Desulfurization performance of biotrickling filter on the removal of flue gas adsorbent produced by dual-alkali flue gas desulfurization process

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

ABSTRACT

A biotrickling filter (BTF) was used to investigate the elimination of flue gas adsorbent containing sulfite, sulfate, and hydrosulfate; it was undertaken to replace the regeneration step of dual-alkali flue gas desulfurization. Sulfate-reducing bacteria (SRB) isolated from landfill leachate were inoculated, and overall desulfurization performance as well as impact resistance was evaluated. The results showed that an efficient SRB could reduce the start-up time to 1 h, which is one third of that required for initial condition, for a sulfite removal efficiency above 80%. Further, the sulfite removal efficiency rose to 98% in 3.9 h with the lower packing load of 5.56 kg SO_3^{2-}-S/(m^3 d), and in 6.4 h for 6.37 kg SO_3^{2-}-S/(m^3 d). In contrast, 85% removal efficiency in 5 h for sulfate and 98% removal efficiency in 0.5 h for hydrosulfite were obtained when the packing loads were 0.95 kg SO_4^{2-}-S/(m^3 d) and 1.76 kg HSO_3^--S/(m^3 d), respectively. Moreover, the BTF could quickly restore after impact shock, such as, 0.5 h restoration time for initial pH which varied from 4.5 to 6.5, 6 d for 27 d shutdown behavior, and 4 d for 5 h high temperature shock of 85 °C. Therefore, the BTF system was an effective method for flue gas adsorbent treatment.

Key words | biotrickling filter, desulfurization, high temperature shock, pH shock, shutdown behavior shock, sulfate-reducing bacteria

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INTRODUCTION

With the ever-increasing resource requirements of human beings, sulfur dioxide (SO_2), which is the primary air pollutant from natural and anthropogenic sources, has caused worldwide atmospheric environmental problems. Moreover, it is the major reason for acid precipitation, which continually affects the natural ecosystem (Schindler 1988; Likens *et al.* 1996), materials of buildings, machinery and municipal facilities (Dincer 2000), and human health (Likens *et al.* 1972; Goyer *et al.* 1985), and exists in both developed and developing countries. Hence, for air pollution control, it is essential to remove the SO_2 mainly from the flue gas of modern industry.

Recently, the dual-alkali flue gas desulfurization (FGD) system (generally Na-Ca dual alkali) has been the most popular process for SO_2 treatment. In the FGD system, aqueous sodium hydroxide (or sodium carbonate) solution is used to absorb the SO_2 of flue gas, and is then regenerated by aqueous lime. However, calcium sulfate (gypsum) by-product, which is of poor quality because of the existence of ash and other desulfurization by-products, is always discarded.

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Moreover, the large-scale gypsum disposal (Teekayuttasakul & Annachhatre 2008) requires further dewatering and a huge area for landfilling. Hence, in order to overcome this disadvantage, a biological reactor has been introduced to replace the regeneration step of dual-alkali FGD. Over the past two decades, the biotrickling filter (BTF) seems to be one of the most promising bioreactors to eliminate waste flue gas. Compared with traditional biofiltration, BTF and its modification process are more effective in facilitating continuous operation for the convenient control of overall pressure drop, pH, and nutrient (Cox & Deshusses 1998; He *et al.* 2012). Furthermore, it is suitable to treat various kinds of pollutants (Kennes *et al.* 2009), especially high-concentration acidifying pollutants containing waste gas streams, such as ammonia- (Moussavi *et al.* 2011; Wu *et al.* 2011), chlorine- (Chan & Peng 2008), or sulfur-containing compounds (Ramírez *et al.* 2009). However, it is hard to maintain a strict anaerobic environment for the desulfurization microorganisms in biofiltration. Therefore, during the previous studies, researchers (Philip & Deshusses 2003; Pandey *et al.* 2005; Teekayuttasakul & Annachhatre 2008; Han *et al.* 2011) always chose to make flue gas containing sulfur dioxide dissolve in water or aqueous solution of BTF, which were then further processed in another biological reactor. However, the separated operation process in two bioreactors occupied a large physical area and incurred high equipment costs. In summary, the BTF was applied to substitute the regeneration step of dual-alkali FGD for the elimination of sulfite-, sulfate- or hydrosulfate-containing adsorbent, which has never been reported in previous research.

In the current study, a BTF was used to investigate the elimination of flue gas adsorbent containing sulfite, sulfate, and hydrosulfate, in which biological methods were undertaken to replace the regeneration step of dual-alkali FGD. Efficient sulfate-reducing bacteria (SRB) were isolated and enriched from landfill leachate and inoculated in a BTF to reduce start-up time, to improve removal efficiency, and to obtain economical operation. In addition, the effect of initial pH, shutdown behavior, and high-temperature on the stable capacity of the BTF was evaluated. It is desirable to explore a steady and high efficiency system for the treatment of flue gas adsorbent, which could provide a scientific basis for BIO-FGD industrial application.

