Biofilter for generation of concentrated sulphuric acid from H_2S

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Abstract

Biofilters are used for the conversion of odorous hydrogen sulphide to odourless sulphate in wastewater treatment plants under the right conditions of moisture and pH. One of the consequences of maintaining the suitable pH and moisture content is the production of large volumes of weakly acidic leachate. This paper presents a biofilter with a maximum H_2S elimination capacity of 16.3 g m^{-3} h^{-1} and removal efficiency greater than 95 % which produces small volumes (1 mL of solution L^{-1} of reactor day^{-1}) of sulphuric acid with a concentration greater than 5.5 M after 150 days of continuous operation. The concentrated sulphuric acid was produced by intermittently trickling a minimum amount of nutrient solution down the upflow biofilter which created a moisture and pH gradient within the biofilter resulting in an environment at the top for the bacterial conversion of H_2S, while sulphuric acid was accumulated at the base. Genetic diversity profiling of samples taken from different sections of the biofilter confirms that the upper sections of the biofilter had the best environment for the bacteria to convert H_2S to sulphate. The formation of concentrated sulphuric acid presents an opportunity for the recovery of sulphur from the waste stream as a usable product.

Keywords: Biofilter; Hydrogen sulphide; Wastewater; Sulphuric acid; Sulphur recovery; Zero leachate

Introduction

Domestic sewage contains organic sulphur, sulphonates and inorganic sulphur (as sulphates) which are sources of hydrogen sulphide (Carrera-Chapela et al. 2014; Gostelow et al. 2001). Hydrogen sulphide is a colourless and toxic gas that is considered a broad spectrum poison and affects the nervous system among other organs (Burgess et al. 2001; Guidotti 2010). It has a characteristic smell of rotten eggs which can be detected by the human nose at concentrations as low as 10 ppb (Shareefdeen and Singh 2005). Typical concentrations of H_2S generated from wastewater treatment plants range from 5 to 100 ppm (Churchill and Elmer 1999; Stanley and Muller 2002). Removal of hydrogen sulphide is considered the most dominant odour control requirement from wastewater (Gostelow et al. 2001). Biofilters are becoming common as a treatment for H_2S emanating from wastewater or sewage treatment plants since they work at ambient temperatures and have low capital costs (Ben Jaber et al. 2016; Dumont et al. 2008; Feng et al. 2011; Lebrero et al. 2014; McNevin and Barford 2000; Mudliar et al. 2010; Romero Hernandez et al. 2013). Biofilters use biofilm—microorganisms immobilised on the surface of porous media that degrade the pollutants to oxidised and less harmful compounds. In biofilters, polluted air flows up through the media and a continuous stream of water trickles down the media to keep the biofilms moist and biologically active. The pollutants in the air come in contact with the active biofilms and are degraded to harmless products. The disadvantage of biofilters is that the microorganisms require sufficient moisture, nutrients and a suitable pH (Mudliar et al. 2010). In the case of biofilters used to remove hydrogen sulphide in an aerobic environment, the overall biological reaction that occurs is given below (Oyarzun et al. 2003; Wang et al. 2003): $H_2S+2O_2 \rightarrow SO_4^{2-}+2H^+$

H_2S can be oxidised to either elemental sulphur or SO_4^{2-} depending on the ratio of H_2S to O_2in the treated air (Chaiprapat et al. 2011; Jensen and Webb 1995). If the oxygen is supplied in a limited amount, incomplete oxidation of H_2S produces elemental sulphur (Chaiprapat et al. 2011; Jensen and Webb 1995). Microorganisms that can oxidise H_2S include *Thiobacillus denitrificans*, *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans*. The pH range for optimal growth of *T. denitrificans* is 6.8 to 7.4, *T. thioparus* is 5.5–7.0 and *A. thiooxidans* is 1.8–2.5 (Aroca et al. 2007; Lors et al. 2009;

Solcia et al. 2014). However, studies have shown that the production of sulphuric acid by these microorganisms can drop the pH in the biofilter to below 1 and *A. thiooxidans* has been shown to operate even at a pH of 0.2 (Lors et al. 2009; Solcia et al. 2014). A common strategy to control pH in conventional biofilters is to wash out the accumulated acidity in the biofilm with a buffered media or chemicals like sodium hydroxide or calcium carbonate (Jover et al. 2012; Shareefdeen et al. 2003b; Solcia et al. 2014). This leads to production of as much as 2000 mL L^{-1} day^{-1} of neutral or slightly acidic leachate (pH = 2) which is treated as waste and requires proper disposal (Abdehagh et al. 2011; Chaiprapat et al. 2011; Park et al. 2011; Solcia et al. 2014). Instead of considering this leachate as waste, the leachate can be thought of as a source of sulphur. The notion of recovering nutrients other than sulphur from the leachate of biofilters is not new (Dumont et al. 2012a; Jung et al. 2005; Rabbani et al. 2015; Rabbani et al. 2016; Zhang et al. 2013). Removal and recovery of elemental sulphur from coal, natural gas and high sulphur crude oils is well-recognised processes, but recovery of sulphur from dilute streams of acid from wastewater treatment plants has not been previously attempted (Babich and Moulijn 2003; Bachmann et al. 2014; Jiang et al. 2015; Meshram et al. 2015; Shu et al. 2014). Dilute sulphuric acid solutions produced in industry are concentrated by energy-intensive processes using high-temperature conversion of acid to sulphur dioxide and subsequent catalytic conversion of sulphur dioxide to concentrated sulphuric acid (Smith and Mantius 1978). Dilute sulphuric acid has also been concentrated in laboratory scale evaporators, where droplets of dilute sulphuric acid undergo a loss in water by evaporation to produce acid with concentrations of as much as 14 M (Zhou and Liu 2007). It has been estimated that the amount of sulphur that can be potentially recovered from polluted air in WWTP can be as high as 17.5 kg of S day^{-1} (Rabbani et al. 2015).

