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Biological Hydrogen Sulphide Removal from Air by Package Column

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Many industrial processes and sewage treatment facilities produce odours, most of which are of decomposed sulphur compounds. Hydrogen sulphide, which is a toxic and corrosive gas, may be the standard indicator among the obnoxious odours and therefore the amount released into the air is required to be regulated strictly. Hydrogen sulphide was efficiently removed from contaminated air by a pilot-scale biofilter; a column prepared with soil, sawdust and activated sludge materials from the leather industry was used for preparation of a biodegradation unit. The biodegradation unit was used under several working conditions which were designed for 48 h repetition intervals, with different hydrogen sulphide concentrations, loading rate increased from 10 to 100 mg m^{-3} and different gas flow rates (25, 50 and 75 m s^{-1}). The removal efficiencies of the biodegradation unit were measured mainly from the outflow concentrations and degradation activity. The main by-product obtained in the biodegradation process was sulphate in the drainage water, as it accounted for more than 90 % of the total sulphur compound decomposed in the packing material. Sulphate removal from the system was carried out by drainage water during the operation periods. In the recent study, about 100 % hydrogen sulphide removal was found at lower gas flow rates by the biologically produced reactor.

Key Words: Biodegradation, Hydrogen sulphide, Removal, Sulphate, Soil column, Air pollution, Treatment, Gas, Mine.

INTRODUCTION

Hydrogen sulphide is a special compound which can be found in natural gases as well as in volcanic gases and hot-springs[1,2]. It is also originated from the anaerobic decomposition of human and animal wastes and from different industrial activities, such as rayon textiles manufacture, pulp and paper mills, oil refinery and natural gas treatment[3], *etc*. It has a typical smell of rotten eggs and can be smelt in fine concentrations as low as 0.5 ppb[4]. However, at 100 ppm, it can no longer be smelt. Breathing hydrogen

sulphide at a concentration higher than 500 ppm can be fatal after a few breaths, due to its broad spectrum toxicity[5]. Extensive study of the effect of hydrogen sulphide on the fish species crayfish and benthic invertebrates, showed that hydrogen sulphide is highly toxic to fish and other aquatic organisms at concentrations frequently found in natural settings. Hydrogen sulphide is reported to be toxic to crustaceans at low concentrations[6,7]. In aquaculture reservoirs, sulphide is typically generated in sediment where anaerobic conditions that enhance sulphate reduction prevail. Episodes of mass mortality of fish have been attributed to hydrogen sulphide release from peaty fishpond sediments.

The gas produced from coal gasification contains hydrogen sulphide and other hazardous sulphur compounds, which must be removed to prevent corrosion and environmental problems. Thus the desulphurisation of hydrogen sulphide in coal-gasified gas has been extensively investigated to be utilized in advanced power generation systems such as integrated gasification combined cycle and in gasification systems the molten carbonate fuel cells. The coal gasification processes should be operated at high temperatures to obtain a high thermal efficiency. Therefore, the desulphurization processes practically operate at high temperatures of 600-700 ºC[2,8].

Several different techniques are available for removing odorous sulphur compounds from waste gases. Techniques such as scrubbing and adsorption on solids recover sulphur either as hydrogen sulphide or organic sulphides or as elemental sulphur or SO_2. Sulphur dioxide or hydrogen sulphide can be recycled by processes such as the Claus process[9]. The Claus process has been most commonly employed to remove hydrogen sulphide from natural gas facilities or refinery plants. Claus plants generally convert 94-98 % of sulphur compounds in the feed gas into elemental sulphur. As the restrictions on sulphur emissions are annually strengthening worldwide, a number of tail gas clean-up processes have been developed to reduce sulphur emission to permissible levels. The development of the new processes to deal with the Claus tail gas is based on the direct oxidation of remaining traces of hydrogen sulphide by oxygen or hydrogen sulphide absorption/recycling technologies[10,11]. Up to now, two main catalytic processes dealing with the selective oxidation of hydrogen sulphide by oxygen into elemental sulphur have been developed. Elemental sulphur recovery is actually a good choice at high concentrations. When sulphur compounds are at low concentration, processing by techniques such as thermal or catalytic combustion, or oxidative scrubbing or bio-filtration may be preferred. Catalytic combustion suffers the possible deactivation of catalysts during extended operation. Both combustion and oxidative scrubbing convert the pollutant gas into another pollutant, although less odorous (SO_2 or SO_3^{2-}/ SO_4^{2-} solutions).