MATERIALS AND METHODS

Source of bacteria and wastewater

The organism described in this article was isolated and extracted from landfill leachate collected at a sanitary landfill in Beijing, China. The chemical oxygen demand (COD), NH_4-N, total phosphorus, and pH of the leachate were 22,848 mg/L, 2,154 mg/L, 23.1 mg/L, and 7.13, respectively. An initial simulant liquid medium consisted of the following composition (g/L): $Na_2HPO_4.7H_2O$, 1.0; KH_2PO_4, 0.5; $Fe(NH_4)_2(SO_4)_2.6H_2O$, 0.2; NH_4Cl, 0.5; $MgCl_2.2H_2O$, 0.4; $CaCl_2.2H_2O$, 0.1; carbon source of $C_3H_5NaO_3$ 5.0 mL; pH, 7.0 to 7.5; trace element solution, 2 mL. The trace element solutions for the bacteria growth were described in previous works (Sublette & Sylvester 1987). In addition, the overall experimental simulant flue gas adsorbent was configured, with the addition of different concentrations of Na_2SO_3, Na_2SO_4, or $NaHSO_3$ in the simulant liquid medium.

Experimental apparatus and operation

All experiments were performed in a BTF system which is shown in Figure 1. The BTF consisted of two segments made of transparent rigid plexiglass each with an inner diameter of 80 mm and a height of 400 mm. The filling medium was ball-shaped fiber packing (diameter, 15–20 mm; bulk density, 1,380 kg/m^3; filling density, 72 kg/m^3; specific surface area, 3,000 m^2/m^3; void ratio,

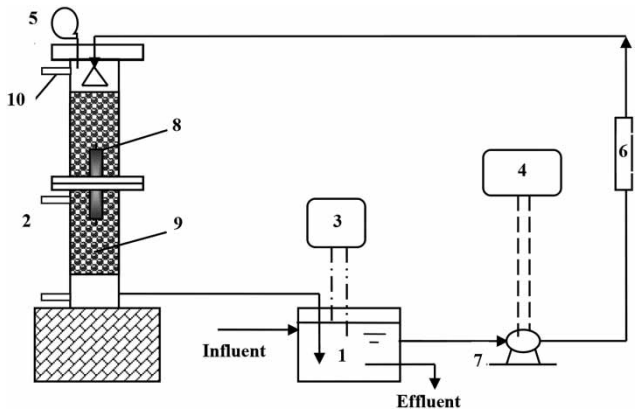

Figure 1 | The setup of BTF system (1, circulation tank; 2, biotrickling filter; 3, automatic temperature controller; 4, dual voltage stabilized power supply; 5, gas sampling bag; 6, flowmeter; 7, micro-circulation pump; 8, temperature sensor; 9, ball-shaped fiber packing; 10, sampling port).

96%). Each segment of the BTF column was packed to a height of 300 mm and the effective volume was 1.5 L. The ball-shaped fiber packing was inoculated with sulfate-SRB inoculum in the BTF. The operating temperature was automatically controlled at $35 \pm 2\,^{\circ}C$ by a temperature-controller and heating tape. Moreover, a temperature sensor was set in the center of the BTF, which was used to monitor the temperature of the flue gas adsorbent treatment system. In addition, there was a gas outlet on top of the BTF to collect waste gas. The flue gas adsorbent trickled by gravity down through the packing of the BTF, flowed into the trickling liquid tank, and then was pumped to the top of the BTF for the overall circulation by micro-circulation pump. A dual voltage stabilized power supply was used to control the flow of trickling liquid.

Analysis method

The indicators of source water, such as, sulfite, sulfate, and sulfide, were determined according to 'Water and wastewater monitoring and analysis method (fourth edition)' (Wei *et al.* 2002). Dissolved oxygen (DO) and pH were measured with a multi-function water quality monitor (Multi 340i, Germany WTW). A precision pH meter (model PHS-3C, Shanghai, China) was used to monitor pH and oxidation-reduction potential (ORP); DO was determined using a DO meter (model HQ30D, Hach, USA); COD was determined using a COD meter (model DRB-200, Hach, USA). Optical density (OD_{600}) was determined by ultraviolet-visible spectrophotometer (model UV-752N, Shanghai, China) at a wavelength of 600 nm. In this study, a confidence limit of 95% was used, and all experimental results represented the mean of at least three runs.

RESULTS AND DISCUSSION

Biofilm formation of BTF

Enrichment, isolation, and purification of SRB

SRB, which are widely used in anaerobic processes for the treatment of sulfate-rich wastewater, eliminated the pollutants through the dissimilation of organic matter. During the reaction phase, the organic matter and sulfate were considered as an electron donor and electron acceptor, respectively. SRB utilized and transferred the sulfate to the reduction sulfur compound (such as, S^{2-}, HS^{-}, and H_2S) by metabolism. Moreover, the SRB could improve the removal efficiency of sulfite in the flue gas adsorbent through the enrichment culture. In addition, landfill leachate which was collected at a sanitary landfill was used as an inoculum for the isolation and extraction of SRB.

