Performance of A Novel Monolith Biotrickling Filter Treating High Concentration of H_2S from Mimic Biogas

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Thesis submitted in partial fulfillment of
the requirements for the degree of
Master of Science in the Department of
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ABSTRACT

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Abstract

Pre-treatment of hydrogen sulfide is required before the utilization of biogas to eliminate the detrimental effects of corrosive hydrogen sulfide to the following combustion engines and pipelines. Biotrickling filters as one of the biotechnological methods have been investigated in desulfurizing biogas in recent years. Although high removal efficiency has been achieved by conventional biotrickling filters, clogging of the biotrickling filter bed due to the accumulation of excess biomass and elemental sulfur, has been widely reported (Janssen et al. 1997, Fortuny et al. 2008). In this context, a novel biotrickling filter using a monolith as its filter bed has been proposed and studied in this work to investigate its performance in removing H_2S and solving the bed-clogging problem through pigging, a common method used for pipeline and tubular reactor cleaning. The inlet H_2S concentration was controlled around 1000 ppm_v, corresponding to a loading rate of 122 g S–H_2S m^{-3} h^{-1}, and the empty bed gas residence time (EBRT) was 41 s. The influence of different H_2S/O_2 ratios on the removal performance was investigated at these conditions and results indicated that at H_2S/O_2 molar ratio of 1:2, an average removal efficiency of 95% was obtained. Under all conditions investigated, elemental sulfur and sulfate were measured to be the two dominant products and covered up to 93% of total end products. The monolith bed design also served to demonstrate that the risk of clogging was greatly reduced under this kind of design and bed-clogging problems

could be resolved when bed pigging was implemented to remove excess biomass and elemental sulfur accumulated inside the bed. Based on the results reported here, the monolith filter bed can be an effective alternative to the conventional packing material with a high specific surface area and a comparable performance could also be achieved by this novel bioreactor.

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1. Introduction

Converting organic wastes to biogas through anaerobic digestion has become an economical method at wastewater treatment plants, animal farms, and other organic waste generating facilities, since biogas is known as a renewable energy resource and can be used as fuel for heating and electricity generation (López et al. 2015). However, hydrogen sulfide (H_2S) is inevitably formed due to the presence of sulfate in the feedstock (Chaiprapat et al. 2015). H_2S is an odorous and corrosive gas and will cause detrimental effects on the following equipment, including pipelines, cogeneration engines, and microturbine units (Soreanu et al. 2008). The combustion of H_2S will also lead to the emission of SO_2, which is known as one of the precursors of acid rain (Chaiprapat et al. 2015). Therefore, the pre-treatment of H_2S is required before the final utilization of biogas. Among all the technologies used for biogas desulfurization, chemical scrubbing is considered as one of the most common and effective technologies, for its high removal efficiency and considerable short contact time of 1.3-2 s (Mannucci et al. 2012). Nonetheless, this method also has significant drawbacks including high operating costs, utilization of hazardous chemicals, and huge consumption of reagents and energy (Gabriel et al. 2003, Charron et al. 2004). In this context, the application of biotechnological alternatives to chemical scrubbing in H_2S has been widely investigated in recent years (Wu et al. 2001, Soreanu et al. 2008). Among all the biotechnological methods, biotrickling filters (BTFs) have been

suggested to be one of the best biological alternatives to chemical methods (Montebello et al. 2014), for BTFs have been shown to be as effective as chemical scrubbing in selected studies. Moreover, this technology avoids the use of hazardous chemicals and possesses more economical and environmental-friendly characteristics (Gabriel et al. 2003, Mannucci et al. 2012).

According to previous studies, conventional BTFs have been proven to successfully control H_2S in biogas with different concentration levels and achieved to remove up to 100% H_2S from biogas depending on conditions (Wu et al. 2001, Soreanu et al. 2008, Mannucci et al. 2012). Microorganisms like Thiobacillus, Hyphomicrobium, Xanthomonas, and Methylophaga sulfidovorans have been found in such BTFs operated at acidic or neutral pH conditions (Chung et al. 1998, Ruokojärvi et al. 2001). Generally, mixed sulfur oxidizing bacteria (SOB) cultures are utilized for the bio-desulfurization process which can be mainly described by following Equations (1), (2), (3), and (4).

$$H_2S(g) \rightarrow H_2S\ (aq) \quad (1)$$

$$H_2S(aq) \rightarrow H^+ + HS^-\ (aq) \quad (2)$$

$$HS^- + \frac{1}{2}O_2 \rightarrow S^0 + OH^- \quad (3)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (4)$$

H_2S is initially transferred from the gas phase into the aqueous phase by absorption and dissociates in the aqueous phase. It is then biologically oxidized to elemental sulfur (S^0), sulfate (SO_4^{2-}), and other sulfur species like sulfide, thiosulfate

and sulfite depending on the oxygen availability in the aqueous phase (Fortuny et al. 2010).

However, even with good performance in treating H_2S in biogas, this technology has not been widely applied in the industry yet, mainly because there are still some technical aspects to be improved (López et al. 2015). One of the biggest obstacles in applying BTFs in the industry is the bed clogging problem caused by the accumulation of elemental sulfur particles in the system (López et al. 2015). According to the published literature, a wide variety of packing materials, including open-pore polyurethane foam (PUF) (Gabriel et al. 2003, Ramírez et al. 2009), polyester fibers (Soreanu et al. 2008), pall rings (Wu et al. 2001), porous lava (Namini et al. 2008), coconut husk (Chaiprapat et al. 2015) and activated carbon (Duan et al. 2005), have been investigated in BTFs. Although for most of them, a high removal efficiency (RE) can be achieved (Soreanu et al. 2008, Mannucci et al. 2012), the excess biomass is difficult to remove in these kind of packing materials and leads to bed clogging problem. This is a serious problem especially for materials with a high specific surface area, and can become the main limitation of high rate treatment (Mannucci et al. 2012). This accumulation can worsen the issue of O_2 availability for the inner layers in the biofilm, which in turn highly increases the proportion of elemental sulfur produced as the end product. Bed clogging cloud also cause the increases of the pressure drop in the reactor and thus increasing the energy consumption of gas pumping (Andreasen et al. 2012, Mannucci et al. 2012,

Montebello et al. 2014).

