Comparison of two-stage and single-stage biofiltration for H_2S and toluene co-treatment

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ABSTRACT. Odorous compounds such as hydrogen sulphide (H_2S) and volatile organic compounds (VOCs) are difficult to remove together because odour oxidation product is acidic and this decreases the pH in the bioreactor causing poor removal of VOCs. Two types of bioreactors (single-stage and two-stage bioreactor) have been used for the co-treatment of gas mixtures. A study was carried out to investigate their comparative performances for the simultaneous removal of an airstream containing H_2S and a VOC represented by toluene.
Results demonstrated that a two-stage bioreactor performance was more effective than a single-stage bioreactor because a two-stage bioreactor allowed for separate media beds of different microorganisms. In a two-stage bioreactor, most H_2S was degraded in the first stage and this protected the second stage from significant acidification. Toluene was removed chiefly during the second stage operated at a neutral pH. GRTs exceeding 3s for H_2S or 12s for toluene were required to obtain high removal efficiency in the two-stage bioreactor. Experiments also revealed that in both single and two-stage reactors, toluene did not have significant influence on H_2S removal. However, inlet H_2S concentration had obvious influence on toluene removal.

1 INTRODUCTION

Few studies have been carried out to investigate biological treatment of off-gases containing both H_2S and VOCs. The typical metabolic product of H_2S oxidation by *Thiobacillus sp*., i.e. sulphuric acid, will decrease the pH inside the bioreactor rapidly. Most *Thiobacillus sp*. are autotrophic organisms and thus do not use VOCs as carbon sources for growth. On the other hand, VOCs are degraded by heterotrophic microorganisms, which are thought most effective at neutral pH. Most biofilter researchers have assumed that removal efficiency for VOCs decreases when pH declines and early researches supported this assumption (Cox *et al*., 2002). In practical applications, it is difficult and expensive to control medium pH at neutral level. These apparently conflicting pH optima for microbial activity are challenges for developing bioreactors for removing both H_2S and VOCs.
The most optimal way to treat polluted air mixture is believed to divide the bioreactor into different levels allowing optimal activity of different organisms under different living conditions. A two-stage bioreactor may solve these problems (Derek *et al*., 1999).

The first stage is designed to remove H_2S at low pH condition. In this stage, an inert, acid resistant medium is used. The second stage is designed to remove VOCs at neutral pH. Because H_2S removal is confined to the first stage, there is no acid production in the second stage. However, there are still some researchers studying co-treatment of a mixture gas of H_2S and VOCs in a single bioreactor and getting some good performances (Todd *et al*., 1996; Ergas *et al*., 1995).
Thus, the performances of a two-stage biofilter and a single-stage biofilter for H_2S and toluene co-treatment were investigated to study their feasibility and applicability. A horizontal style was designed to realize two stages in one tank and lower the pressure drop.

2 MATERIALS AND METHODS

The horizontal biofilter consisted of six segments. The size of each segment was 15cmx15cmx10cm (WidthxHeightxLength) with a volume of 2.25L. Five of them were packed with Calgon carbon and the other one was kept empty for flexible operation. Water and nutrients were added by a sprinkler recycling system. The upper two sumps were for two-stage biofilter and the lower sump was for single-stage biofilter. There were two water valves to contact the upper and lower sumps. When the reactor operated as single-stage biofilter, the water valves were open. Or else when as a two-stage biofilter, they were closed. The schematic diagram of the biofilter is shown in Figure 1.