This paper describes an aerobic biofilter that removes H_2S while producing concentrated sulphuric acid as a product. The setup, which also minimises leachate production, encourages sulphur recovery rather than producing waste streams of diluted sulphuric acid. A moisture and pH gradient are maintained in the biofilter by adding a minimal amount of solution to the top, so that the top section of the biofilter is favourable for the growth of microorganisms, while the bottom section accumulates sulphuric acid.

Materials and methods

Experimental setup

The investigation was carried out in a lab-sale upflow biofilter, and the schematic of the experimental setup is given in Fig. 1. H_2S was supplied to the reactor using Tedlar gas sampling bags (CEL Scientific Corp.) made of Dupont's 2mil Tedlar PVF film with PTFE fittings which were non-reactive to hydrogen sulphide. Concentrated H_2S in a Tedlar bag was dosed using a peristaltic pump (Masterflex L/S economy variable-speed drive, Cole-Palmer Instrument Company) into the pressure-regulated laboratory compressed air leading to the biofilter. The flow rate of the peristaltic pump was adjusted to obtain the desired H_2S concentration. The flow rate from the peristaltic pump never exceeded more than 0.1 L min^{-1}, and this was done to ensure that the oxygen to H_2S ratio at the inlet of the biofilter was always high providing an aerobic environment during the operation of the biofilter. The Tedlar bags, stored at room temperature, were changed every 30 h and the H_2S concentration and humidity of the gas entering the biofilter were monitored in real time.

Biofilter column

The biofilter was constructed from acid-proof PVC piping (Holman Industries) with an internal diameter of 5.5 cm. The biofilter had three detachable sections (the top, middle and bottom sections as shown in Fig. 1) and a glass flask at the bottom for the collection of acidic product. Each section was filled with equal amounts of acid resistant polyethylene packing material (AMB Biomedia Bioballs (ABB media), The Tech Den Pty. Ltd.) with dimensions of 11 mm × 7 mm and a total surface area of 850 m^2 m^{-3}. The packing material was chosen for its large surface area and its inertness to low pH. The sections were filled with the ABB media to a height of 13.0 cm in each section giving a total working volume of 308.86 cm^3 or 0.309 L for each section. The number of packing material was about 1200 ABB media/L of reactor resulting in free space of 20 % inside the biofilter. The packing material in each section was supported by sieve plates made of Plexiglas. Empty Bed Residence Time (EBRT) is the time that a gaseous pollutant spends in a biofilter and is defined as the bed volume of the reactor divided by the air flow rate (Shareefdeen and Singh 2005). In this system, the bed volume

was 0.926 L and the flow rate was set at 0.9 L min^{-1} giving a gas velocity of 23 m h^{-1} and an EBRT of 62 s.

Seeding procedure

At the start-up period, the biofilter was seeded with a mixture containing 1 L of activated sludge (sourced from a local wastewater treatment facility in Woodman Point, Perth) and 1 L of nutrient solution with the following composition modified from the *Thiobacillus novellus*medium as described in Atlas (2005): KH_2PO_4 (4.0 g), K_2HPO_4 (1.5 g), $MgCl_2 \cdot 6H_2O$ (0.2 g), NH_4Cl (0.1 g) and 10 mL of trace metal solutions (Na_2EDTA 50 g L^{-1}, NaOH 11 g L^{-1}, $CaCl_2 \cdot 2H_2O$ 7.34 g L^{-1}, $FeCl_2$ 2.3 g L^{-1}, $MnCl_2 \cdot 7H_2O$ 2.5 g L^{-1}, $ZnCl_2$ 1.0 g L^{-1}, $CoCl_2 \cdot 6H_2O$ 0.5 g L^{-1}, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ 0.5 g L^{-1}, $CuCl_2$ 0.73 g L^{-1}). To ensure that the incoming H_2S was the only source of sulphur in the biofilters, there was no thiosulphate or sulphate in the nutrient solution. The magnesium sulphate, ammonium sulphate, zinc sulphate and copper sulphate were replaced with equimolar amounts of the respective metal chlorides. After the initial incubation period, a peristaltic pump (Masterflex C/L Dual-Channel Variable-Speed Tubing Pump, Cole Palmer Instrument Company), controlled by a connected computer using a Labjack USB interface and National Instruments LabView 7.1 control software, was used to control the amount of nutrient added to the top of the column.

