Biological Removal of Carbon Disulfide from Waste Air Streams

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A pilot-scale biological control system for the treatment of 3400 m$^3$ h$^{-1}$ of a gaseous stream containing up to 7.8 g CS$_2$ m$^{-3}$ and trace amounts of hydrogen sulfide (H$_2$S) was installed in a cellulose sponge manufacturing facility. The objective was to demonstrate the capability of the process to attain sustained removal efficiencies of 90% for CS$_2$ and 99% for H$_2$S. The system consisted of two sequential biotrickling reactors, which had been previously inoculated with an adapted microbial consortium. During the pilot test, stable removal efficiency and elimination capacity of +90% and 220 g CS$_2$ m$^{-3}$ h$^{-1}$, respectively, were attained with an empty bed residence time (EBRT) of 33 seconds for a period of several weeks. Efficiencies greater than 99% were always obtained for H$_2$S. Based on the results, the system was determined to be an effective process to remediate waste air streams containing reduced sulfur compounds generated at cellulose sponge facilities.

INTRODUCTION

In the United States, Carbon disulfide is classified as a hazardous air pollutant under Title III of the Clean Air Act Amendment of 1990 (CAAA), triggering an increased interest in finding reliable, cost effective technologies for its control. Carbon disulfide is emitted both by natural and industrial sources [16]. In the traditional process for the production of cellophane, rayon and cellulose sponges, high amounts of exhaust air contaminated with both hydrogen sulfide, (H$_2$S), and carbon disulfide, (CS$_2$), are generated when the dissolved sodium cellulose xanthogenate (Viscose) is precipitated in an acid bath. CS$_2$ concentrations on these gases may reach up to 4.7 g m$^{-3}$ in air. While there are many alternatives to remove H$_2$S from gases [4], fewer have proved to be adequate for CS$_2$ emissions control. The processes currently available are based on absorption, adsorption and thermal or catalytic oxidation [5].

Biotechnological processes, such as biofilters and biotrickling filters, represent an interesting alternative to the traditional methods due to their wide range of application, high removal efficiency and reduced operating costs [18]. Several microbial processes have been described in the literature for the removal of H$_2$S [7]. These include the use of very different species including photosynthetic, chemotrophic and heterotrophic bacteria and even molds. Also, mixed chemical-biological systems have been proposed utilizing ferric ions as chemical reactant [13]. Some of these processes have reached industrial scale. The microbiological degradation of CS$_2$ is not as ubiquitous and has been less investigated. Smith and Kelly [16], reported that only one strain of Thiobacillus thioparus, from eight different Thiobacilli studied, was able to use CS$_2$. The reaction proceeds through the formation of H$_2$S and Carbonyl sulfide (COS) which is further transformed in H$_2$S and CO$_2$. The H$_2$S produced is then oxidized to elemental sulfur and subsequently to sulfonic acid. Sulfur accumulation in the reactors is highly dependent on dissolved oxygen availability (Janssen et al., [6]). An unidentified Thiobacillus sp, was reported by Plas et al., [14], that also utilizes CS$_2$: small consumption rates based on respirometry were observed. More recently four bacterial strains from the CS$_2$ producing tree Quercus lobata, three of them Thiobacillus have been isolated which could use CS$_2$ and a wide range of other reduced sulfur compounds as their sole energy source [8]. Some of these strains have been recently reclassified part size Paracoccus [9].

A limited number of publications describe the biological degradation of CS$_2$ in biofilters. A pilot plant installed to treat a sulfur-laden waste gas from an organic synthesis process reported 99% of odor removal for H$_2$S and 90% for CS$_2$ [3]. Berzacy et al., [2], reported a microbial process for the treatment of an exhaust gas from a rayon manufacturing plant attaining elimination capacities of 70 g H$_2$S m$^{-3}$ h$^{-1}$ and 70 g CS$_2$ m$^{-3}$ h$^{-1}$ using a fixed bed reactor. Carbon disulfide and H$_2$S removal has also been reported with a conventional biofilter configuration [19].