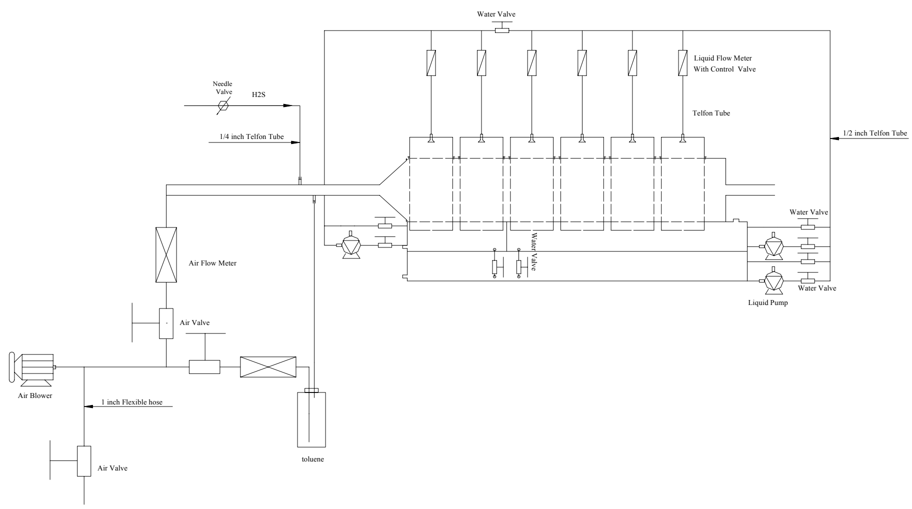

Figure 1. Schematic diagram of the horizontal biofilter.

The toluene waste gas was produced by passing air through a bottle containing pure liquid toluene. High concentration H_2S in gas cylinder was controlled by a regulator and a flow meter to get the desired H_2S gas stream. With dilution of bulk ambient airflow, the combined gas stream was channeled through the reactor.
In the two-stage biofilter, *Thiobacillus sp.* were inoculated at low pH in the first stage. *Pseudomonas putida* was then inoculated in the second stage at neutral pH. This provided the optimum survival environment for bacteria growth thus enhancing the overall efficiency and effectiveness in the biofilter system. The neutral pH biofilter (single-stage) was inoculated by a mixture of *Thiobacillus sp.* and *Pseudomonas putida*.

These two species of bacteria are ubiquitous and symbiotic at neutral pH in wastewater treatment.

The packing material was granular activated carbon (GAC) of diameter 4 mm, supplied by Calgon Co. (Pittsburgh, PA). Gas samples were collected using Tedlar bags and measured immediately after sampling. H_2S concentration was measured by Jerome 631-X Hydrogen Sulfide Analyzer (USA). Toluene analysis was accomplished with a Hewlett Packard 5890 gas chromatograph (GC) with a Flame Ionization Detector (FID). Sulfate content was measured by gravimetry according to 4500-SO_4^{2-} Standard Method. The operating parameters are shown in Table 1.

Table 1. Operating Parameters of the horizontal biofilter.

Operating Parameter		Single-stage biofilter	Two-stage biofilter	
			First stage	Second stage
Packing media volume (L)		11.25	2.25	9
Inlet gas Concentration(ppm)	H_2S	5-50		
	Toluene	10-300		
GRT(s)		9-60	1.5-15	6-60
Gas flow rate (L/min)		9-90		
pH of recirculation solution		6.0-8.0	1.0-3.0	6.0-8.0

3 RESULTS AND DISCUSSION

3.1 Biofilter performances

At the beginning, only toluene gas was fed in. *Pseudomonas putida* was inoculated after carbon bed breakthrough. When toluene removal was stabilized above 95%, H_2S was introduced. Gas retention time (GRT) and inlet concentration was changed step by step to test these two key parameters influence on system performance (Figure 2~5).

3.1.1 Two-stage biofilter

GRT in Figure 2 and 3 refers to first stage GRT and second stage GRT, respectively. The legend "RE I" represents the first stage removal efficiency. "Outlet I" is gas outlet concentration from the first stage. Most H_2S was removed by the first stage. Overall H_2S removal was higher. After 60 days' operation, the second stage was contaminated by H_2S degraders. A number of H_2S degrading bacteria were detected in the second stage leachate.