Sampling and chemical analysis

The H_2S concentration was measured in real time by means of an inline sensor (GD 2529 Hydrogen Sulphide Sensor, GasTech Australia Pty. Ltd). Humidity and temperature of the gas mixture were measured using the HOBO Pro v2 external temp/RH probe and data logger (Onsetcomp). Five pieces of randomly chosen ABB media were added to 10 mL of distilled deionised water in a 30 mL glass vial and shaken for 10 min. 1 mL of solution with the extracted water soluble ions was then analysed for sulphate (SO_4^{2-}), sulphide (HS^-), thiosulphate ($S_2O_3^{2-}$), elemental sulphur (S) and hydrogen ion (H^+) concentration. Sulphate was determined based on precipitation as $BaSO_4$ followed by photo spectrometric quantitation at 420 nm with the HACH DR 2700 Portable Spectrophotometer (Rice and Bridgewater 2012). Sulphide (HS^-) was determined based on the reaction of copper sulphate ($CuSO_4$)

in an acidic solution producing CuS precipitate which was measured photometrically at 480 nm (Cord-Ruwisch 1985). Thiosulphate ($S_2O_3^{2-}$) was determined based on the standard method for the standardisation of sodium thiosulphate with potassium iodate (Vogel and Mendham 2000). Elemental sulphur was determined using extraction with chloroform and HPLC analysis (Henshaw et al. 1997). A 0.8 mL chloroform (ChemSupply) and 0.2 mL of 10 % nitric acid were added to 1 mL sample and shaken for 15 min. The tube was then centrifuged at 1350 rpm for 5 min. The bottom 0.5 mL chloroform layer was added to 1 mL of methanol and injected into Agilent 1200 HPLC Liquid Chromatography System with an Eclipse DB C-18 column (4.6 × 150 mm) with a diode array and multiple wavelength detector set at 254 nm. The eluent was HPLC grade methanol (Honeywell Burdick & Jackson) at a flow rate of 1.5 mL min^{-1}. The pH of the medium was determined by titration with NaOH using methyl orange as indicator. The moisture content in the different sections of the biofilter was expressed as the gravimetric water content (Margesin and Schinner 2005):

$$M_n = \frac{M_w}{M_o}$$

where M_n is the moisture content, M_w is the mass of medium with water and M_o is the mass of the medium without water

Results and discussion

Removal of H_2S from the inlet air

The biofilter initially operated continuously for more than 24 weeks with H_2S in the inlet air. Inlet mass load of a biofilter is defined as the product of flow rate and concentration of pollutant divided by the reactor volume (Shareefdeen and Singh 2005). During the first 17 weeks of the operation of the biofilter, the inlet mass loading of H_2S varied between 8.4 to 7.2 g m^{-3} h^{-1} (102 to 87 ppm min^{-1}) (Fig. 2). Removal efficiency (RE) is a measure of how effective the biofilter is at removing the pollutant (Shareefdeen and Singh 2005). After an initial 7 day incubation period, the removal efficiency of H_2S was continuously greater than 95 % for the first 17 weeks, indicating that the

biofilter was removing H_2S from the contaminated air. The mass loading was increased to between 18 and 15 g m^{-3} h^{-1} (216 to 177 ppm min^{-1}) from week 17 to week 22 (Fig. 2). After an initial decline in removal efficiency to 35 %, the response of the biofilter was rapid as the removal efficiency reached 95 % within 4 days of continued operation under the same conditions. Finally, the mass loading was increased to greater than 33 g m^{-3} h^{-1} (380 ppm min^{-1}) after week 22 (Fig. 2). The removal efficiency at this stage reduced to less than 10 % and did not improve after more than 10 days of continued operation under the same conditions. This is similar to examples in the literature which show a drop in removal efficiency of a biofilter at higher concentrations of H_2S because of sulphate accumulation which inhibits microbial activity (Ben Jaber et al. 2016; Chaiprapat et al. 2011; Romero Hernandez et al. 2013; Solcia et al. 2014; Yang and Allen 1994).

The parameters for this biofilter are summarised in Table 1. Volumetric load (V_L) is a term used to normalise the volume of air entering the system and is defined as the airflow rate divided by the volume of the reactor (Shareefdeen and Singh 2005). Elimination capacity (EC) is the mass of pollutant removed by the biofilter and normalised for the flow rate and the volume of the reactor (Shareefdeen and Singh 2005).

There is a wide range of mass loading rates (3–162 g m^{-3} h^{-1}) in the literature for biofilters that remove H_2S based on different operating conditions and types of support medium (Table 2). The maximum elimination capacity of 16.3 g m^{-3} h^{-1} in this study is within the range of similar lab-scale biofilters (Chaiprapat et al. 2011; Converse et al. 2003; Kim et al. 2008; Park et al. 2011; Roshani et al. 2012; Solcia et al. 2014).