Enrichment culture medium was configured by the addition of different concentrations of Na_2SO_3 in the simulant liquid medium. A 1,000 mL enrichment medium was equally separated into five 250 mL glass flasks with sponge stoppers, and then the amount of 0.1, 0.2, 0.4, 1.0, and 2.0 g of Na_2SO_3 was separately added, that is to say, the concentration of Na_2SO_3 was 0.5, 1.0, 2.0, 5.0, and 10 g/L in five glass flasks. Finally, 10 mL landfill leachate or 5% inoculation was added to each one and N_2 was aerated for 2 min to ensure an anaerobic environment. Culturing took place for 48 h at a temperature of 33 °C and centrifugation speed of 160 rev/min. After the measurement of OD_{600}, the cultural bacteria were centrifuged. Then, the supernatant was discarded and the lower bacterial inoculum was transferred to fresh enrichment culture medium. The overall culture process was repeated for six periods and the variation of OD_{600} in different sulfite concentrations followed the change of culture period as shown in Figure 2.

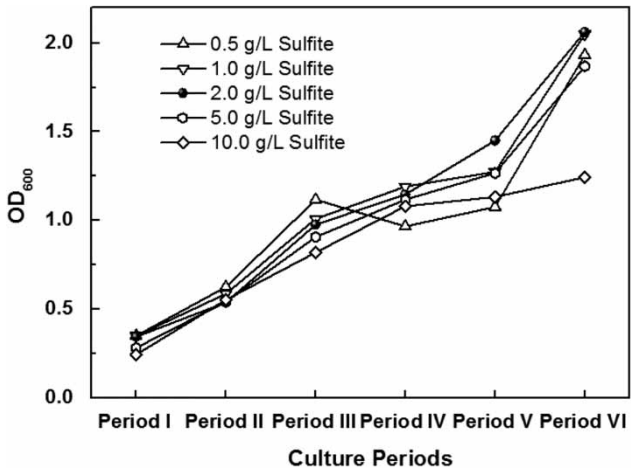

Figure 2 | The variation of OD_{600} in different sulfite concentrations followed the change of culture period.

As shown in Figure 2, OD_{600} apparently increased with each successive period. When the sulfite concentration was 0.5 g/L, OD_{600} slightly decreased in the fourth and fifth periods. That was maybe because the bacteria growth was limited by the low sulfite concentration. On the contrary, when the sulfite concentration was 10 g/L, the growth rate of bacteria sharply decreased in the last culture period. This suggests that a great number of bacteria were inhibited by the high sulfite concentration. In addition, the growth curve of the bacteria presented similar trends when the sulfite concentration was 1.0, 2.0, and 5.0 g/L. Moreover, the sulfite concentration of 2.0 g/L might be the most suitable condition for the enrichment culture SRB. Besides, following the six-period culture phase, the bacterium concentration maintained a high level and trended to saturation, which illustrated the end of the enrichment stage.

Although some infectious microbes were eliminated after enrichment, there still existed a variety of bacteria in the bacterium suspension. In order to get a higher degradation purified SRB, bacterium suspensions were further isolated and purified. STARKEY's medium was used, which was composed of the following salts (g/L): NH_4Cl, 1.0; K_2HPO_4, 0.5; $MgSO_4.7H_2O$, 2.0 $CaCl_2.2H_2O$, 0.1; Na_2SO_4, 1.0; 70% of $C_3H_5NaO_3$, 5.0; $(NH_4)_2Fe(SO_4)_2.6H_2O$, 0.1; H_2O, 1,000 mL; pH, 7.0 to 7.5; and included 2 mL trace elements. The plate smearing method was carried out with 0.1 mL bacterium suspension, which was then set at 33 °C in a constant-temperature incubator. Black colony growth continuously appeared after 4 days. Single colony growth was picked and inoculated in liquid culture medium at the same time. The overall culture process was repeated three times. Finally, a microscopic examination was carried out on the single colony growth, and the results showed that a single species, rod shape, and negative gram were observed, which indicated that the isolation and purification of SRB was fairly complete.

Biofilm culturing

Prior to being used to fill the BTF, the ball-shaped fiber packing was placed into the landfill leachate for one week, which facilitated bacterial attachment to the surface of the packing materials. The micro-pump was then started and biofilm culturing took place at the temperature of 27–32 °C and trickling density of 9–18 $m^3/(m^2 h)$ in the BTF with the inoculated packing. Nutrient solution, which was changed at regular intervals, consisted of the following composition (g/L): NH_4Cl, 0.5; $MgSO_4.7H_2O$, 2.0; Na_2SO_4, 1.0; $CaCl_2 2H_2O$, 0.1; $(NH_4)_2Fe(SO_4)_2.6H_2O$, 0.1; vitamin C ($C_6H_8O_6$), 0.1; KH_2PO_4, 1.2; K_2HPO_4, 0.7; KNO_3, 1.1; $NaHCO_3$, 0.5; 70% of $C_3H_5NaO_3$ 5.0 mL; pH, 7.0 to 7.5; trace element solution, 2 mL. The variation of pH and sulfite concentration in the BTF was monitored. When the biofilm was successfully formed, the sulfite removal efficiency was investigated with 634.8 mg/L initial SO_3^{2-}-S concentration in the BTF. During the same operation and control condition, the sulfite removal efficiency was also studied with the addition of 100 mL SRB, which was isolated and purified from the landfill leachate. The compared results are shown in Figure 3.