Multiple reactions have been suggested in recent years to describe the initial reaction between the various iron species and sulphide. However, it is widely accepted that under anaerobic conditions the reaction consists of two principal steps: surface dissolution of the iron oxide followed by a redox reaction and (if the solubility product is exceeded) FeS precipitation. For simplification reasons, the following two equations are often used to describe the initial stage of iron-sulphide reactions[12-14]. Ferric (Fe^{3+}) is reduced by sulphide together with the precipitation of colloidal sulphur (eqn. 1) and ferrous (Fe^{2+}) reacts with S^{2-} to precipitate as insoluble FeS (eqn. 2). The second reaction is pH dependant and will rarely occur at pH values lower than 6. Eqn. 3 combines eqns. 1 and 2 and the equilibrium equation between S^{2-} and HS^- to show the overall reaction at conditions exceeding the solubility product of ferrous sulphide and assuming eqn. 2 has reached equilibrium.

$$2Fe^{3+} + HS^- \longrightarrow 2Fe^{2+} + S^0 \quad (1)$$

$$Fe^{2+}S^{2-} \longrightarrow FeS \ (K_{sp} = 3.7 \times 10^{-19}) \quad (2)$$

$$2Fe^{3+} + 3HS^- \longrightarrow 2S^0 + 3H^+ + 2FeS \quad (3)$$

According to eqn. 3, each mol of Fe^{3+} can potentially remove 1.5 mol of S^{2-} while releasing 1.5 mol of acidity. Despite the frequent use of eqns. 1 and 2, a variety of different oxidation products have been reported for reactions of sulphide with iron oxides, depending on both the type of iron oxide involved and environmental conditions. However, despite a large data bank, the exact conditions giving rise to a specific end product have not been properly quantified to date. Other than elemental sulphur, sulphate has also been reported to be the product of sulphide oxidation, especially when hematite was the iron source[15]. Thiosulphate ($S_2O_3^{2-}$) and sulphite (SO_3^{2-}) are unstable and generally will not be encountered in the presence of even small concentrations of oxygen[13]. But under strict anaerobic conditions, such as in sediments, they have occasionally been reported as the end products of sulphide oxidation by iron oxides[15,16]. Various other end products, such as pyrhotite, varying in composition from FeS to Fe_4S_5, ferric sulphide Fe_2S_3, smythite Fe_3S_4 and pyrite and marcasite, both having the formula FeS_2 have also been cited as the end products of iron-sulphide reactions[17].

However due to the elevated pH in the reactor, only a small amount of S^{2-} was in the form of hydrogen sulphide and thus the odour problem normally associated with biological sulphate reduction was not present[18,19]. Sulphate-reducing bacteria utilize sulphate as an electron acceptor in the oxidation of an energy substrate with the production of sulphide, which may react with heavy metals to precipitate them out as metal sulphides[20,21]. Biological sulphate reduction has been cited as a method for the treatment of sulphate and metal-rich waters originating from the mining industry as it has a number

of advantages over other processes. Bioremediation mineralizes sulphur in a natural environmental friendly way. The objective of this study was hydrogen sulphide removal from the contaminated air at low gas flow rate by a biological reactor.

EXPERIMENTAL

The experimental design used in the present study is given in Fig. 1. The gas flow, treated in the biofilter was obtained in the laboratory by mixing hydrogen sulphide with ambient air (1000 ppm hydrogen sulphide in air, BOS Com., Konya, Turkey). The hydrogen sulphide flow, which was controlled by a Flow Meter-Controller, was mixed with the air stream, which was saturated with water by bubbling the air through a humidification column filled with deionized water. Nutritive solution, which was at 250 mg L^{-3} starch solution for feeding micro-organisms, was used 12 mL d^{-1} in the biofilter. The volume of the bioreactor itself is 510 mL and the dimensions are 18 cm in length and 6 cm cylinder internal diameter. It is made of PVC and is divided into three pieces (1, 2 and 3), which are located 2 is biofilter and 1 and 3 are empty species before and after biofilter. Total volume of the unit is 710 L with two empty spaces, before and after stuffing closed with 0.01 diameter mesh filter. Room temperature was within 17-22 ºC range which led to a temperature in the biofilter in the 20 ºC. The continuous operating time of the biofilter was 24 h repetitions intervals. The velocities of the gas in the bio-filter were 25, 50 and 75 m s^{-1} and the retention time was 4 h. The hydrogen sulphide mass loading rate, defined as the amount of hydrogen sulphide introduced into the system/unit time and unit volume of the packing material ranged from 0.4 to 5900 mg hydrogen sulphide m^{-3} s^{-1}.