The pressure drop in the biofilter was periodically measured during the course of the operation of the biofilters with an in-house water differential manometer. Pressure drop occurs in biofilters due to excessive growth of biomass or the compaction and breakdown of the medium (like soil or wood chips) leading to a reduction in the porosity of the medium (Chung et al. 2001; Elias et al. 2002; Kennes and Veiga 2002; Kim et al. 2008; Yang and Allen 1994). The maximum pressure drop in this biofilter was 4 Pa m^{-1} filter bed, and the value is lower than the pressure drop in conventional biofilters treating H_2S (Chung et al. 2001; Dumont et al. 2012a; Elias et al. 2002; Kim et al. 2008;

Yang and Allen 1994). This is due to the inert ABB media maintaining its structure during the course of this study and the low gas velocity in this biofilter (23 m h^{-1}) compared to other studies in the literature. For example, a study conducted by Dumont et al. showed that a biofilter using expanded schist for the removal of H_2S had a pressure drop of 10–80 Pa m^{-1}, but the gas velocity in that study was considerably higher (89–229 m h^{-1}) (Dumont et al. 2012a). The conversion of H_2S to H_2SO_4 is dependent on the ratio of H_2S and O_2, and since the intention of this study is to harvest H_2SO_4, it was important to avoid the formation of anaerobic zones inside the biofilter (Chaiprapat et al. 2011; Jensen and Webb 1995). In their study of aerobic acidic biofilters for the removal of H_2S, Chaiprapat et al. showed that the highest efficiency of conversion of H_2S to sulphate or sulphuric acid was obtained when the H_2S to O_2 ratio was 1:4 (Chaiprapat et al. 2011). The aerobic environment in the biofilter in this study was ensured by always maintaining that H_2S to O_2 ratio was greater than 1:10 at all times.

Production of leachate

One of the objectives of the biofilter is the production of a minimum amount of leachate, and since the amount of leachate produced in a biofilter is dependent in the humidity of the air, both the humidity of the incoming waste gas and the outgoing air from the biofilter were monitored using the HOBO Prov2 external temp/RH probe and data logger (Onset Computer Corp.). The mixture of H_2S from the Tedlar bag and the in-house supply of air was found to have an average relative humidity of 44 ± 3.2 % during the study period. Unlike other examples in the literature, where the incoming waste gas was humidified before entering the biofilter, the incoming waste gas in this biofilter was not humidified to allow the production of a minimum amount of concentrated leachate at the bottom (Dumont et al. 2012a; Gonzalez-Sanchez et al. 2008; Shareefdeen et al. 2003b; Solcia et al. 2014). As the gas travelled up the biofilter, it picked up moisture resulting in the outlet to have an average relative humidity of 100 % (23.00 g m^{-3} at 25 °C). The amount of moisture lost due to the difference in humidity between the inlet and outlet was calculated to be 0.70 g h^{-1} (approximately 16.8 mL day^{-1}), and this water loss was compensated by delivering 3 mL of nutrient solution at the top of the reactor every 4 h (18 mL day^{-1}) or excess water of about 1.2 mL day^{-1}. Experimentally 178.59 mL of excess liquid was collected over the 172 days of operation of this biofilter. This figure

is comparable to the excess nutrient solution added over this period considering possible inaccuracy in metering of the small volume of nutrient solution intermittently added and the estimation of water loss through calculating the difference between moisture content of air at the inlet and outlet of the biofilter. The acidic product produced per volume of biofilter was a 1.15 mL L^{-1} day^{-1}. This is considerably less than similar systems which produced leachate in the range of 38 to 2000 mL L^{-1} day^{-1} (Abdehagh et al. 2011; Chaiprapat et al. 2011; Gabriel and Deshusses 2003; Shareefdeen et al. 2003b; Solcia et al. 2014; Yang and Allen 1994). With careful monitoring and control of the moisture in the biofilter, it is possible to operate a biofilter with a little or no leachate. The concept of operating a biofiler with no leachate has been explored previously in a biochemical ammonia removal process, where the amount of water percolating through a biofilter is controlled, and this results in a pH and soluble ion gradient with the production of no leachate (Vitzthum von Eckstaedt et al. 2013). The biofilter in this study is similar in that it produces a minimal amount of leachate, but the biofilter removes H_2S instead of ammonia. The amount of sulphur that can be recovered from the leachate can be considerable in industrial biofilters that remove H_2S which currently produce large volumes of dilute waste stream (Rabbani et al. 2015). The recovery of sulphur was explored in a pilot scale study that was recently conducted where H_2S was removed from air generated at a wastewater treatment plant using a biofilter similar to the one described in this study (Rabbani et al. 2016). The pilot scale biofilter removed H_2S from air with a 92 % removal efficiency and produced a very small amount of acidic leachate (0.2 mL L^{-1} day^{-1}), and sulphur was recovered as ammonium sulphate (Rabbani et al. 2016).