In recent years only a few studies have investigated strategies for the reduction of elemental sulfur accumulated in BTF reactor. One possible approach to unclog a bed is to oxidize S^0 under sulfide starvation period (Fortuny et al. 2010). According to a study by Fortuny et al., the accumulated S^0 can be utilized as the substrate for the sulfur-oxidizing bacteria (SOB) and oxidized to SO_4^{2-} based on Equation (5). Therefore, bed cleaning is achieved through the consumption of the solid sulfur particles. However, the process was found to be slow, and incomplete sulfur removal could also be observed when the oxygen supply was insufficient to the reactor (Fortuny et al. 2010).

$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow {SO_4}^{2-} + H^+ \quad (5)$$

Other solution to avoid bed clogging is to optimize the filter bed. Fortuny et al. (2008) suggested that a firm, open and regular structure of the filter bed could reduce the chance of compaction. In the present study, a 3D-printed honeycomb monolith was proposed to replace the traditional packing material in BTF, which could help solving bed-clogging problems. The connected channels in this honeycomb monolith greatly reduced the risk of bed clogging and provided the possibility of using the pigging process for removing the excess biomass and accumulated sulfur particles. Pigging is an operation typically used in pipelines and tubular bioreactors during construction and regular system maintenance for different purposes, including debris removal, gauging, separation of products, and line

cleaning, etc. Therein, the device utilized in this operation is called “pig” and this name is usually used to describe the device that passes through a pipeline driven by the pipeline fluid (Tiratsoo 1992). In the experiment presented in this thesis, this new approach has been evaluated for solving the bed-clogging problem in BTFs and reclaiming sulfur particles for their economic values.

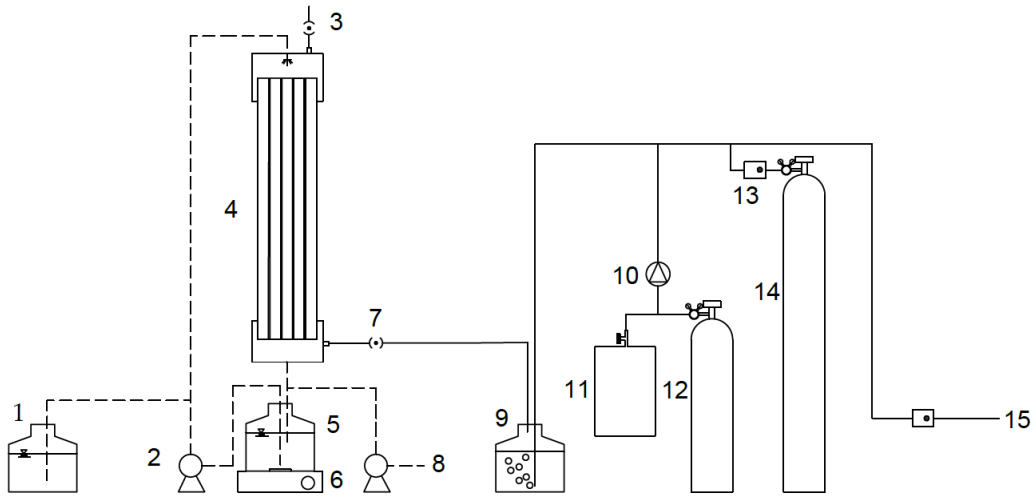
In this study, a laboratory-scale honeycomb monolith BTF reactor was operated for more than one year to investigate the overall performance of this novel bioreactor in treating high concentration H_2S (1000 ppm_V). The influence of the molar ratio H_2S/O_2 on the H_2S removal efficiency (RE), elimination capacity (EC), and the products of different sulfur species was investigated first. Then, the pigging process was conducted to demonstrate the ability of using the pigging approach to remove excess biomass and accumulated sulfur particles inside of the system.

2. Materials and Methods

2.1 Experimental Installation and Operating Conditions

The experimental laboratory-scale setup (Fig. 10) was comprised of an upflow counter-current BTF made of a 3D-printed honeycomb monolith as the filter bed (220 mm in height). Inside of the monolith column, 19 hexagonal channels are equally distributed and each channel has a width of 7.8 mm. The walls between channels were designed as meshes with a width of 1 mm and each square hole in the mesh is 1×1 mm, leading to an empty bed volume of 204 cm^3. This mesh design for the wall provided more surface area for the growth of microorganisms. The reactor was inoculated with activated sludge from the local wastewater treatment plant, which led to mixed SOB cultures to immobilize on the inside surfaces of the monolith to remove H_2S from biogas. The synthetic biogas consisted of a minute stream of air (as needed per H_2S:O_2 ratio imposed), mixed with metered streams of N_2, and H_2S in controlled amounts. The inlet H_2S concentration was controlled to around 1000 ppm_v, corresponding to a loading of 122.4 g S–H_2S m^{-3} h^{-1}. During the entire experimental period, the synthetic biogas was humidified by bubbling in DI water and then fed to the bottom of the BTF at a constant flow rate of 0.30 L min^{-1}, which was also the gas flow rate of N_2 since the flows of air and H_2S were small enough that they could be neglected. All the gas flows were regulated with Alicat flow meters (Alicat, MC-5SLPM-D/5M and MC-50SCCM-D/5M). The empty bed residence time

(EBRT) was 41 s, which was close to the range of 10-40 s based on the reference EBRT from previous studies (Namini et al. 2008, Mannucci et al. 2012). During normal operation, the liquid volume in the accumulation tank below the column was usually controlled to 0.4 L, and the liquid was recycled to the top of the monolith column and then sprayed downward to the packing bed with a recirculation rate of 0.2 L min^{-1}, using a peristaltic pump (Master-Flex, model 7518-00). The nutrients required by for the growth of SOB were provided by a mineral medium (in grams per liter) KH_2PO_4 0.5 g, $MgCl_2$ 0.1 g, $CaCl_2$ 0.05 g, $NaHCO_3$ 1 g, $FeSO_4$ 0.01 NH_4Cl 1 g, and pH was adjusted to approximately 6.8. Fresh mineral medium was replenished into the accumulation tank at the same flow rate of 0.2 L d^{-1} as the liquid was discarded from the accumulation tank. The discarded liquid was then collected in a bottle stored in the refrigerator, and together with the liquid in accumulation tank, was sampled for sulfur species measurement. Throughout the experimental period, the system was operated at the room temperature (20-25 °C).