According to Figure 3, the biofilter was re-inoculated on day 12 because the system was shut down for maintenance of the recirculation system. On day 63, toluene removal efficiency dropped quickly due to biofilm clogging and then recovered after washing. From day 113 to 118, no data were recorded because of GC malfunction. Toluene removal of the first stage was unstable. The first stage outlet concentration was found sometimes higher than inlet concentration. No toluene degraders were found in the first stage during bacteria counting. The removal mechanism was mainly carbon adsorption, not bacteria degradation. Toluene was mainly treated in the second stage. Inlet H_2S concentration increased approximately to 50ppm on day 154. The second stage was acidized quickly because of the high H_2S outlet from the first stage. pH of the second stage dropped to 1.9. Biofilm with carbon power sloughed into the recirculating water and made it dark. To assure overall high performance, H_2S outlet from first stage is suggested to be lower than 3ppm. GRT not shorter than 3s/12s (H_2S/toluene) is suggested for high gas mixture removal efficiency.

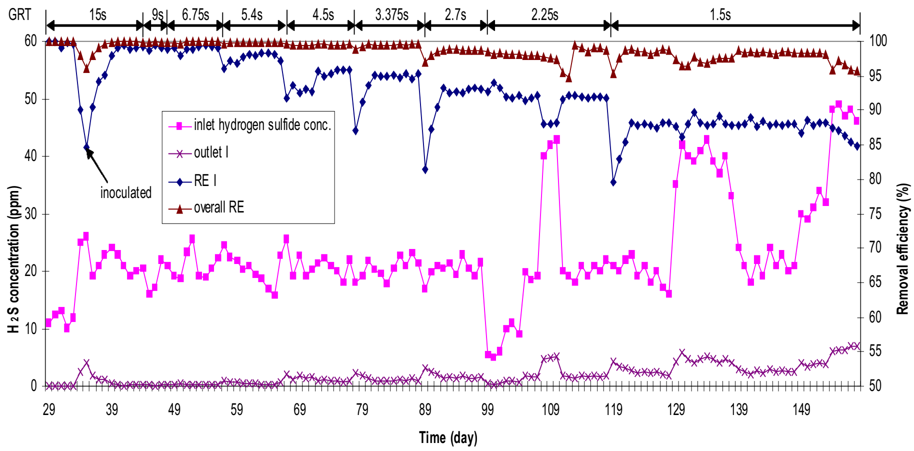

Figure 2. H_2S removal in two-stage biofilter.

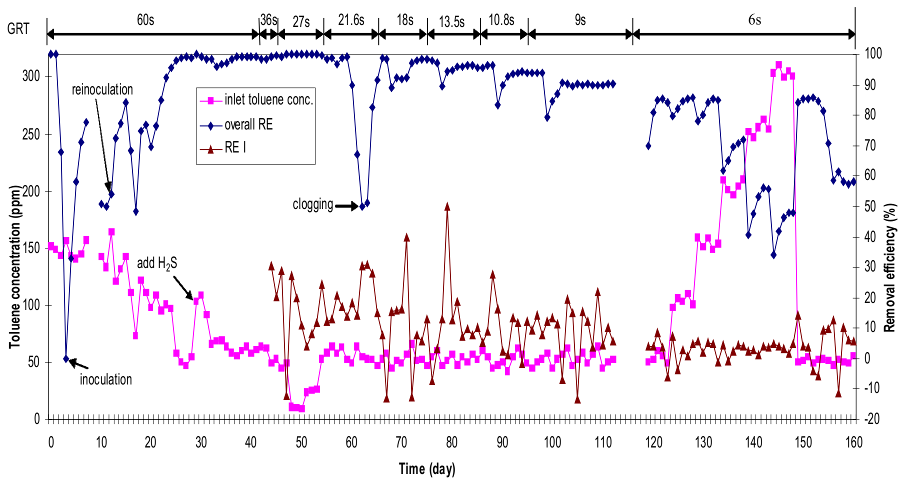

Figure 3. Toluene removal in two-stage biofilter.