Accumulation of ions in leachate

Water soluble ions produced by the biological oxidation of H_2S are washed down and accumulated at the bottom. The ions that accumulated in the leachate were monitored during the study period and are shown in Fig. 3. There was an increase in the amount of both the sulphate and hydrogen ion in the leachate over time, and the hydrogen ion concentration is twice that of the concentration of sulphate in the leachate. This is expected since the biological oxidation of H_2S produces H_2SO_4 (Eq. 1). As shown in Fig. 3, the dashed line represents the H^+ that is expected from the amount of SO_4^{2-} in the

leachate ('expected H^+'). The amount of H^+ experimentally detected ('detected H^+'), which was determined as described in 'Sampling and chemical analysis' section, shows a good agreement with the expected H^+, especially after the first 8 weeks.

The average concentration of sulphuric acid collected in the leachate from week 17 to week 22 was 5.5 M (Fig. 4) and is much more concentrated than the sulphate concentrations of similar biofilters in the literature where the concentrations in the leachate are 0.2 M or less (Chen et al. 2014; Solcia et al. 2014). It is important to note that in this study, the average relative humidity of the air in equilibrium with the acid is 44 % (10.15 g m^{-3} at 25 °C) and, according to the literature, the maximum sulphuric acid concentration that can be achieved in equilibrium at this relative humidity is 6 M (Perry and Chilton 1973).

There was no sulphide (HS^-) and thiosulphate ($S_2O_3^{2-}$) in the leachate at any time during the operation of the biofilter, providing further evidence that the biofilter operated in an aerobic environment. It should be noted that elemental sulphur was detected in the leachate after 10 weeks of the operation of the biofilter; however, the amount formed was less than 1 % of the total sulphur in the system. Biological oxidation of H_2S even in an aerobic environment has been shown to produce small quantities of elemental sulphur (Chaiprapat et al. 2011; Jensen and Webb 1995).

Removal of H_2S by each section of the biofilter

The biofilter was constructed so that each of the sections could be detached and the performance of each section in removing H_2S was measured. A summary of the results of the H_2S removed by each section is summarised in Fig. 5. Interestingly, the bottom section did not remove any significant amount of the incoming H_2S (Fig. 5) indicating that these parts of the biofilter did not have an environment conducive to the formation of microorganisms for the removal of H_2S. This is further explored in 'Moisture and ion gradient in biofilter' section. When the inlet concentration of H_2S was around 100 ppm (for example week 14 in Fig. 5), the middle section removed almost all of the H_2S. When the inlet H_2S concentration was stepped up to 200 ppm (for example week 21 in Fig. 5), the bottom section continued to be poor in removing H_2S and the middle section removed about half of

the H_2S. The addition of the top section removed H_2S from the inlet gas at greater than 98 % removal efficiency. With the increase in the inlet concentration of H_2S, the top section was almost as important as the middle sections in removing H_2S from the inlet, whereas in previous weeks, with lower inlet H_2S concentration, the middle section alone was sufficient to remove most of the H_2S. Stepping up the inlet concentration once again to 400 ppm led to the failure of the whole biofilter in removing H_2S.

Moisture and ion gradient in biofilter

One of the expected characteristics of this biofilter was that there would be a gradient of moisture content and ion concentrations in the different sections of the biofilter.

The moisture content in each section was determined and is shown in Fig. 6. Since air with low humidity (44 %) entered the biofilter from the bottom, the average moisture content of the bottom section was lower than the top and middle sections of the biofilter. Previous studies have shown that operating conditions such as the mass loading rate and the amount of moisture in a biofilter have to be carefully controlled to avoid accumulation of sulphate in the biofilter which has an inhibitory effect (Ben Jaber et al. 2016; Yang and Allen 1994). Yang and his co-workers have shown that microorganisms that convert H_2S to sulphate are inhibited when the sulphate concentration is greater than 0.8 M (Yang and Allen 1994). In this study, it was evident that the bottom section did not remove any H_2S from the air (Fig. 5) and with the sulphate concentration in the bottom section being on average greater than 2 M; this was no surprise. The middle and top sections of the biofilter with an average sulphate concentration of 0.83 and 0.12 M, respectively, however, do allow the biological oxidation of H_2S to take place.

Samples from each section at the end of week 14 were sent to Australian Genome Research Facility (AGRF) at the University of Queensland for diversity profiling using the two bacterial 16 s amplicons of 16S:27F – 519R (V1-V3), and the results are summarised in Table 3. Organisms identified as being of the *Acidithiobacillus* family, which live in a low pH, were found in all sections of the biofilter, but only the top and middle sections contained organisms identified as being of the *Thiobacillus* family.

The bottom section did not have a pH favourable for the growth of *Thiobacillus*. In the middle section, there were four times more sequences of the *Acidithiobacillus* family than in the top and bottom section indicating that the middle section has the most number of *Acidithiobacillus* which correlated to the fact that the middle section was doing most of the work in removing H_2S from the inlet (Fig. 5).