1. Discarded-liquid bottle
2. Liquid recirculation pump
3. Outlet gas sampling port
4. Monolith biotrickling filter
5. Nutrient accumulation tank
6. Magnetic Stirrer
7. Inlet gas sampling port
8. Fresh mineral medium supply
9. Fine bubble humidifier
10. Gas pump
11. 10 L storage bag
12. H_2S gas cylinder
13. Gas flow meter
14. N_2 gas cylinder
15. Clean air supply line

Figure 1: The schematic of the laboratory-scale biotrickling filter

2.2 Analytical Methods

2.2.1 Gas Sampling and H_2S Measurement

The inlet and outlet gas samples were collected in 1 ml syringes from the inlet/outlet sampling ports and then injected into 1-liter Tedlar bags for dilution. The H_2S concentration was determined using a portable Jerome 631-X Hydrogen Sulfide Analyzer which has a range of 0.003-50 ppm_v of H_2S. The performance of the BTF treating H_2S can be evaluated by the H_2S removal efficiency (RE) and elimination capacity (EC), and the calculations of both factors were based on the Equation (6) and (7).

$$RE = (C_{in} - C_{out})/C_{in} \quad (6)$$

$$EC = (C_{in} - C_{out}) \times Q/V \quad (7)$$

Where the C_{in} and C_{out} are the inlet and outlet H_2S concentrations in the gas flows (g m^{-3}), the unit of RE is % in the Equation (6), while, Q is the gas flow entering the BTF (L h^{-1}), V is the empty bed volume (m^3), and the unit of EC is g m^{-3} h^{-1} in Equation (6) (Fortuny et al. 2008).

2.2.2 Sulfur Species Measurement

To investigate the impact of the inlet H_2S/O_2 ratio on the fraction of different sulfur species on the end products, sulfur species measurements in the liquid phase of both the accumulation tank and the discarded-liquid bottle were conducted at three different H_2S/O_2 condition of ratio 2:1, 1:1, and 1:2. In the experiment, the sulfur species, including sulfate (SO_4^{2-}), sulfide (S^{2-}), elemental sulfur (S^0), sulfite (SO_3^{2-}), and thiosulfate ($S_2O_3^{2-}$) were measured to establish a sulfur mass balance over a period of time (generally 3 to 5 days). The sulfate concentration was analyzed with the USEPA SulfaVer 4 method, which can be used to measure the sulfate concentration in a range of 2 to 70 mg L^{-1}. The sulfide formed was measured by the USEPA Methylene Blue method where the method of using spectrophotometer has been adopted in the experiment. The colorimetric determination method proposed by Bartlett et al. (1954) was used to measure the elemental sulfur in the liquid phase. The measurements of both sulfite and thiosulfate concentration were conducted by using the testing kits from Chemetrics (Titrets® Titration Cells K-9602 and K-9705).

2.2.3 Pigging Process

At the end of the operation, pigging was conducted by using a steel hexagonal bar with a width of 3/16 inches (4.8 mm) to physically remove the extra biomass and sulfur particles clinging on the inside surface of the monolith column. The pressure drop of the BTF at different gas flow rates were measured by a U-shaped tube and the differential pressure experiments were conducted before and after the pigging process to evaluate the effectiveness of the pigging process. After the pigging process, the deposits were collected for further analysis. The dry/wet mass ratio was obtained by first weighing certain amounts of the wet deposits removed by pigging, putting the samples into a vacuum oven for 6 hours, then reweighing the samples when the samples were totally dried. To analyze the fraction of biomass and elemental sulfur deposits, the deposits were firstly disaggregated by a sonicator to lyse the cells and then the biomass concentration was determined from the concentration of the total Kjeldahl nitrogen (TKN kit TNT828, Hach) by considering a typical biomass composition ($C_5H_7NO_2$) (Montebello et al. 2014). The fraction of the elemental sulfur was measured with the same method mentioned before for the elemental sulfur measurement in the liquid phase.

3. Results and Discussion

3.1 Performance of the Monolith BTF

The system was continuously operated for more than one year and all the experiments of this study were conducted in 162 days after stable operation was achieved. During the entire operation, the inlet H_2S concentration was controlled at 1000 ± 150 ppm_v, corresponding to the loading rate (LR) of 127 ± 18 g H_2S m^{-3} h^{-1}. To investigate the influence of different H_2S/O_2 ratios on H_2S removal performance, REs at different H_2S/O_2 ratios of 2:1, 1:1, and 1:2 were measured and the results are shown in Fig. 2. As can be seen, the experiment was conducted in two rounds and each round showed similar performance in H_2S removal for the specific H_2S/O_2 supplied ratio. The REs of the system ranged from 42% to 100%, with the highest RE achieved at H_2S/O_2 ratio 1:2 and lowest RE obtained at H_2S/O_2 ratio 2:1. The low RE at ratio 2:1 can be explained by the low O_2 availability in the aqueous phase, when the dissolved oxygen was not enough to fully remove H_2S from the biogas. At these conditions, formation of elemental sulfur is preferred and since it is less favorable for the microorganisms, lower rates of removal are observed. Therefore, the ratio 1:2 could be considered as the optimal H_2S/O_2 ratio condition in this study, where the stable performance and high REs were observed, while the REs at other two ratios were low and fluctuated. According to the previous literatures, the 90-100% RE was obtained when the H_2S/O_2 ratio was 1:49.2 and the EBRT was set to 130 s in the study

of Montebello et al. (2014), while a longer EBRT of 313 s was required to get the 80-90 % RE of around 2000 ppm H_2S in the study of Chaiprapat et al. (2011). Although up to 100% RE was only achieved at H_2S/O_2 ratio 1:2 by this monolith BTF, the monolith BTF was stable over time, and thus it can be considered providing robust performance and high efficiency with a relatively low EBRT and O_2 supply.