As can be seen from Figure 3, the sulfite removal efficiency with the addition of SRB was 72.2% at 0.5 h, compared to 23% with the initial condition in the BTF. Even at 1 h, the efficiencies with the addition of SRB and for the initial condition were 82.4 and 40.1%, respectively. After 5 h, the removal efficiency for both conditions was approximately the same, and above 96.0%. Moreover, for the sulfite removal efficiency to reach more than 80%, the time for the addition of SRB was approximately 1 h, which was only one third of the time required to reach 80% removal efficiency for the initial condition in the BTF. The results indicated that the addition of SRB could greatly reduce the start-up time of the BTF, withstand a high packing load, and improve the adaption capacity of the microbial community. Therefore, the SRB which was isolated and purified from landfill leachate was efficient.

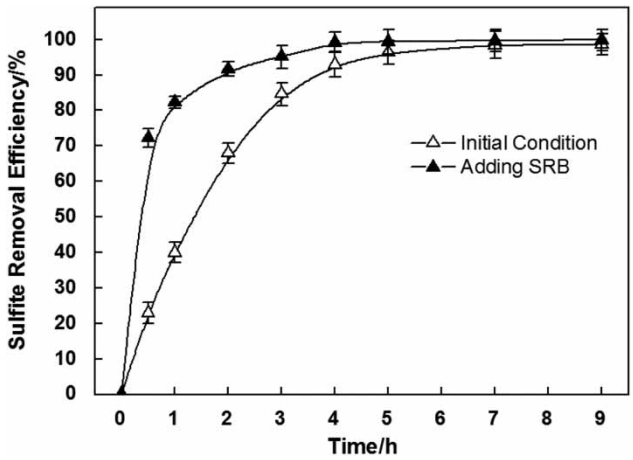

Figure 3 | The variation of sulfite removal efficiency before and after the addition of SRB suspension.

Overall desulfurization performance of BTF during the stable operation period

The overall desulfurization performance of the BTF was investigated during the steady operation period. Two kinds of packing loads including 5.56 kg SO_3^{2-}-S/(m^3 d) and 6.37 kg SO_3^{2-}-S/(m^3 d) were compared, and the variation of sulfite and sulfide were analyzed. The experiment results are shown in Figure 4.

From Figure 4, it can be seen that the sulfite removal efficiency quickly rose up to 98% in 3.9 h and the accumulated sulfide concentration was stable at 647.9 ± 16.7 mg/L during lower sulfite packing load. However, during the higher packing load of sulfite, the time required for the sulfite removal efficiency to increase up to 98% was 6.4 h and the steady concentration of sulfide was 962.6 ± 8.6 mg/L. More interestingly, the elimination process of sulfite concluding adsorption phase (0 to 0.5 h) and elimination phase (defined as: up to 98% removal efficiency after the adsorption phase) is clearly shown in Figure 4. During the adsorption phase, the adsorption rate of the high packing load in 0.5 h was 1,996.6 mg/L (SO_3^{2-}-S)/h, which was 2.3 times more than that of the low packing load. However, the elimination rate of sulfite for the high packing load was only 105.0 mg/L (SO_3^{2-}-S)/h, which was 0.8 times that of the low packing load during the elimination phase. These results indicated that the degradation rate of the elimination phase of the high packing load was inhibited. Besides, compared to the low packing load (464.3 ± 148.3 mg/L), the accumulated average sulfide concentration was as high as 656.4 ± 228.8 mg/L. However, in the previous work, Okabe's research (Okabe *et al.* 1995) described that the cell yield was reduced by 50% at a sulfide concentration near 250 mg/L at pH of 7.0 in a chemostat. Reis *et al.* (1992) found that the complete inhibition concentration of sulfide for SRB in the treatment of lactate was about 550 mg/L at pH of 6.2 to 6.6. Krishnakumar & Manilal (1999) thought that there was no sulfide inhibition for SBR when the sulfide concentration was less than 400 mg/L. Therefore, the activity of SRB was inhibited because of the accumulation of sulfide (656.36 ± 228.78 mg/L) for the high packing load in the BTF. In addition, with the utilization of ball-shaped fiber packing, the removal efficiency of sulfite at the high packing load was up to 98.64% at 6 hours, this could be because granular biomass and biofilms are more resistant to toxicity (Omil *et al.* 1997; Lens *et al.* 1998; Celis-Garcia *et al.* 2004).

