lactate. At 5 h, SO₂⁻ was completely removed with sodium acetate as a carbon source, and the EC was 467 g-S/(m³ h). The maximum RE of SO₂⁻ with sodium lactate as a carbon source was 98.4% at 6 h. Sodium lactate and sodium acetate could both be used as carbon sources for SRB. Acetate was superior, by taking both C/S and RE into account (Wang 2011).

An obvious difference was observed in TDS yields with the two carbon sources, which are demonstrated in Figure 5. The TDS yields were over 70% with sodium acetate as a carbon source, which was 15–20% higher than the yield with sodium lactate.

The values of pH and ORP with different carbon sources are shown in Figure 6. All ORP values were lower than –370 mV, indicating a perfect anaerobic condition in the BTF, which was a very important condition for SRB to survive and normally metabolize. Minor differences in ORP were observed with lactate or acetate as a carbon source.

However, the pH in the effluent significantly decreased at 25 h, and all values of pH were lower with lactate as a carbon source than those with acetate as a carbon source, indicating that sodium lactate was not completely degraded and that acetic acid was produced (see Equations (5) and (6)). Based on their metabolic capabilities, SRB are categorized as either complete oxidizing SRB, which are able to oxidize the organic compounds to CO₂, or incomplete oxidizing SRB, which carry out an incomplete oxidation of the organic source, usually to acetate as an end product (Colleran et al. 1995; Muyzer & Stams 2008). A complete lactate oxidation is not achieved by most Desulfobacter species and particular
Desulfo bacterium species. Desulfnema magnum does not grow on lactate (Widdel 1988). The oxidation process stayed at the acetic acid stage, and the produced acetate cannot be further used as a carbon source. Acetate production during the BSR process is actually a major drawback of sulfate-reducing reactors because SRB cannot completely oxidize acetate even with excess sulfate levels (Lens et al. 2002). The acetate remaining in the effluent largely contributes to the residual COD (Omil et al. 1996; Lens et al. 1998). Overall, acetate is a more suitable carbon source.

The values of pH were higher with acetate as a carbon source, and sulfate could be completely degraded, perhaps indicating the presence of a complete oxidizer SRB. These SRB can completely degrade acetate to CO2 and H2O; thus, they do not cause the accumulation of acetic acid and do not lead to environmental acidification, or failure of the wastewater treatment system. Furthermore, complete oxidation of acetate favors the recycling of carbon. As such, these SRB have been paid more and more attention.

CONCLUSIONS

The BTF was revealed to treat sulfite, sulfate, and hydrosulfite in FGD wastewater, and it could replace the regeneration stage of the dual-alkali process. The BTF could completely remove SO2−4 within 3 h with an EC of 296 g-S/(m3-h). With an SO2−4 concentration of 0.60 g-S/L packing, the RE of SO2−4 reached 90.3% at 5.25 h and 95% at 24 h. The RE of HSO3− was above 95% at 0.5 h, and HSO3− could not be detected in the trickling liquid at 2 h with an EC of 370 g-S/(m3-h). Sodium lactate and sodium acetate could both be used as carbon sources for SRB reduction. Acetate was superior when C/S and RE was taken into account. In addition to FGD, the potential applications of BTF include the treatment of sulfate/sulfite-laden wastewater from pulp and paper, petroleum, mining, and chemical industries.

REFERENCES


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