Sulphur balance

The mass balance in this system over the study period is shown in Fig. 7. The amount of sulphur entering the biofilter was calculated by considering the H_2S (g) removed by the biofilter as the only source of sulphur. The mass of H_2S entering the biofilter per volume of air is given as (C_{in}–C_{out}), where C_{in} and C_{out} are the H_2S concentration (in g m^{-3}) of the inlet and outlet, respectively. If the flow rate is designated as Q (in m^3 min^{-1}), then the mass of H_2S entering the biofilter (in g min^{-1}) is given as (C_{in}–C_{out}) X Q. Mass of sulphur entering the biofilter as H_2S is indicated in Fig. 7 as 'S (from H_2S)'. The total amount of all forms of sulphur in the biofilter was indicated in Fig. 7 as 'S (in biofilter)' and was determined by measuring the amount of sulphate (SO_4^{2-}) and elemental sulphur (S) in the accumulated leachate and on the biofilm in all the sections of the biofilter. Sulphide (HS^-) and thiosulphate ($S_2O_3^{2-}$) were not detected in this biofilter. Table 4 contains representative data used to construct Fig. 7 which shows the distribution of sulphur as different forms in the biofilter. In this biofilter, the sulphur from the sulphate in the leachate accounted for more than 90 % of the mass of sulphur in the system after the initial acclimation period showing that almost all the sulphuric acid produced in the biofilter had been collected in the leachate as sulphate. Previous researchers have shown that almost all the H_2S removed by an aerobic biofilter is converted to sulphuric acid (Chaiprapat et al. 2011; Moghanloo et al. 2010).

Conclusion

This study describes an aerobic biofilter that removes H_2S with a maximum H_2S elimination capacity of 16.3 g m^{-3} h^{-1} and produces sulphuric acid with a concentration of 5.5 M. The amount of leachate

produced was very low (1 mL L^{-1} day^{-1}) compared to similar biofilters in the literature, and this was achieved by intermittently trickling a minimum amount of nutrient solution down the upflow biofilter. The system created a moisture and pH gradient within the biofilter resulting in an environment at the top for the bacterial conversion of H_2S, while sulphuric acid was accumulated at the base.

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Table 1 Biofilter parameters during the operational period

	Weeks 1–17	**Weeks 17–22**
Average H_2S concentration of inlet air	0.14 g m^{-3}	0.28 g m^{-3}
Volume of reactor	0.00093 m^3	0.00093 m^3
Inlet flow rate	0.0009 m^3 min^{-1}	0.0009 m^3 min^{-1}
EBRT	62 s	62 s
Volumetric load	58 m^3 m^{-3} h^{-1} [a]	58 m^3 m^{-3} h^{-1} [a]
Mass loading rate	7.8 g m^{-3} h^{-1} [b]	16.2 g m^{-3} h^{-1} [b]
Elimination capacity	7.6 g m^{-3} h^{-1}	16.3 g m^{-3} h^{-1}
Removal efficiency	96 %	99 %

[a] m^3 m^{-3} h^{-1} refers to m^3 of air flow m^{-3} of reactor volume per hour

[b] g m^{-3} h^{-1} refers to gram of H_2S m^{-3} of reactor per hour

Table 2 Summary of operating conditions and supporting material information of biofilters that remove H_2S

	Supporting material	**EBRT (s)**	**Mass loading rate (g m^{-3} h^{-1})**	**Removal efficiency (%)**	**Ref.**
1	Lava rock	85	144	98	(Ramirez-Saenz et al. 2009)
2	Coconut fibre	78	162	90	(Chaiprapat et al. 2011)
3	AMB Biomedia Bioballs	62	16	95	This study
4	Mixture of compost and perlite	50	3	100	(Lebrero et al. 2010)
5	Proprietary synthetic inorganic media	30	6	100	(Shareefdeen et al. 2003a)
6	Expanded schist	16	30	100	(Dumont et al. 2012a)
7	Mixture of compost, perlite and oyster shells	15	8	99	(Converse et al. 2003)
8	Open pore polyurethane foam	1–6	30	95	(Gonzalez-Sanchez et al. 2008)

Table 3 Distribution of *Thiobacillus* and *Acidithiobacillus* in the biofilter

	Total sequences	**Sequences with *Acidithiobacillus***	**Sequences with *Thiobacillus***
Top section	125279	15	186
Middle section	104996	61	24
Bottom section	99915	20	0

Table 4 Representative data showing the distribution of sulphur as different forms in the biofilter

Week	S from SO_4^{2-} in leachate	S from elemental S in leachate	S from SO_4^{2-} in biofilter	S from elemental S in biofilter
	g	mg	g	mg
2	0.90	0.00	0.06	0.00
10	11.05	1.02	0.74	0.00
17	19.36	1.42	0.33	52.1
21	26.74	1.62	0.87	66.7