3.1.2 Single-stage biofilter

To maintain the biofilter pH at neutral level, caustic soda was added every day. To avoid comsumption of large amount of alkali, H_2S concentration was set at a lower level (5ppm). In the following figures, RE I is H_2S removal efficiency of the first cell. RE I decreased from 99% to 90% as GRT decreased. However, the overall removal efficiency was always 100% because of the long overall GRT. Toluene removal followed similar to H_2S. When GRT varied from 60s to 9s, the removal efficiency fell from about 100% to 87%. With increasing inlet concentration, both RE I and toluene removal efficiency dropped accordingly at a short constant GRT.

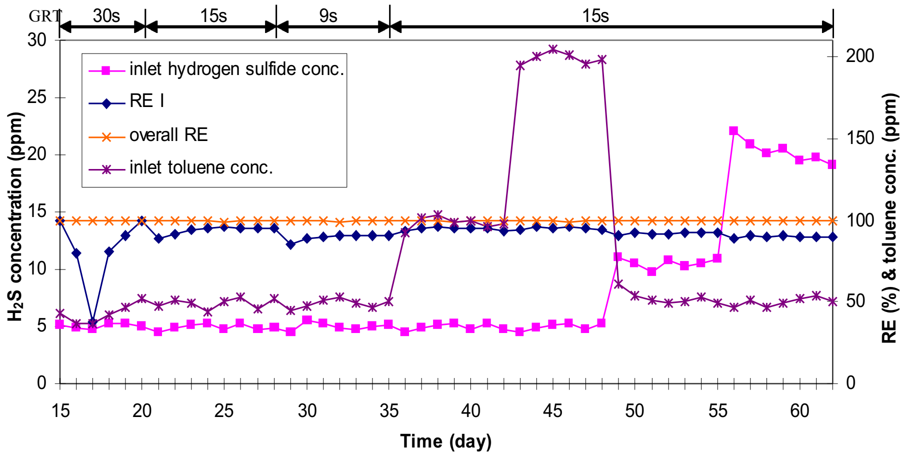

Figure 4. H_2S removal in single-stage biofilter.

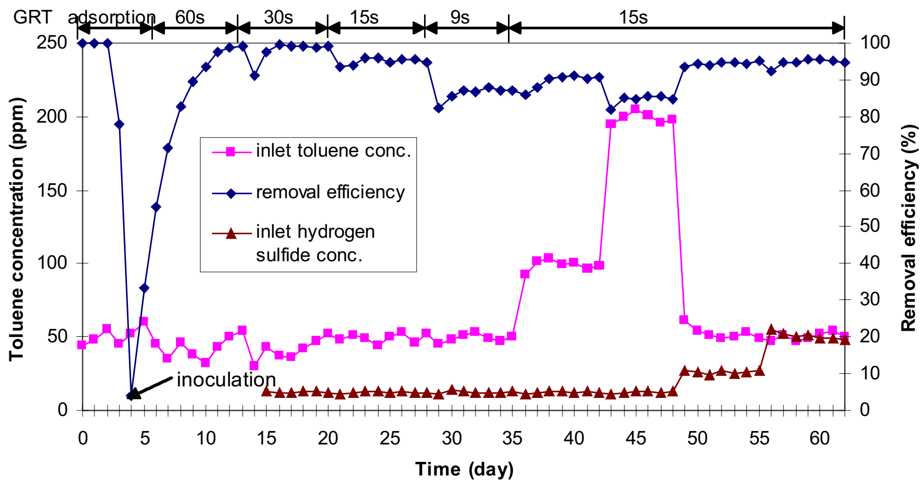

Figure 5. Toluene removal in single-stage biofilter.