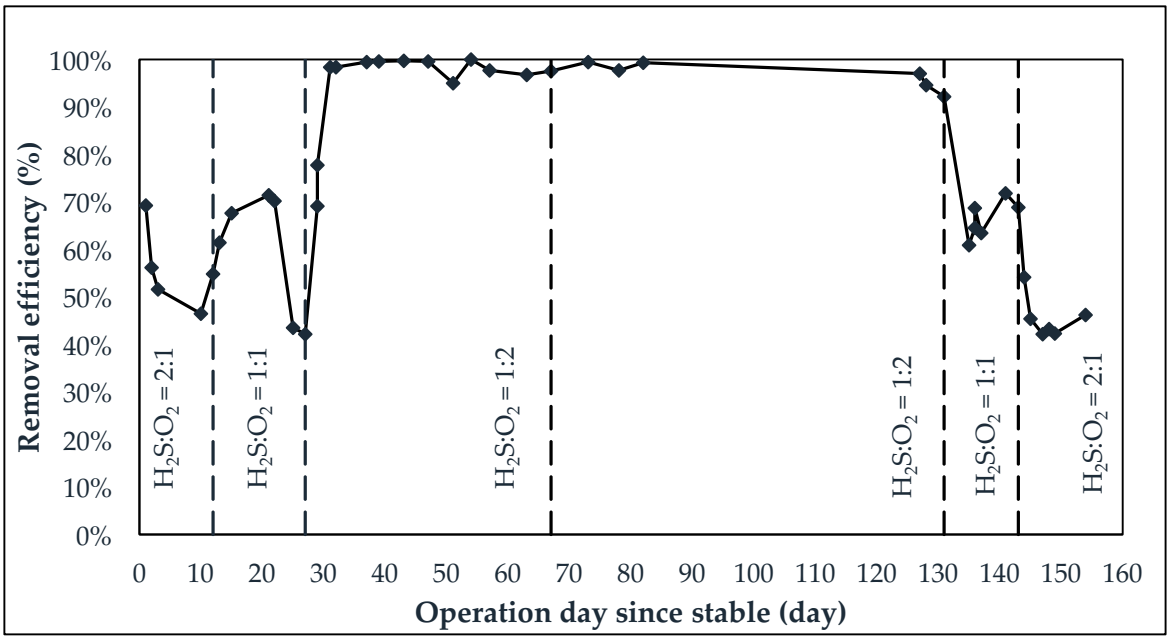


Figure 2: Effects of different H_2S/O_2 molar ratios on removal efficiency

The results of average REs at these three H_2S/O_2 ratios are shown in Table 1, where the average RE was ranged from 50% to 95%. Since the inlet H_2S concentration was controlled around 1000 ppm_v, the lowest average RE of 50% corresponded to the outlet H_2S concentration of 500 ppm_v. According to Fortuny et al. (2008), the concentration of 500 ppm_v is also the highest H_2S concentration that can be withstood by following combustion engines without causing corrosion problems. Based on this

fact, the industrial application of this kind of BTF should be conducted with the H_2S/O_2 ratio lower than 2, and ratio 1:2 can be considered as the optimal H_2S/O_2 ratio for its stable removing performance and high RE.

Table 1: Average removal efficiency and elimination capacity at different H_2S/O_2 molar ratios

H_2S/O_2 ratio	2:1	1:1	1:2
Removal efficiency (RE,%)	50	63	95
Elimination capacity (EC, g $m^{-3} h^{-1}$)	62.5	78.2	122.2

Fig. 3 is showing the elimination capacity (EC) at different H_2S/O_2 ratios. The ECs ranged from 52.9 to 133.6 g H_2S $m^{-3} h^{-1}$, where the highest EC was achieved at H_2S/O_2 ratio 1:2, while the lowest EC was observed at H_2S/O_2 ratio 2:1. The average ECs at different H_2S/O_2 supplied ratios are shown in Table 1, indicating (as expected) an increasing trend in the average EC with the increase of oxygen levels in the inlet gas flow. Here, the value of the highest average EC of 122.2 g H_2S $m^{-3} h^{-1}$ is comparable to the highest ECs range of 110–140 g H_2S $m^{-3} h^{-1}$ in the previous studies (Fortuny et al. 2008).

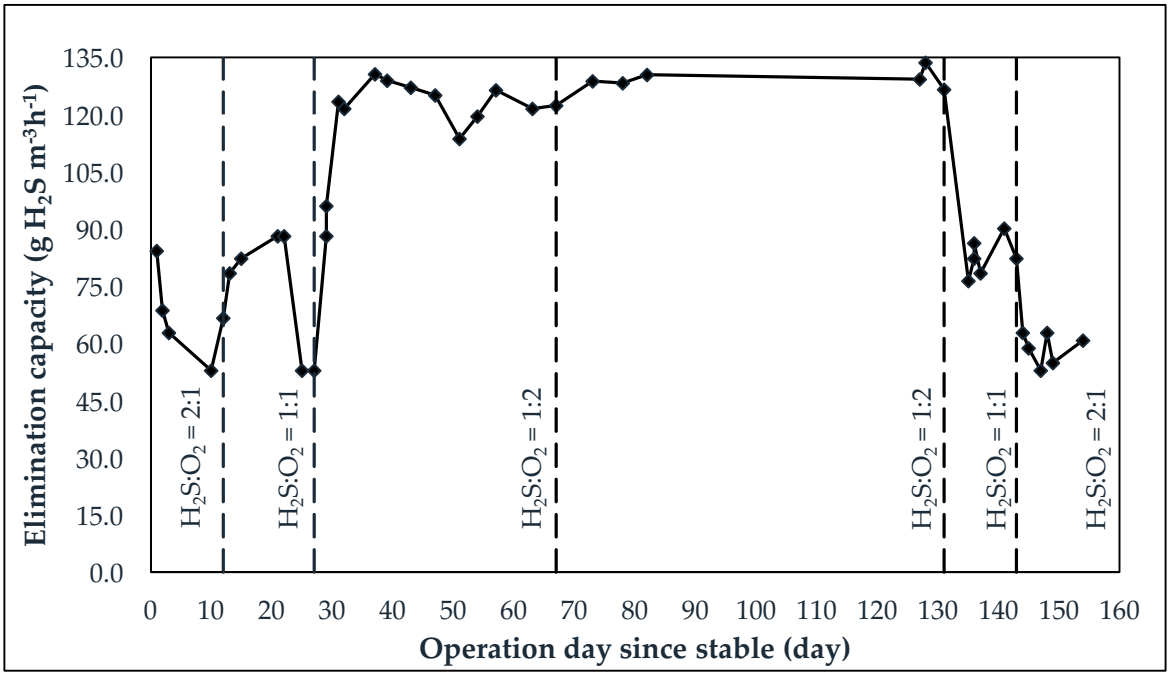


Figure 3: Effects of different H_2S/O_2 molar ratios on elimination capacity

During the entire operating period, the pressure drop in the system measured by U-shape tube was kept below 1 cm of water column. This is a low value, but consistent with the relatively long gas residence time. Even at the end of the operating stage, no major clogging was observed inside the channels. This contrasts with the study of Fortuny et al. (2008) who observed a pressure drop of 10 cm of water column and found that elemental sulfur particles gradually accumulated inside the PUF packing material leading to full clogging of the BTF system. When compared with the results in the study of Fortuny et al. (2008), the application of a honeycomb monolith as the packing bed in this study shows a large advantage by greatly reducing the bed-clogging risk when treating high concentrations H_2S.