Fig. 1 Schematic diagram of experimental setup

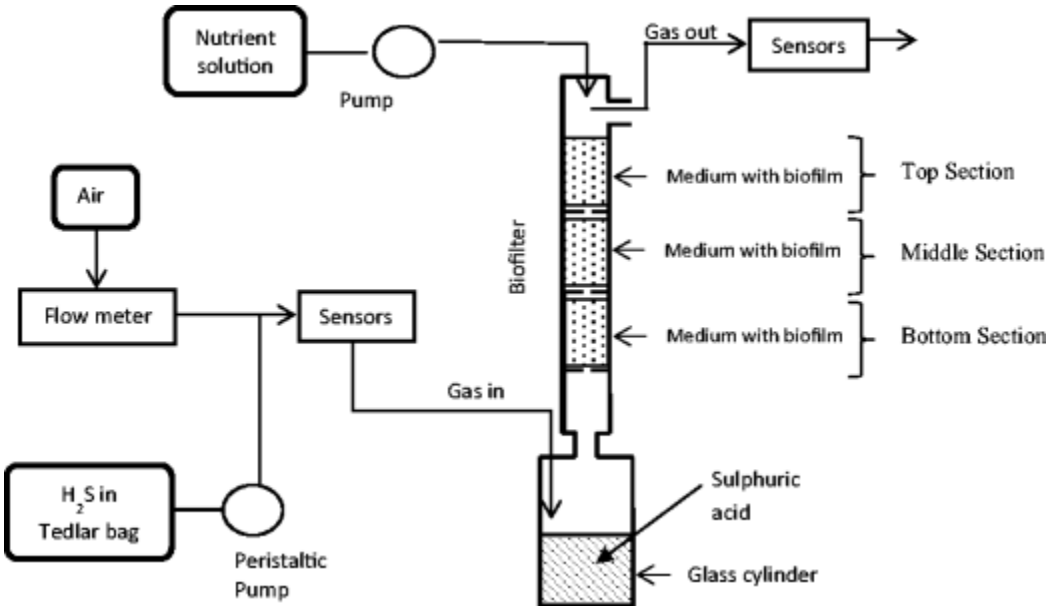

Fig. 2 H_2S concentration in the inlet and the outlet of the biofilter during the operational period