3.2 Effects of GRT on biofilter performances

From Figure 6, we can see removal efficiency of two-stage biofilter was better than single-stage biofilter at the same GRT. Different pH resulted in different species of H_2S degraders in the two-stage and single-stage biofilters. Islander *et al.* (1991) hypothesized microbial succession in sewer pipes with decreasing pH. At neutral pH, *T. intermedius, T. novellus* and *T. denitrificas* tend to dominate. As the pH decreases to 6, *T. neapolitanus* dominates. When pH declines to 3, *T. thiooxidans* dominates. This same microbial succession is expected to occur in biofilters. The removal rates of various microorganisms are different, accordingly. Tanji *et al.* (1989) reported H_2S removal rate 0.73 mmol/L·h using *Thiobacillus thioparus* TK-m in a neutral pH system, while *Thiobacillus thiooxidans* got a very high removal capacity of 396~428 g-S/m^3·h (12.375~13.375 mmol/L·h) in a low pH biofilter (Cho *et al.*, 2000). In two-stage bioreactor, different microorganisms for H_2S and toluene degradation were under separate optimum living environment. While in single-stage reactor, all kinds of organisms lived in a complex ecosystem together.

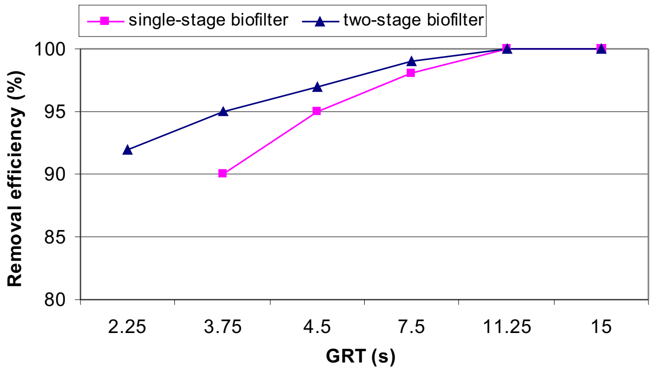

Figure 6. H_2S removal efficiency vs. GRT.

As for toluene removal, two-stage biofilter were still better than single-stage biofilter at the same GRT. Firstly, microorganisms' number decreased because H_2S degraders shared a part of carbon surface area. Secondly, the removal efficiency might be adversely affected through the accumulation of high salt concentrations and increased ionic strength because a large quantity of alkali was added (Dolfing *et al*., 1993). Sulfate concentration in the second stage lechate of the two-stage biofilter was 21 mg/L before acidification, while it was up to 267 mg/L in the single-stage biofilter lechate. Thirdly, maintaining the uniformity of the neutral pH in the medium might be difficult, because the irrigation water might not trickle through it uniformly.

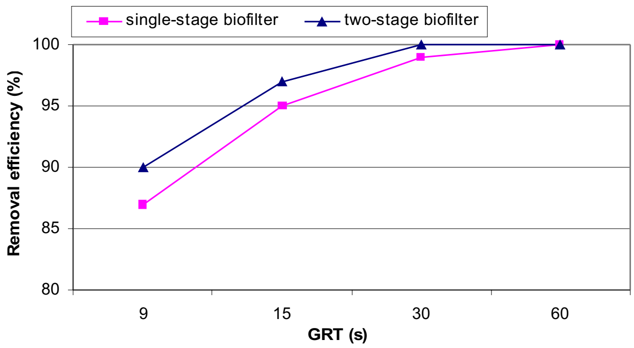

Figure 7. Toluene removal efficiency *vs.* GRT.

3.3 Substrate interaction

3.3.1 Toluene influence on H_2S removal

H_2S concentration input was held constant, while toluene concentration was increased gradually. According Figure 2~4 and 8, the fluctuation of toluene concentration (10~300ppm) had little influence on H_2S removal in both two-stage biofilter and single-stage biofiler. H_2S removal efficiency was still remained at high level. Similar result was reported by other researchers (Cox *et al*., 2001).