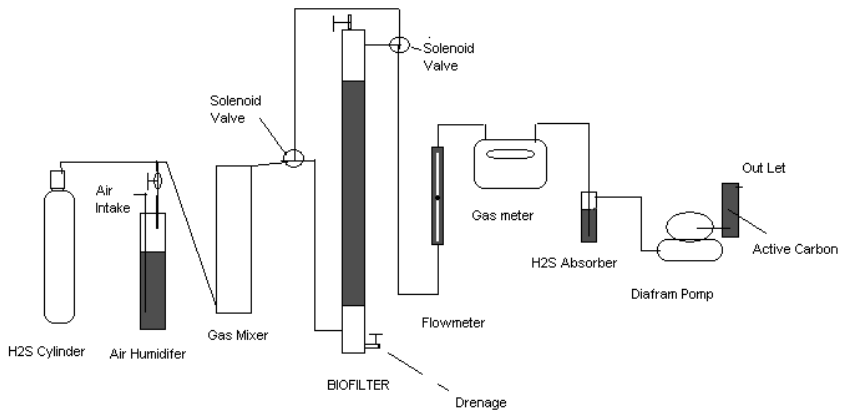

Fig. 1. Hydrogen sulphide biodegradation filter system used in present study

The packing materials used in the study were soil which was collected from top organic layer of the soil surface, saw dust of 10 year old 14 cm diameter beech wood and activated sludge from leather industry final precipitation pond. These materials, mixing 100 g of soil and 100 g of sawdust, with the addition of 20 mL activated sludge, were filled up in a 6 cm diameter PVC pipe and closed on both sides by a 0.01 mm pore size plastic filter to keep the filling materials stable. The filling content was wetted with distilled water to get moisture content of 80 % and drained.

Hydrogen sulphide was supplied from the hydrogen sulphide cylinder, 1000 ppm concentration that was mixed with humidified air to get the desired hydrogen sulphide concentration for each experimental run. Before each experimental run, the mixed gas bypassed the biofilter unit *via* a solenoid valve passed through direct to the gas absorber to measure gas concentration; then the fixed gas was passed to the biofilter. After adaptation of microorganisms in the filter unit, hydrogen sulphide gas passed through the filter unit for 8 d with concentration ranging from minimum to maximum. Daily, a 12 mL starch solution was added in the biofilter from the top of unit and drainage water was collected from the bottom tap. The content of sulphate in the drainage water and sulphide in the absorber was measured by the Cuvette test method[22].

RESULTS AND DISCUSSION

Continuous operation of the hydrogen sulphide biodegradation was carried out at 24 h repetition intervals. The hydrogen sulphide loading rate was increased in three steps for 24 h experimental periods. During this experimental period, the operation was carried out with gas flow rates of 25, 50 and 75 m s^{-1} and a retention time down to 4 s^{-1}. Removal efficiency rates of up to 100 % were reached with low concentrations of hydrogen sulphide and higher retention times periods (Fig. 2). It was decreased to *ca.* 80 % with increasing concentrations of hydrogen sulphide up to100 mg m^{-3}. For each experimental run, three different velocities of hydrogen sulphide were used with 5 different concentrations, in order 10, 20, 40, 80 and 100 mg m^{-3} (Figs. 3 and 4).

Microorganisms are able to degrade the contaminant up to concentrations of 45 g m^{-3} h^{-1}, which is within the rate of many industrial emissions[23]. In order to test the performance of the biofilter under more severe conditions, the superficial gas velocity was increased from 100 to 200 m h^{-1} between 1000 and 1250 h of operation, which decreased the residence time from 27 to 13.5 s[24]. In present study, increasing concentration and gas flow rate gives high hydrogen sulphide mass loading into the biofilter, so that removal efficiency was decreased down to about 50 % (Fig. 4). Analysis of drainage water showed that hydrogen sulphide was oxidized to sulphate and pH of the solution was over 7.5.