In addition, the removal efficiency of SO_4^{2-} and HSO_3^-, which exist in small quantities in the simulated flue gas adsorbent, was also investigated. When the packing load of sulfate was 0.95 kg SO_4^{2-}-S/(m^3 d), operated at similar parameters in the BTF, the sulfate removal efficiency quickly reached up to 85% in 5 h and 95% in 24 h. Besides, when the packing loads of hydrosulfite were 1.45, 1.76, and 1.90 kg HSO_3^--S/ (m^3 d), the corresponding removal efficiencies of hydrosulfite were 97%, 98%, and 95% in 0.5 h, respectively. Moreover, the concentration of hydrosulfite was lower than the detection limit in 2 h. Interestingly, the removal rates of sulfite and hydrosulfite were apparently quicker than that of sulfate, which might be because the long step and reversible character from sulfate to sulfite affected the sulfate elimination during the biological

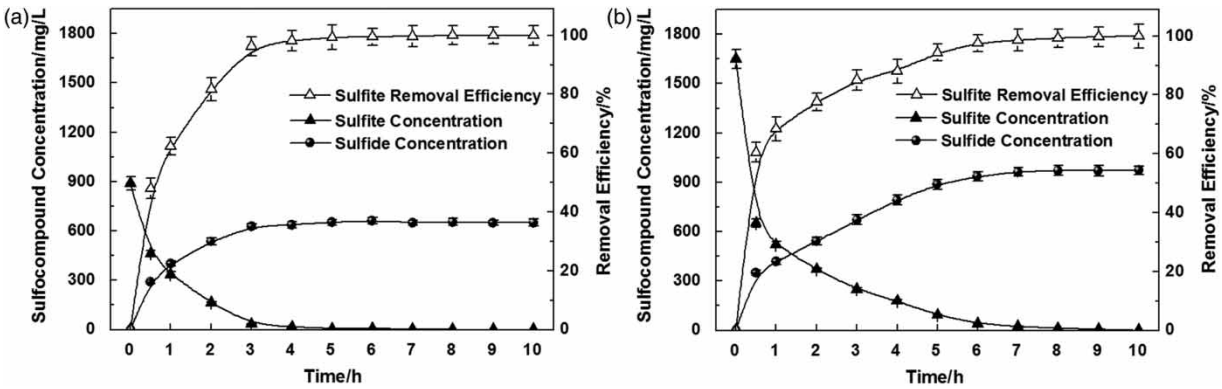

Figure 4 | The variation of sulfite and sulfide sulfur under different sulfite volume load, for lower sulfite packing load (a) and for higher sulfite packing load (b).

desulfurization process. In previous research, Canfield (2001) found that the step in which the sulfate reduced to sulfite was reversible; in contrast, the final reduction of sulfite to hydrogen sulfide was not reversible. Therefore, the reduction sulfite from sulfate could be retransferred to sulfate again during specific conditions. Moreover, when the sulfite and sulfate acted as electron acceptors in the anaerobic biotechnology process for industrial wastewater treatment, the biomass yield of the former was two times more than that of the latter under different electron donors (such as, acetate and H_2) (Speece 1996). Thus, the reduction rate was relatively faster for the sulfite and hydrosulfite within the BTF. However, the BTF could efficiently eliminate simulated flue gas adsorbent containing SO_3^{2-}, SO_4^{2-}, and HSO_3^-.

Influence of unexpected operation factors on the stable performance of BTF

In the current study, there were a few actual accidents which took place in the microbial desulfurization process of the BTF, which might occur in real life practical applications under potential operational situations. For example, the sharp fluctuations of pH in flue gas adsorbent, the shutdown behavior of the machine due to equipment failure or production interruption, and high temperature shock. Therefore, it is necessary to study the stability of the reactor.

Effect of initial pH on the desulfurization performance of BTF

According to the acid dissociation constant (pK_a) of H_2SO_3, for which pK_1 and pK_2 were 1.81 and 6.91, respectively, when the pH of the flue gas adsorbent was 4.5 to 6.5, the main formation of SO_3^{2-} was HSO_3^-. $NaHSO_3$ was used to configure the simulated flue gas adsorbent and HCl for the adjustment of pH. The influence of initial pH on the desulfurization performance of the BTF was investigated in four periods. With the addition of $NaHSO_3$ concentrations of 2,060, 4,000, 4,000, and 6,500 mg/L in the initial simulant liquid medium, the initial pH values were adjusted to 6.38, 5.51, 4.99, and 4.99, for which the corresponding packing loads of hydrosulfite were 1.20 kg HSO_3^--S/ (m^3 d), 1.45 kg HSO_3^--S/ (m^3 d), 1.90 kgHSO_3^--S/ (m^3 d), and 1.76 kgHSO_3^--S/ (m^3 d), respectively. Finally, the simulated flue gas adsorbent was introduced into the BTF and recycle startup. Besides, the variation of pH is shown in Figure 5.