3.2 Sulfur Species Measurement in Liquid Phase

Sulfur species, including sulfate (SO_4^{2-}), sulfide (S^{2-}), elemental sulfur (S^0), sulfite (SO_3^{2-}), and thiosulfate ($S_2O_3^{2-}$), were measured in the liquid phase to determine the fate of sulfur in the system. The fractions of each sulfur species produced at different H_2S/O_2 supplied ratios are shown in Fig. 4. Sulfate and elemental sulfur were the two predominant sulfur species in the liquid phase; the sum of these two species accounted for up to 93% of all end products, while the sulfide was less than 1% in all three H_2S/O_2 supplied conditions. The sulfite and thiosulfate as the intermediate sulfur species were also detected in all three H_2S/O_2 conditions and made up to 3-13% of the total end products. However, the concentration of thiosulfate species was reported minimal by some previous studies of BTF treating H_2S in an acidic condition (Montebello et al. 2014, Chaiprapat et al. 2015). The study of Van den Bosch et al. (2008) indicated that the formation of thiosulfate can be influenced by the pH, where a higher pH could lead to an increase of the selectivity of thiosulfate formation. Thus, the detection of thiosulfate in this study could be explained by the pH setting (around 7) in the system and the incomplete oxidation, due to the low oxygen availability in the aqueous phase. Fig. 4 also shows the increasing trend of sulfate fraction along with the decreasing trend of elemental sulfur fraction in the liquid phase with the supplied H_2S/O_2 decreases from 2 to 0.5, which is in consistent with the reaction mechanisms that the higher oxygen

level would favor the formation of the sulfate.

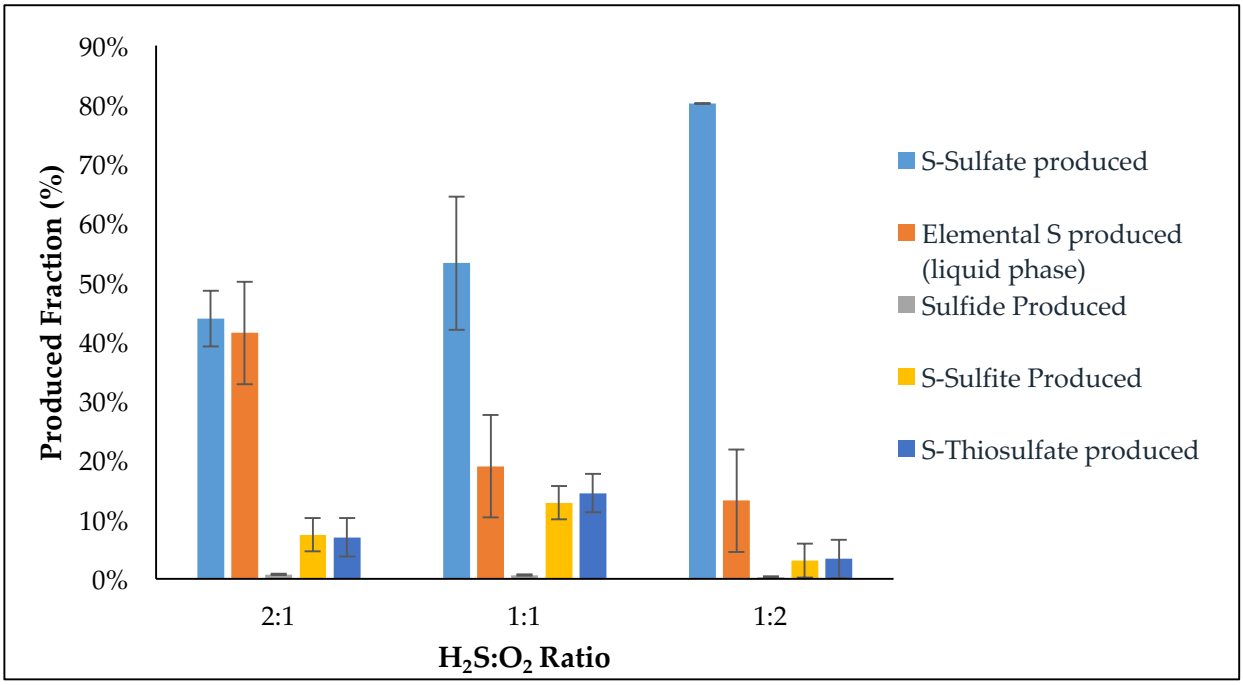


Figure 4: Different sulfur species fractions in the liquid phase at different H_2S/O_2 molar ratios

Based on the results of the measurement on different sulfur species in the liquid phase, a low recovery rate of sulfur in the liquid phase was observed. Under all H_2S/O_2 supplied conditions, the productions of all sulfur species in the liquid phase only made up around 3% of the total S- H_2S removed from the gas phase. With such a low recovery rate in liquid phase, one possible hypothesis is that most H_2S in the biogas was oxidized and immobilized as elemental sulfur, and then accumulated inside the channels of the filter bed. Based on this hypothesis, sulfur mass balance on different ratio conditions was established and final recovery rates were calculated in Table 2, where the sulfur production rates in solid were calculated based on the

weight increase rates with an average sulfur content of 62.13% extracted from latter discussion (section 3.3.3). During the operation, the production of solid elemental sulfur in a period of time was hard to precisely measure, so this result was calculated based on the weight increase rate of the column. Although the result might not be precise, it did reveal a general picture of the fractions of the removed sulfur both in liquid phase and solid phase. The high fraction of sulfur production in solid phase also conformed to the previous hypothesis that most H_2S was converted to elemental sulfur and accumulated in the system. 100% recovery rate under H_2S/O_2 ratio 2:1 and 1:1 was achieved and the less than 100% recovery rate at ratio 1:2 might be caused by the standard errors during the experiment and the missing measurement of other sulfur species in solid phase.