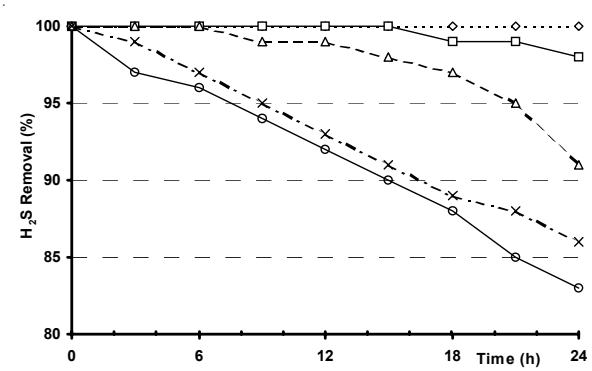

Fig. 2. Removal efficiency of biofilter unit at 25 m s^{-1} gas velocity throughout the 24 h of continuous operation with 5 different concentrations of hydrogen sulphide (H_2S); ◇ 10, □ 20, △ 40, × 80 and ○ 100 mg m^{-3}

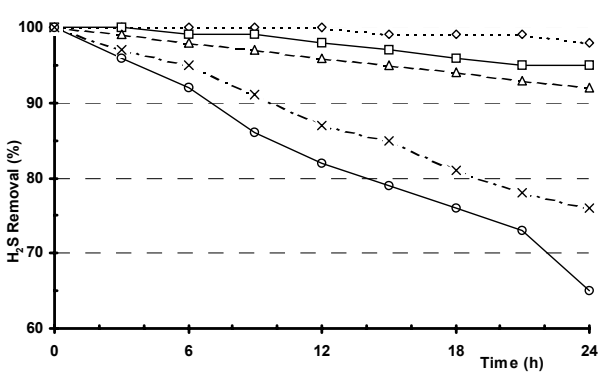

Fig. 3. Removal efficiency of biofilter unit at 50 m s^{-1} gas velocity throughout the 24 h of continuous operation with 5 different concentrations of hydrogen sulphide (H_2S); ◇ 10, □ 20, △ 40, × 80 and ○ 100 mg m^{-3}

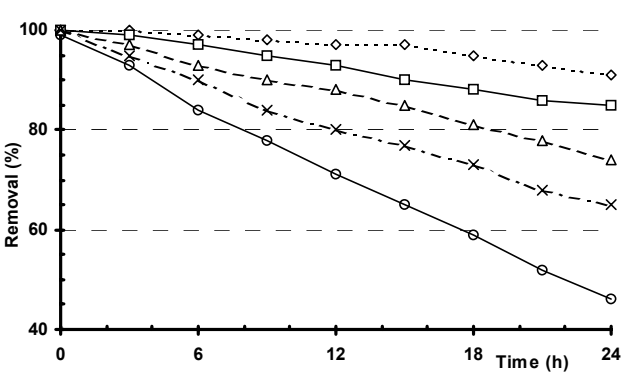

Fig. 4. Removal efficiency of biofilter unit at 75 m s^{-1} gas velocity throughout the 24 h of continuous operation with 5 different concentrations of hydrogen sulphide (H_2S); ◇ 10, □ 20, △ 40, × 80 and ○ 100 mg m^{-3}

Previous investigation showed that microorganism populations develop most rapidly near the inlet of the reactor, as this is the region where the majority of the contaminant degradation occurs[25,26]. The hydrogen sulphide loading mass was increased in the following experimental runs. High removal efficiencies were found of different loadings at the beginning of the operation, but started to decrease when the removal capacity of the microorganisms was not enough to remove the high loaded hydrogen sulphide.

Conclusion

A packing material based on organic soil, sawdust and leather industry activated sludge, used as a biofilter, has proven to effectively decompose the hydrogen sulphide in gas streams, with a concentration loading rate of 10 to 100 mg m^{-3}. The superficial gas velocity has been a determining parameter in the operation of the biofilter, as an increase from 25 to 75 m s^{-1} led to a decrease in the removal efficiency to below 50 %. The removal efficiencies of the whole biofilter were mainly due to the degradation activity of the low flow rate and high retention time. The main by-product obtained in the biodegradation process was sulphate, as it accounted for more than 74 % of the total sulphur amount accumulated in the packing material. Other by-products were thiosulphates and tertationate, which accounted for 26 % of the remaining total sulphur content. Produced sulphate, easily removed by drainage water through the outlet, was removed form the bed for operation periods of 24 h and the bioreactor was not reduced sulphate elemental sulphur or hydrogen sulphide.

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