During the four periods of different hydrosulfite packing loads, the removal efficiency of hydrosulfite was more than 95% in 0.5 h, and was under the detection limit in 2 h. In addition, Figure 5 shows that the pH values of different periods have similar trends, which all sharply rose up to 7.0 in 0.5 h and stabilized at 7.0 to 7.5, which was consistent with the optimum pH (7.0 to 8.0) in the BTF of previous researchers (Mudliar *et al.* 2010). This could be because the following reaction in the desulfurization process of the BTF.

$$3CH_3COO^- + 4HSO_3^- \rightarrow 3HCO_3^- + 4HS^- + 3H_2O + 3CO_2 \quad (1)$$

As shown in Equation (1), when four moles HSO_3^- were reduced, three moles alkalinity of CH_3COO^- and four moles H^+ were consumed, as well as the alkalinity including three moles HCO_3^- and four moles HS^- being produced. That is to say, there were two moles alkalinity net increment when one mole SO_3^{2-} was deoxidized. The conclusion was similar to the change of sulfate reduction process in previous research (Drury 2000; Kim *et al.* 2003; Sheoran *et al.* 2010). Therefore, the variation of initial pH had little effect on the desulfurization performance, which indicated that the BTF had stronger resistance capacity.

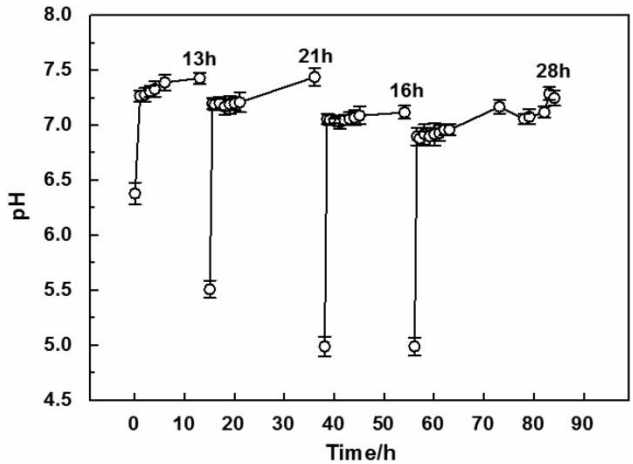

Figure 5 | The variation of pH for the four periods of different hydrosulfite effective packing loads.

Effect of shutdown behavior on the desulfurization performance of BTF

The shutdown behavior was investigated because of a few minor incidents in the BTF. After an outage of 27 days, the microbial community on the ball-shaped fiber packing had almost collapsed. In addition, great loss of biofilm, apparent gaps within the packing, and rust-colored biofilms were observed. The fresh nutrient solution, which was described in the 'Biofilm culturing' section previously, filled into the circulation of the BTF, and then restarted the system. The color of packing placed in the bottom layer of the BTF quickly went black in the first day, the same happened after 2 days for the middle layer, and after 4 days for the whole system. At the same time, the fresh simulant flue gas adsorbent was used to examine the recovery capacity of the BTF, and the results are shown in Figure 6.

Figure 6 shows that the BTF had a relatively rapid recovery, in which the recovery removal efficiency of sulfite surpassed that of the original steady operation in 8 h. In addition, during the adsorption phase, the adsorption rate of the recovery operation stage in 0.5 h was 672.4 mg/L (SO_3^{2-}-S)/h, which was 92% of that of the steady operation stage. Moreover, the elimination rate of sulfite for the recovery operation stage was 24.48 mg/L (SO_3^{2-}-S)/h, which was 1.3 times than that of the steady operation stage during the elimination phase. However, the effluent color was relatively dark because the reproduction speed of SBR exceeded the absorption ability of the microbial community during the initial recovery stage. After 6 days, the effluent was clear. Therefore, the BTF could be efficiently recovered within 4 days for biofilm culturing and 6 days for stable operation. Similar observation was reported by other researchers, Balasubramanian *et al.* (2012) tested the shutdown behavior in a BTF, where the system was regained within 72 h after 9 days long term shutdown without air and volatile organic chemicals supply; Namini *et al.* (2012) investigated the shutdown performance in a BTF, the results showed that the recovery time was 32 h for 2 days of complete shutdown, whereas for complete recovery of the removal efficiency at least 12 days were necessary when the shutdown period was increased to 5 days.

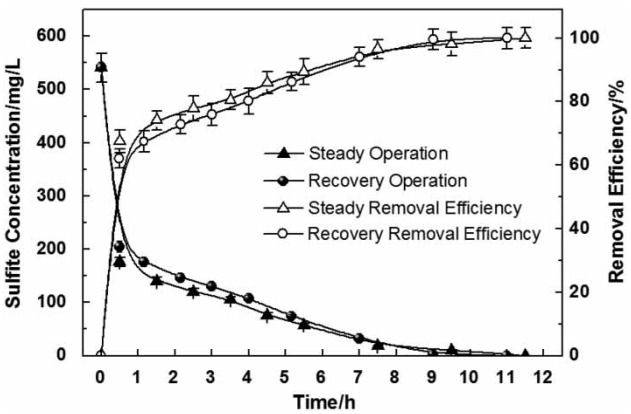

Figure 6 | Contrast of desulfurization in the reactor outage before and recovery.