A modified biotrickling filter was proposed to treat air polluted with a mixture of CS$_2$ and H$_2$S from regenerated
cellulose processes by Morales et al. [12] and Torres et al. [17]. In this system, an enriched autotrophic consortium immobilized on an inert support performs oxidation of the sulfides. Continuous medium addition and recirculation through the bed allows for sulfur and sulfate removal and pH control. Analyses of the capacity of this system have recently been proposed by Lobo et al. [10]. Elimination capacities of 300 g H\textsubscript{2}S m\textsuperscript{-3} h\textsuperscript{-1} and 180 g CS\textsubscript{2} m\textsuperscript{-3} h\textsuperscript{-1} have been reached while treating gaseous emissions at Rayon, Cellophane and Sponge plants using single tower systems with capacities of up to 51,000 m\textsuperscript{3} h\textsuperscript{-1} [11, 15]. The current work discloses the results obtained on treatment process simulations using actual sponge plant operation). The air stream is then forced through the packing by means of a fan, and it is purified as the sulfur compounds transfer to the liquid phase to be finally oxidized within the biofilm producing elemental sulfur and sulfates. The pH is measured and controlled on line using a gel electrode and control loop (ABB-Kent Taylor, Stonehouse, UK). An alkaline solution (5-25% w/w NaOH) was provided as needed to control the pH with a metering pump. Process parameters such as flows (waste gas and re-circulating liquids), pressure drop across the packing beds and temperature were monitored and registered in real time by means of a programmable logic controller (Allen-Bradley Corp.; Milwaukee, USA). Table 2 shows relevant operating condition ranges used during test period. Inoculation of the reactors was accomplished using a consortium already adapted to H\textsubscript{2}S and CS\textsubscript{2} extracted from a pilot plant previously described [12].

Empty Bed Residence Time, EBRT, in [h] is defined as volume packed bed/gas flow rate. Load and Elimination Capacity, (EC), are expressed as g CS\textsubscript{2} m\textsuperscript{-3} h\textsuperscript{-1} and are defined as (CS\textsubscript{2} inlet/EBRT) and [(CS\textsubscript{2} inlet - CS\textsubscript{2} outlet)/EBRT] respectively. Efficiency, in %, is ((CS\textsubscript{2} inlet-CS\textsubscript{2} outlet)/ CS\textsubscript{2} inlet).

**Analytical Methods**

Infrared mass spectrometry (IRM S). Routine analysis for CS\textsubscript{2} concentration in the incoming (inlet) and treated (outlet) air stream was performed by IRMS using an online continuous analyzer (Servomex Group Ltd; Nor-

**Table 1. Equipment Components of BIOCYD-SR Unit**

<table>
<thead>
<tr>
<th># of Units</th>
<th>Equipment Name and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>BIOREACTOR. 1.98 m diameter; 6.1 m long packed bed. Mist demister. Nozzle type PVC liquid distributor:</td>
</tr>
<tr>
<td>1</td>
<td>FAN. 3400 m\textsuperscript{3} h\textsuperscript{-1}</td>
</tr>
<tr>
<td>2</td>
<td>LIQUID PUMP. 29.5 m\textsuperscript{3} h\textsuperscript{-1}</td>
</tr>
<tr>
<td>1</td>
<td>CLARIFIER. 4 M\textsuperscript{3} capacity.</td>
</tr>
<tr>
<td>1</td>
<td>CAUSTIC STORAGE TANK. 0.57 m\textsuperscript{3} nominal size</td>
</tr>
<tr>
<td>1</td>
<td>CAUSTIC PREPARATION TANK. 0.57 m\textsuperscript{3} nominal size</td>
</tr>
<tr>
<td>1</td>
<td>NUTRIENT SOLUTION TANK. 0.57 m\textsuperscript{3} nominal size</td>
</tr>
<tr>
<td>2</td>
<td>CAUSTIC MELTERING PUMP. 49 lph, electronic driven</td>
</tr>
<tr>
<td>1</td>
<td>NUTRIENT SOLUTION METERING PUMP. 42 lph, electronic driven</td>
</tr>
<tr>
<td>1</td>
<td>SUMP TANK. 3.8 m\textsuperscript{3} capacity.</td>
</tr>
</tbody>
</table>