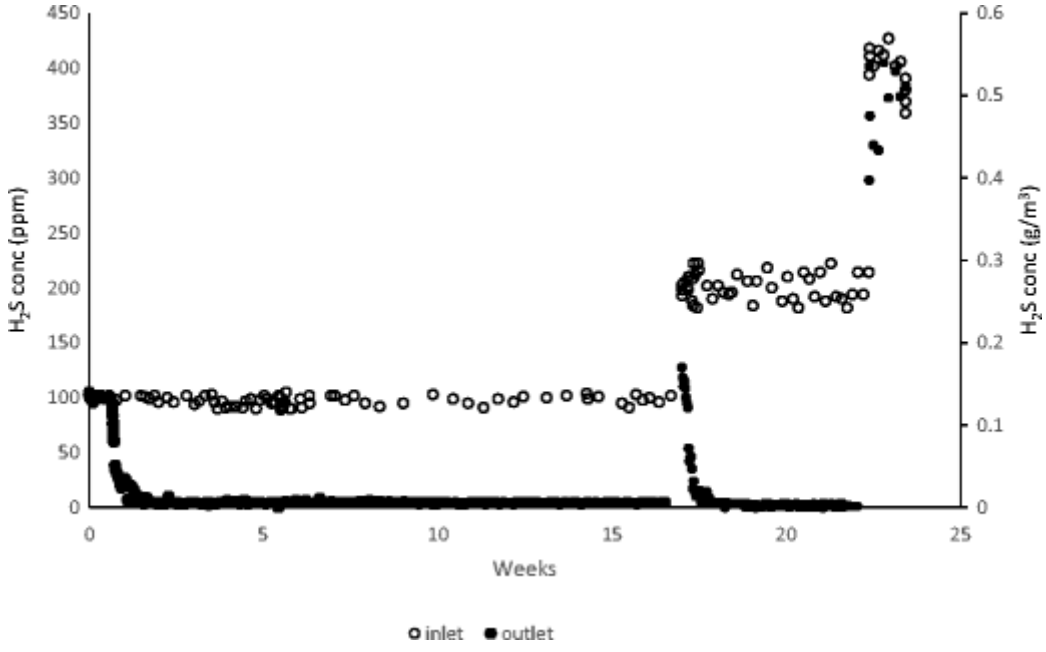

Fig. 3 Cumulative amount of sulphate and hydrogen ion in the leachate

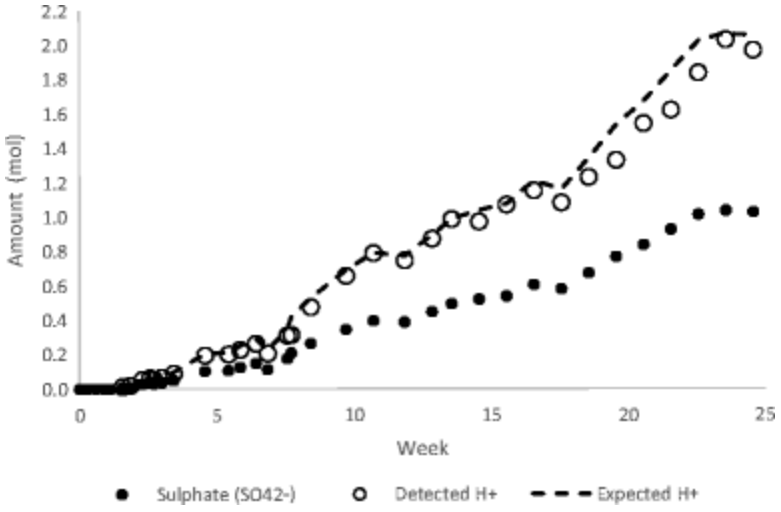

Fig. 4 Concentration of sulphuric acid in the leachate

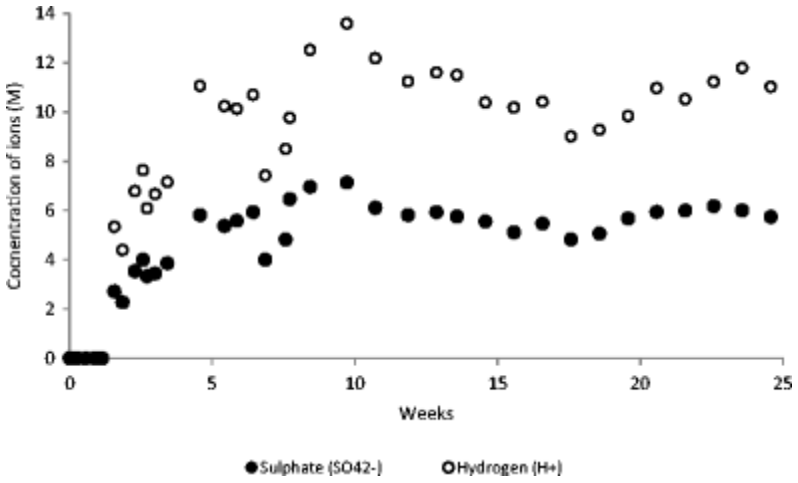

Fig. 5 H_2S in the outlet from different points of the biofilter

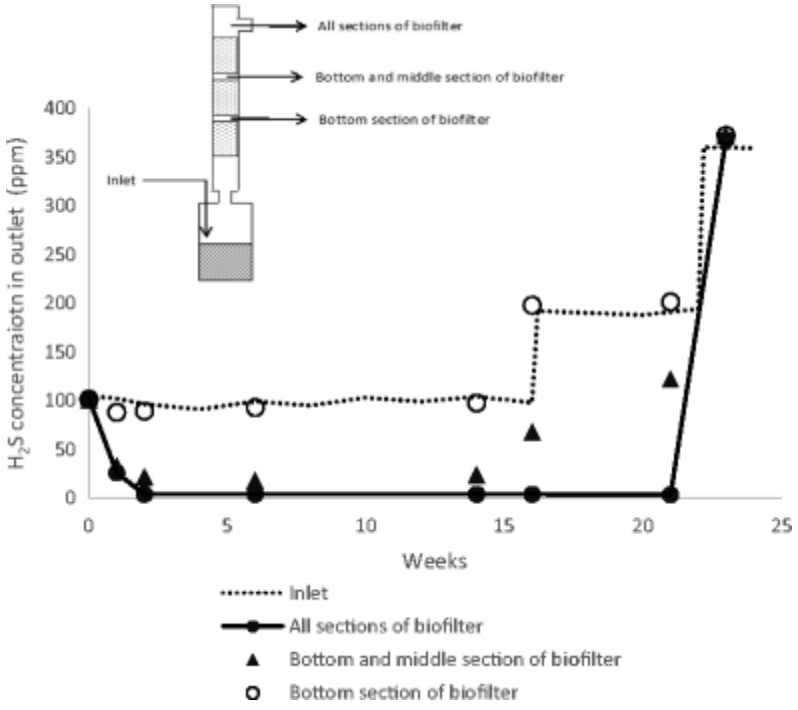

Fig. 6 Average moisture content and concentration of sulphate and hydrogen ion over 17 weeks in the different sections of the biofilter

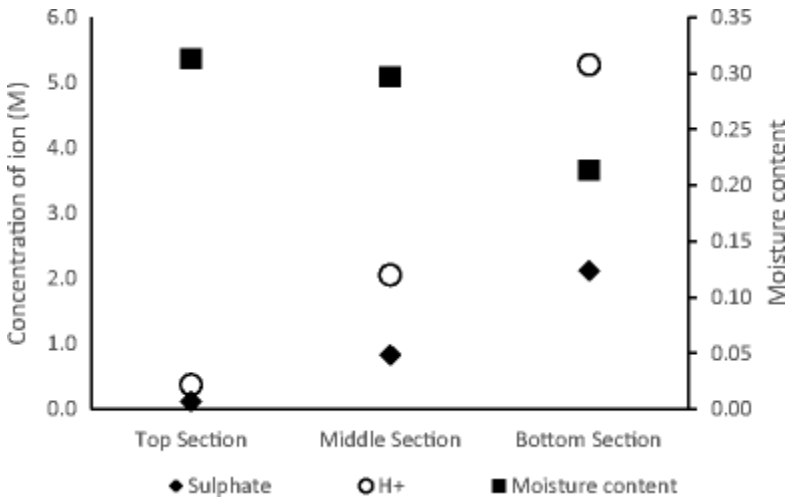

Fig. 7 Mass balance of sulphur in the system