Effect of high temperature shock on the desulfurization performance of BTF

To study the influence of high temperature shock on the desulfurization performance of the BTF, which might be caused by the erosion of the temperature sensor shell, the temperature of the flue gas adsorbent in the BTF was adjusted to 85 °C by an automatic temperature controller. The test duration lasted at least 5 h at the high temperature, and the results showed that the microbial community on the ball-shaped fiber packing in the BTF had been severely destroyed. The color of the biofilm changed from black to yellow, and the packing was exposed with a great loss of biofilm. The result was similar to the previous researchers, such as Zamir *et al.* (2014), who reported that the biofilter was exposed to a high temperature continuously which led to a significant decrease of the microbial population. LaPara *et al.* (2001) also found that the elevated temperature of 55 °C had adverse effects on process performance within aerobic biological wastewater treatment reactors. In addition, Konopka *et al.* (1999) revealed that the microbial communities growing in high-temperature bioreactors at 62 °C had difficulty maintaining membrane integrity under starvation conditions. Hence, the high temperature had a serious effect on the microbial community. Further, after the high temperature shock, the fresh simulant flue gas adsorbent was configured with the addition of sulfite in the initial simulant liquid medium, and then continuously filled into the BTF without the automatic temperature controller. When the influent temperature was 26 ± 2 °C, the desulfurization performance of the BTF was investigated.

During the 2 days at the beginning, there were a large amount of bubbles among the packings and circulation tank. In addition, the color of the biofilm and effluent were grey and milk white, respectively. With the microbial community gradually being restored, the black packing color in the BTF was observed. Moreover, there was a faint smell of H_2S. At the same time, compared with the steady operation (flue gas adsorbent temperature: $35 \pm 2\,^{\circ}C$), the variation of sulfite during the 2 days after the high temperature shock (flue gas adsorbent temperature: $26 \pm 2\,^{\circ}C$) and 4 days after the high temperature shock (flue gas adsorbent temperature: $26 \pm 2\,^{\circ}C$) is shown in Figure 7.

As can be seen from Figure 7, during the adsorption phase, the adsorption rate of sulfite for the steady operation period in 0.5 h was 852.78 mg/L (SO_3^{2-}-S)/h. Besides, the rates 2 and 4 days after the high temperature shock were 628.81 mg/L (SO_3^{2-}-S)/h and 700.85 mg/L (SO_3^{2-}-S)/h, respectively. These results indicate that there was no significant difference in the adsorption phase before and after the high temperature shock. This might be because the high temperature shock had little effect on the physical character of the ball-shaped fiber packing. However, during the elimination phase (defined as: up to 98% removal efficiency after the adsorption phase), compared with the sulfite elimination rate of the steady operation period (117.75 mg/L (SO_3^{2-}-S)/h), 2 days after the high temperature shock the sulfite elimination rate was zero and the rate 4 days after the high temperature shock was only 58.81 mg/L (SO_3^{2-}-S)/h. This showed that the SRB was strongly inhibited not completely inactive after the high temperature shock at 85 °C. Besides, a small portion of the SRB restored their activity, because a little sulfite removal was observed during the 2 days after the high temperature shock. Moreover, the rate 4 days after the high temperature shock was 50% higher than that of the steady operation period. However, the sulfite removal efficiency could be up to 98.8% in 7 h after the restoration of 4 days, which was similar to the removal efficiency of steady operation. More interestingly, the temperature of the flue gas adsorbent in the recovery period was $26 \pm 2\,^{\circ}C$, which was appropriately 10 °C less than that in steady operation (flue gas adsorbent temperature: $35 \pm 2\,^{\circ}C$). This shows that the lower recovery temperature obtained the same total desulfurization amount as the steady operation condition during the long duration biological process. This could be explained by previous studies. Okabe & Characklis (1992) reported that the maximum specific growth rate (μ_{max}) was relatively constant in the range 25 °C to 43 °C. Moosa *et al.* (2005) observed that the maximum specific growth rate (μ_{max}) was found to be constant at $0.061 \pm 0.001\ h^{-1}$, at the 99% significance level using a *t*-test, while the temperature varied from 20 to 35 °C. Therefore, the BTF could well resist the high temperature shock and be quickly restored.

For a comprehensive representation of the BTF situation during the high temperature shock, the pH and ORP were monitored. The result is shown in Figure 8.

Figure 8 shows that the ORP was −410 mV during the steady operation period, a value situated at a normal level

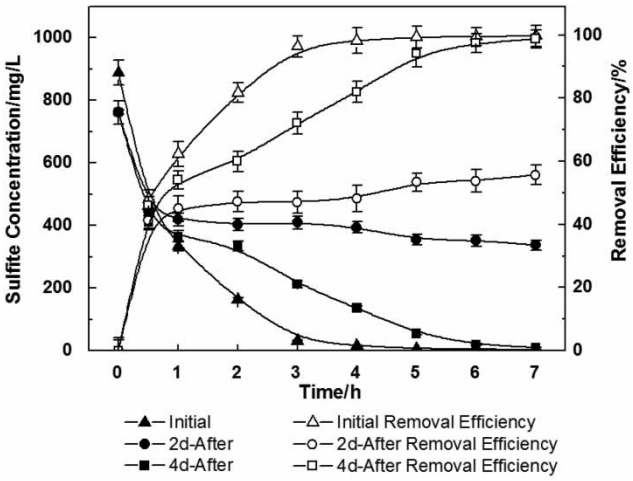

Figure 7 | Contrast of desulfurization of BTF in the high temperature shock.