Table 2: Sulfur balance and recovery rate at different H_2S/O_2 ratios

H2S:O2 ratio	2:1	1:1	1:2
Sulfur removal rate (g h^{-1})	0.0111	0.0166	0.0249
Sulfur production rate in liquid (g h^{-1})	0.0003	0.0002	0.0005
Sulfur production rate as solid (g h^{-1})	0.0264	0.0167	0.0192
Recovery rate (%)	100%	100%	79%

3.3 Performance of Pigging Process in Cleaning Up Filter Bed

3.3.1 Pigging Process Observations

As described in the methods section, a 3/16-inch hexagon steel bar was used

at the end of the BTF operation to demonstrate the feasibility of using pigging for removing excess biomass and elemental sulfur accumulated inside the system. The pictures of the filter bed before the initial startup, at day 165 before and after the pigging process are presented in Fig. 6. Observing the top and bottom sections of the column at day 165 before the pigging process, the blue surface of the honeycomb monolith was fully covered with yellowish solids, which was assumed to consist mainly of elemental sulfur and biomass. When looking through the honeycomb channels inside monolith, some solids could also be observed in the channels. Comparing the top and bottom sections of the filter bed, the bottom section showed more sulfur accumulation than the top section indicating that either the desulfurizing process mainly happened at the bottom section of the filter bed, close to the H_2S inlet port, or that deposits were carried downward in the bed to accumulate at the bottom. The former explanation is more likely and is consistent with what is reported in previous studies that the highest sulfur removal rate takes place near the gas inlet port of the reactor, where the H_2S and oxygen concentrations are the highest and elemental sulfur washed from the upper column accumulated (Fortuny et al. 2008, Montebello et al. 2014).

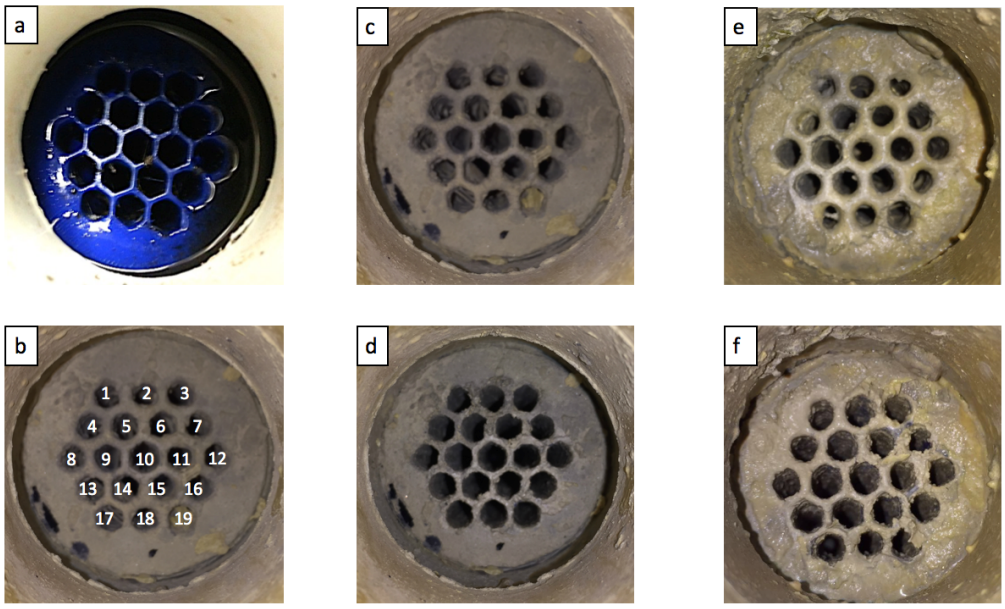


Figure 6: Filter bed of the monolith biotrickling filter: (a) monolith filter before inoculation, (b) is the numbers of all channels, (c) and (d) are the top sections of the filter bed at day 165 before and after pigging, and (e) and (f) are the bottom sections of the filter bed at day 165 before and after pigging process.

During the pigging process, all 19 channels were pigged with the hexagonal bar and total 7.8 g of deposits were collected from this process. The weights of deposits from each channel are presented in Fig 7. The results showed that the accumulated elemental sulfur and biomass were not evenly distributed in the monolith column, and the differences among the weights of pigging deposits from 19 channels were noticeable since the biggest difference was 0.83 g or a factor of about 5 between the lowest and the largest deposit amount. One possible reason for this result is the unevenly distributed recirculation liquid. Due to the small scale bioreactor and the existence of 19 channels inside the monolith column, it was hard to ensure equal distribution of recirculation liquid to every channel. A more uniform

liquid distribution is needed to solve this issue for further laboratory-scale application of this monolith BTF. At large scale, industrial spray nozzles exist and can provide uniform wetting.