**Table 2. Operating Condition Ranges of BIOCYD-SR Unit**

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>Units</th>
<th>Operating Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load Rates</td>
<td>g CS\textsubscript{2} m\textsuperscript{-3} h\textsuperscript{-1}</td>
<td>95 - 275</td>
</tr>
<tr>
<td>CS\textsubscript{2} concentration</td>
<td>g CS\textsubscript{2} m\textsuperscript{-3}</td>
<td>1.7 - 24</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>m\textsuperscript{3} h\textsuperscript{-1}</td>
<td>3400 - 4080</td>
</tr>
<tr>
<td>EBRT</td>
<td>Seconds</td>
<td>33 - 40</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>°C</td>
<td>20 - 40</td>
</tr>
<tr>
<td>Liquid re-circulation rate</td>
<td>m\textsuperscript{3} h\textsuperscript{-1}</td>
<td>12.5 - 20.5</td>
</tr>
<tr>
<td>Liquid pH</td>
<td>PH units</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Liquid temperature</td>
<td>°C</td>
<td>10 - 27</td>
</tr>
<tr>
<td>Sulfate concentration</td>
<td>g SO\textsubscript{4} 1\textsuperscript{-1}</td>
<td>20 - 40</td>
</tr>
</tbody>
</table>
wood, USA); the readings were hand-recorded in an analytical data log form.

Gas chromatography (GC). In order to determine the presence of intermediate sulfur species (specifically COS and H$_2$S) and validate IRMS data, process performance was followed by GC analysis during a one month period. The equipment utilized is a QUAD 400 portable GC analyzer (MTI Analytical Instruments Inc., USA) equipped with an OV-1 column (CS$_2$ detection), a PoraPlotU column (for COS and H$_2$S) and a thermocconductivity detector. The analyzer was operated by means of a portable computer and EZ-Chrom 200 software (Microsensor Technology Inc., USA). The analyzer was calibrated on a daily basis using appropriate CS$_2$/N$_2$ standards. For each analysis, four consecutive runs were performed reporting the arithmetic average of the last three.

RESULTS AND DISCUSSION

The inlet conditions for the system during the complete pilot test period are shown on Figure 2. From start up the flow rates were periodically increased up to 4,080 m$^3$ h$^{-1}$ as the efficiency of the system improved. Average CS$_2$ concentration in the gas fell between 1.7 and 2.5 g CS$_2$ m$^{-3}$.

The evolution of efficiency, load and EC of the BIOCYD-SR is depicted in Figure 3. A week after inoculation, the first IRMS analysis reported 30% efficiency in CS$_2$ removal. As shown, process stabilization took several months as a consequence of difficulties with control loop’s tune up and discontinuities in the waste gas supply to the system. These operational problems were eventually solved and during late August, the bioreactor reached performance stability and CS$_2$ removal efficiencies higher than 95%, with a monthly average above 90%. The highest efficiency values obtained with IRMS and GC analysis were 97.6% and 99.6%, respectively; discrepancies among the techniques might be attributable to interference by CO$_2$ in the IR measurement. High removal efficiencies (>90%) remained even at EBRT of 33 seconds (4080 m$^3$ h$^{-1}$) as shown in Figure 3. The CS$_2$ concentration at the outlet from the second tower attained values lower than 0.06 g CS$_2$ m$^{-3}$, as measured by IRMS, and 0.006 and 0.016 g CS$_2$ m$^{-3}$ by GC for a fairly wide range of loads (150 - 275 g CS$_2$ m$^{-3}$ h$^{-1}$) during the stable performance period (Sept.-Oct). The system was operated under these conditions for five weeks.

Following this period, the source of waste gas fed to the reactors was switched from point 2 to point 1; this stream exhibited highly fluctuating CS$_2$ concentrations as shown in Figure 4. Results from this adjustment, as seen in Figure 5, show that the new waste air characteristics had an immediate deleterious impact on performance, probably due to wider, localized pH variations caused by the transformation into sulfuric acid of the unsteady loads of CS$_2$. Some corrections on the operation parameters such as reducing the pH set point and increasing the liquid flow to the first tower were performed in order to re-stabilize the process. After a few days, the system performance showed some improvement reaching removal efficiency and an EC of 78% and 190 g CS$_2$ m$^{-3}$ h$^{-1}$, respectively, before the pilot tests were terminated.