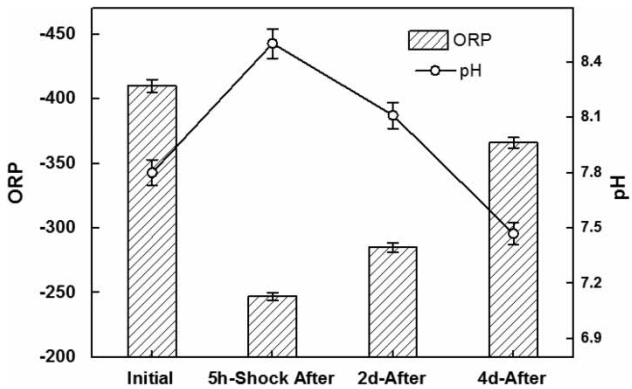

Figure 8 | The variation of ORP and pH during the high temperature shock.

which was controlled from −350 to −420 mV in the current study. In contrast, it was known that when the ORP became more negative than −420 mV (Ag/AgCl), biological inhibition occurred due to too-high sulfide concentrations (Klok *et al.* 2012). Therefore, the ORP value of the steady operation period remained at a normal level. However, with exposure to the high temperature of 85 °C for 5 h, ORP quickly increased to −247 mV, which indicated that the suitable environment for desulfurization was totally destroyed. After this, the ORP decreased to −285 mV in 2 days and reduced further to −366 mV in another 2-day period. The value after 4 d was close to the normal level, indicating that the SRB activity of the BTF was almost recovered, which was consistent with the results shown in Figure 7. In addition, compared with the variation of ORP, the pH presented an opposite trend. During the steady operation period, the pH was nearly 7.8, whereas the anaerobic microbial community was deeply depressed in pH of 8.4 after the 5 h high temperature shock. Similarly, the pH sharply decreased to 7.5 after 4 d, which was lower than that of the steady operation period. Interestingly, the higher sulfite removal efficiency of the steady operation stage could produce a greater amount of hydrogen sulfide, which caused the relatively lower pH. However, the result was not consistent with the pH value in Figure 8. This might be because a portion of sulfide was oxidized to sulfur when the ORP value (steady operation period: around −400 mV) remained between −330 and −400 mV. In previous research, ORP values were situated in the range of −330 to −400 mV which was within the range of ORP usually reported for dissolved sulfide oxidation to elemental sulfur (Fortuny *et al.* 2008; Vannini *et al.* 2008; Montebello *et al.* 2010). Moreover, the dark yellow sulfur-like matter was observed on the inner wall of the reactor, which could further verify the explanation. In short, the BTF could quickly restore after the high temperature shock, which indicated that the BTF had a better performance for the unexpected situation.

CONCLUSION

The efficient SBR which was isolated and purified from landfill leachate could greatly reduce the start-up time of the BTF, withstand a higher packing load, and improve the adaption capacity of microbial community. Moreover, for a sulfite removal efficiency of more than 80%, the time for the addition of SRB was approximately 1 h, which was only one third of that required for the initial condition in the BTF.

The BTF with ball-shaped fiber packing was used to eliminate simulated flue gas adsorbent containing SO_3^{2-}, SO_4^{2-}, and HSO_3^-. The results showed that the sulfite removal efficiency quickly rose up to 98% in 3.9 h with the low packing load of 5.56 kg SO_3^{2-}-S/(m^3 d), and in 6.4 h with the high packing load of 6.37 kg SO_3^{2-}-S/(m^3 d) during the overall desulfurization performance of the BTF. In addition, the removal efficiency of SO_4^{2-} and HSO_3^-, which exist in small quantities in the simulated flue gas adsorbent, was investigated. The sulfate removal efficiency which reached up to 85% in 5 h and 95% in 24 h was observed, when the sulfate packing load was 0.95 kg SO_4^{2-}-S/(m^3 d). When the packing loads of hydrosulfite were 1.45, 1.76, and 1.90 kg HSO_3^--S/ (m^3 d), the corresponding removal efficiencies of hydrosulfite were 97, 98, and 95% in 0.5 h, and the concentration of hydrosulfite was lower than the detection limit in 2 h.

The BTF showed good performance and could quickly recover from the impact shock of unexpected operation factors, such as recovery within 0.5 h for initial pH, 6 d for 27 d shutdown behavior, and 4 d for 5 h duration high temperature (85 °C) shock.

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