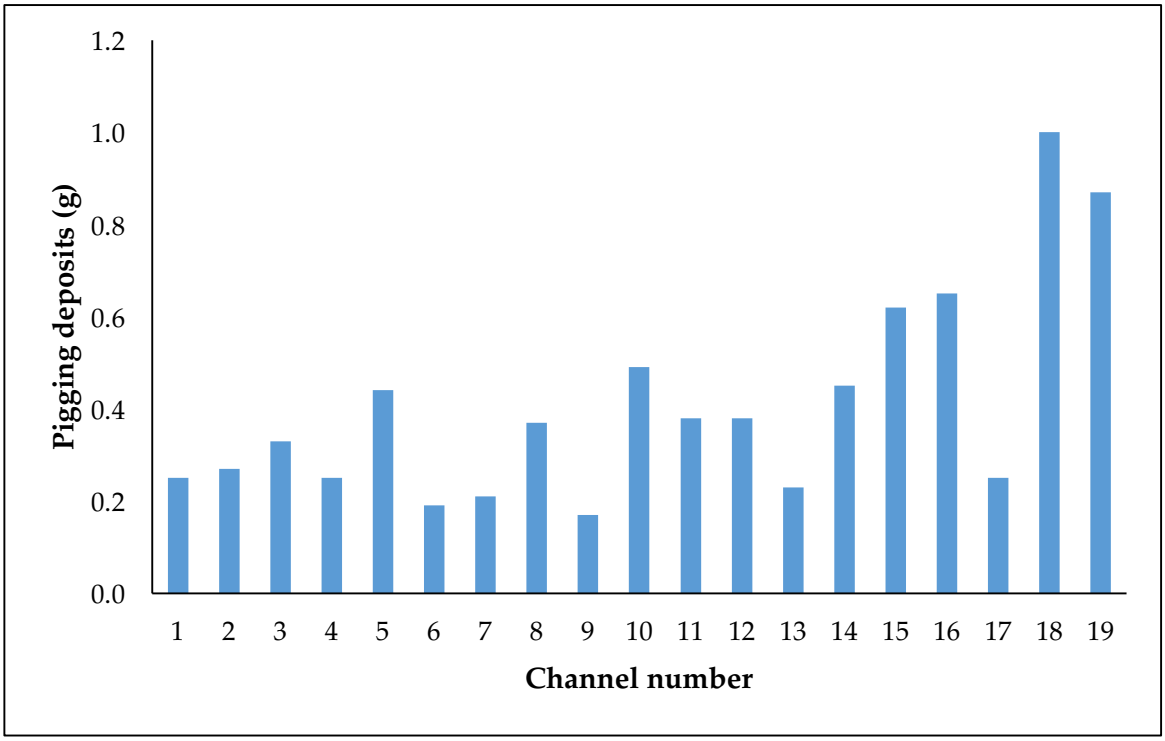


Figure 7: Weights of pigging deposits from each channel

After the pigging process, the channels inside the monolith column seemed much cleaner than before. When the BTF operation was resumed and the liquid recirculation pump was turned on, more solids was observed to wash out from the inside surfaces of the channels. The amount of wet solid was 16.52 g collected from the bottom cap. Its aspect (yellow-gray slurry) was very similar to material removed during pigging albeit slightly more liquid. These solids probably came from the biofilm and elemental sulfur that were loosened by the pigging process and flushed out by the recirculation liquid. Through the entire pigging process, total 24.32 g of

wet solids from both pigging process and flushed solids collection were obtained. The dry/wet ratio of these deposits was 0.47, and thus this corresponded to 11.4 g of dry matter. The mixed deposits were then subjected to further analysis to determine their biomass and elemental sulfur contents (results discussed in Section 3.3.3).

3.3.2 Pressure Drops Before and After Pigging Process

During the entire experiment, the pressure drop of the biotrickling filter was always lower than 1 cm of water column, indicating that there was no significant clog inside the reactor. As mentioned earlier, this is an improvement over an earlier study which reported that a pressure drop of greater than 10 cm of water column had been observed in a PUF-packed biotrickling filter, leading to the eventual shutdown of the system (Fortuny et al. 2008). The relationship of the pressure drop of the filter column with gas flow rate was measured before and after the pigging process hoping to illustrate the effect of pigging. The results presented in Fig. 6 show that there were no large differences between the pressure drop before and after pigging. It is only at a few points that the pressure drop slightly decreased after the pigging process. Since all the channels inside the column had been almost cleaned up after the pigging process, the result of the differential pressure experiment proved that this monolith BTF was not clogged even after 165 days of operation. Even so, applying pigging in this monolith BTF was proven to be effective in removing the accumulated biomass and elemental sulfur allowing to extend stable operation indefinitely. These findings demonstrate that the design of this monolith BTF greatly reduced the risk of bed

clogging, and that pigging provided a means to remove accumulated biomass and sulfur. Altogether, this leads to significant process improvement and simplification.

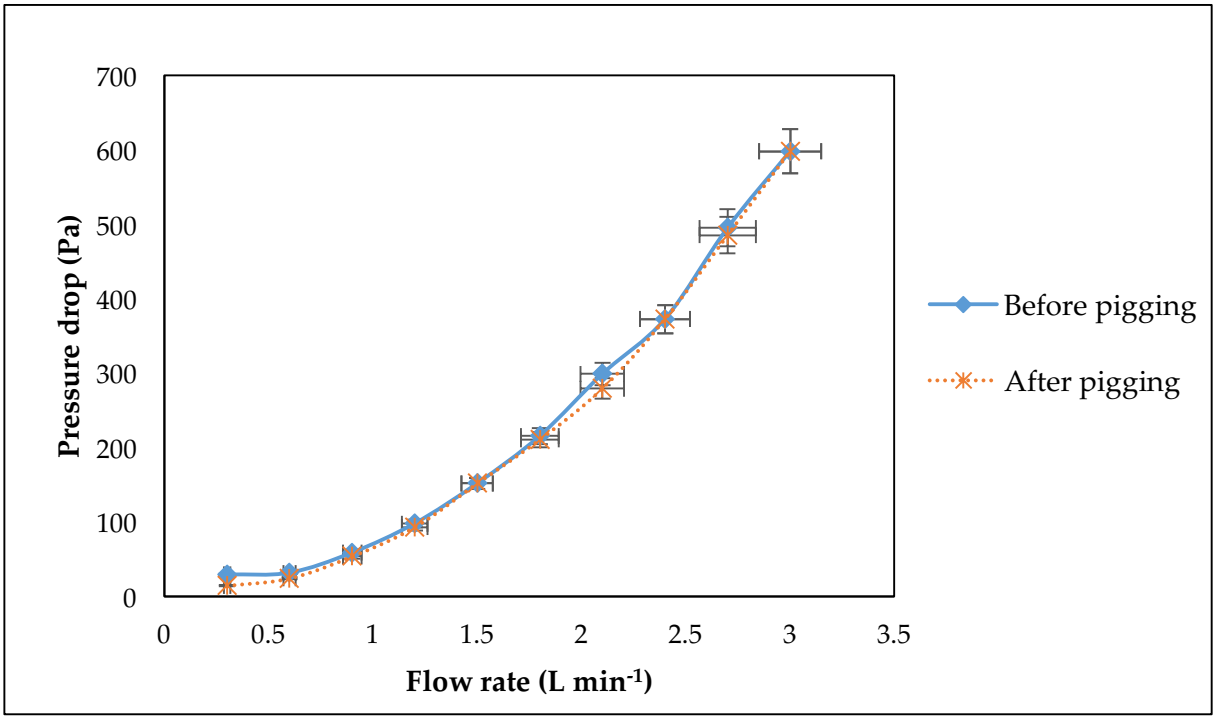


Figure 8: Relationship between pressure drop and flow rate in filter bed before/after pigging process

3.3.3 Pigging Deposits Analysis

The analysis of the collected solids from the pigging process revealed a high content (62.13% of dry mass) of elemental sulfur, while the TKN analysis revealed the low content of 7.03% of (dry) biomass in the deposits. The remainder of the dry mass is unknown. One possible component of the rest proportion is the inorganic material washed out from the filter bed. Trace metal ions like iron and sodium as well as other sulfur species were detected in one previous study (Montebello et al.