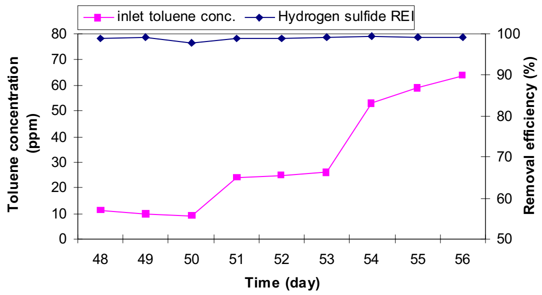

Figure 8. Toluene influence on H_2S removal.

3.3.2 H_2S influence on toluene removal

In the two-stage biofilter, the effect of H_2S on toluene removal was not found when H_2S concentration entering the second stage was below 3ppm. The high buffering capacity of the recycle liquid was sufficient to keep a near neutral pH. However, toluene removal efficiency and pH of the second stage leachate decreased when H_2S concentration was further increased. This was due to the acidification of the second stage as a result of high H_2S inlet concentration.

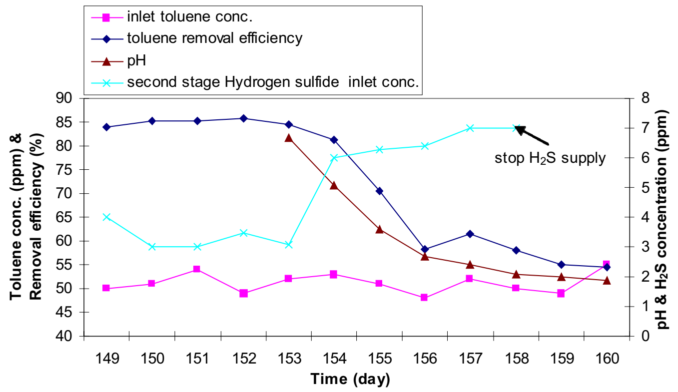

Figure 9. H_2S influence on toluene removal in two-stage biofilter.

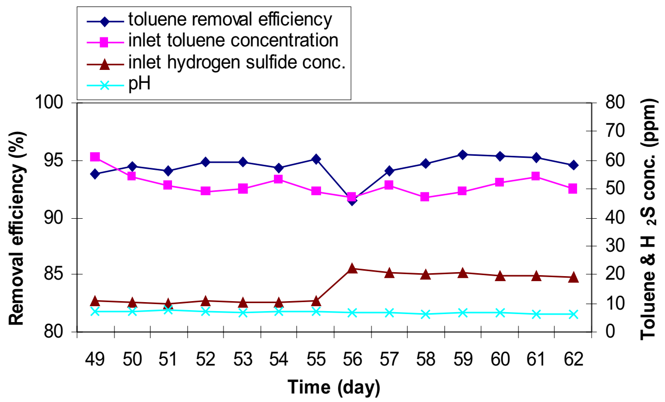

Figure 10. H_2S influence on toluene removal in single-stage biofilter.

In the single-stage biofilter, pH had no effect on toluene removal. However, under H_2S shock loading, toluene removal needed a longer time to recover to the original level. When H_2S concentration increased, more sulfate salt was produced.

4 CONCLUSIONS

In summary, two-stage biofilter was better than single-stage biofilter for gas mixture treatment because of high removal efficiency and low operation cost. In a two-stage biofilter, H_2S was mainly removed in the first stage and the most effective section for toluene removal was the second stage. GRT exceeding 3s/12s (H_2S/toluene) is suggested for high removal efficiency. Toluene at low concentration had no influence on H_2S removal. H_2S would affect toluene removal through pH drop and sulfate accumulation. H_2S outlet from first stage is suggested lower than 3ppm for good performance. This technique would be useful for removing gas mixture whose degraders grow in different environments, including odour and VOCs; H_2S, methanethiol and dimethyl sulfide; and other mixtures.

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