2014). The results, to some extent, explain the low recovery rate of sulfur in the liquid phase discussed earlier (Fig. 5) and also support the previous hypothesis that the inlet H_2S was mostly oxidized to elemental sulfur and then accumulated inside the system. The low biomass content indicates a low growth rate of SOB, which then negatively affects the capacity of the reactor to completely oxidize H_2S to sulfate (Mannucci et al. 2012, Montebello et al. 2014). The high percentage of elemental sulfur in the pigging deposits is favored in this system, since the generation of elemental sulfur does not change the pH in the trickling liquid, while the process of producing sulfate will reduce the pH, thereby adding costs for pH control. Moreover, elemental sulfur is a valuable raw material, and the high sulfur-content deposits could be further purified and used for its commercial value, or used as is as a fertilizer.

3.3.4 System Recovery After Pigging Process

After the continuous operation for 157 days to investigate the influence of H_2S/O_2 supplied ratio on the performance of the system, the system was operated at the reference conditions with the H_2S/O_2 ratio of 1:2 in preparation for the pigging investigations. The performance of the system, including RE and EC was recorded prior to and after pigging and the results are shown in Fig 9. After pigging, the system went through gradual declines of both RE (from 100 to 13%) and EC (from 132 to 15.7 g H_2S $m^{-3}h^{-1}$) and the lowest RE and EC were observed on the third day (at 69 hours) after the pigging process. A recovery trend was then observed on the

fourth day after the pigging process, even though a second drop in performance was observed during the system maintenance, but up to now, the RE reached back to 42% and the EC recovered to 52.9 g H_2S $m^{-3}h^{-1}$. These changing trends indicate that the pigging process removed most of the active SOB, leading to the drop on both RE and EC. This was also observed as the detachment of solids with recirculation liquid mentioned before. With the re-growth of SOB in the reactor, the RE and EC was found to moderately increase and complete recovery of the system is expected in the next few days. The experiment is ongoing.

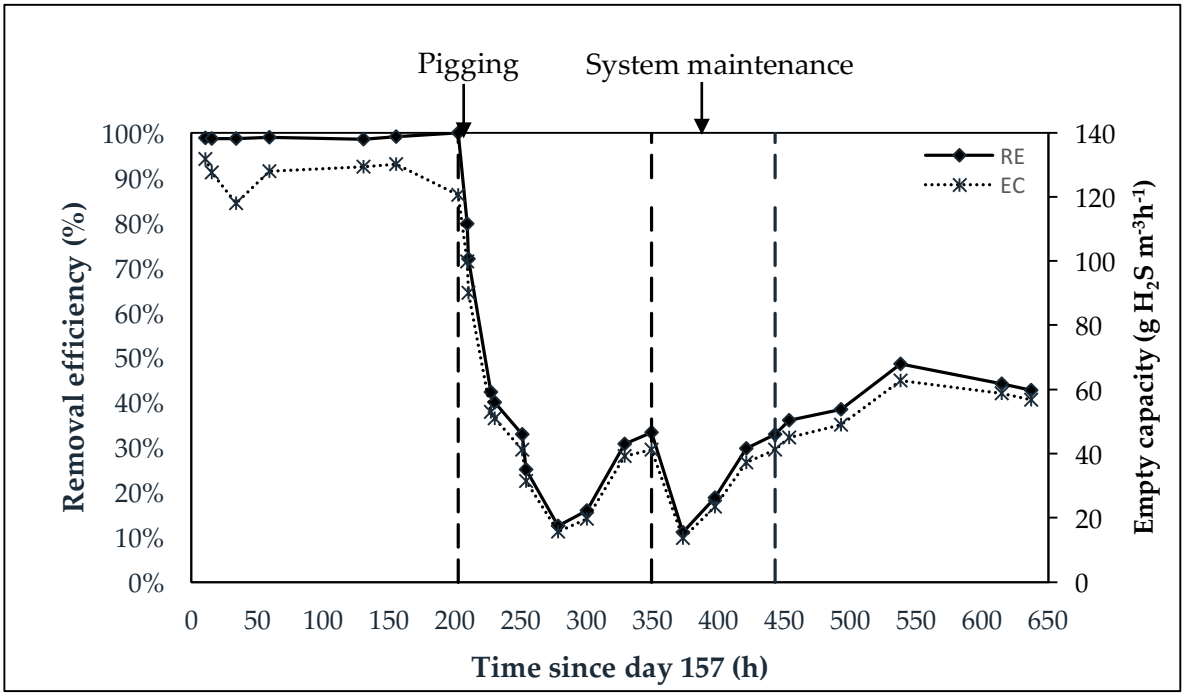


Figure 9: System recovery after the pigging process

Although a complete recovery is expected within 7-10 days, there is no doubt that the pigging process did have a negative effect on the H_2S removal performance of the system. Since all 19 channels were pigged at once in this case, reducing the

numbers of channels being pigged at one time may be a method to mitigate the effects of the pigging on the performance of the system. Possibly, in a large biotrickling filter system, a robot could conduct pigging of a few channels at regular intervals thereby minimizing the impacts on the overall performance of the system. The size of the pig and the control of its position inside the channel undergoing pigging are also two critical factors in the application of this technology.

4. Conclusion

Overall, the results presented and discussed herein indicate that the monolith biotrickling filter bed can be applied as a novel alternative for replacing traditional packing materials with the high specific surface area in BTF to treat high concentration H_2S from biogas. This monolith BTF reactor has been stably operated for more than five months and was able to effectively treat the synthetic biogas contaminated with 1000 ppm_v H_2S, and obtained 52.9 to 133.6 g H_2S m^{-3} h^{-1} EC at H_2S/O_2 supplied ratios from 2:1, 1:1, and 1:2. To fulfill the typical regulation of lower than 500 ppm_v H_2S in the outlet gas flow, the supplied H_2S/O_2 should be smaller than 2. During the operating process, up to 100% RE was achieved at H_2S/O_2 ratio 1:2, and the dominant product, elemental sulfur, was primarily accumulated inside the filter bed. While such accumulation is generally a cause for system upset, the monolith design of the filter bed greatly reduced the risk of the bed-clogging problem when compared with other packing materials. Further, pigging was shown to efficiently remove deposited sulfur and biomass thereby indefinitely extending the life of such biotrickling filters. This constitute the first demonstration of pigging in biotrickling filters; possibly the method can be applied for other biotrickling filter applications where significant biomass or plugging is observed. The high sulfur-content deposits pigged from the reactor could possibly be reused as fertilizers or to produce raw elemental sulfur. Further studies could address the influence of other parameters,

including pH, inlet concentration, and inorganic carbon concentration, on the performance of biotrickling filters removing H_2S from biogas, the optimization of the pigging process, including the optimization of the pig geometry and the mode or frequency of pigging, or further application at larger scale.

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