During the pilot test there were several episodes of discontinuous CS$_2$ supply to the biological unit caused by shutdowns on the activated carbon adsorber which fed the system. When these waste gas supply shortages
lasted a day or less, they had a modest deleterious effect on the process performance (reductions < 10% efficiency), and previous removal efficiencies were recovered within several hours (data not shown). From measurements performed with gas chromatography, H₂S and COS, which are believed to be intermediates of CS₂ biodegradation [16] were not detected at the gas outlet.

Fresh nutrient medium was continuously added in order to sustain growth. The ammonia concentration in the system was reduced as microbial biomass built up in the system from substrate uptake as depicted in Figure 6. Sulfate levels were controlled by purging a fraction of the recirculating liquid at a sulfate concentration of 40 g/l, which has shown to be a practical limit to reduce end product inhibition [15]. An average caustic consumption of 1.4 kgs NaOH/kg CS₂ removed was obtained during the pilot tests; such rate does not take into account full neutralization of the recirculating liquid since it was purged from the system at the pH of operation and subsequently neutralized in an external sump tank. No analysis were performed to quantify the formation of intermediate sulfur species in the liquid such as elemental sulfur or polythionates.

Figure 7 shows the load/elimination capacities relation for start up and steady state operation. Start up phase characterized by a condition where no complete elimination was reached even at low load rates (120-150 g CS₂ m⁻³ h⁻¹); a possible explanation for such behavior is an incomplete biological film coverage of the packed bed’s surfaces which provokes a by-pass effect. On steady state operation, the maximum inlet concentration of CS₂ reached 2.5 g CS₂ m⁻³ corresponding to an equilibrium concentration of CS₂ at the biofilm surface of 3.5 mg CS₂ l⁻¹. Previous respirometric studies performed with biomass extracted from a similar system reported a Monod saturation constant (Ks) of 9 mg CS₂ l⁻¹ [15]. These observations suggest that saturation of the biological capacity of the system was never reached, which in turn justify the observed global first order kinetics obtained throughout the test. The possibility of mass transfer control due to the unfavorable equilibrium conditions (ie. low concentration and solubility) has been proposed recently by Lobo et al. [10].

The elimination capacities in both reactors were dependent on the inlet concentration as shown on Figure 8. The first reactor exhibited a higher elimination capacity (> 416 g CS₂ m⁻³ h⁻¹) than the second reactor as a consequence of receiving the highest load. Average efficiencies during the month of September were 71.4% and 72.4% for reactor 1 and 2, respectively. The configuration of the system allowed for an independent control of each packed-tower which was set according to their respective elimination capacities; Tower 1 required a stricter pH control and larger recirculating liquid flow than tower 2. One of the possible disadvantages associated with countercurrent operation is the stripping of the dissolved pollutant from the liquid at the top of the packed towers [10]; this issue was resolved by pumping the recirculating liquids of both packed-towers to a clarifying tank, thus allowing sufficient residence time for the residual CS₂ to be biodegraded by the suspended microorganisms and favoring absorption on the top of both reactors.

**CONCLUSION**

The pilot tests demonstrated that biological filtration, using the embodiment of a multiple trickling filter, is an effective technology to treat waste-air streams generated at cellulose sponge manufacturing facilities containing high concentrations of CS₂. During the pilot test demonstration project, stable efficiencies and EC of 90% and 220 g CS₂ m⁻³ h⁻¹, respectively were attained by independent control of operational parameters under the high and low loads which are found in each reactor. Furthermore, an additional test proved that for streams

![Figure 6](image-url)  
**FIGURE 6.** Variation of ammonium ion with the elimination capacity.

![Figure 7](image-url)  
**FIGURE 7.** Elimination capacity as a function of the load rate for the start up and the steady state periods.

![Figure 8](image-url)  
**FIGURE 8.** Elimination capacity for reactors 1 and 2 as a function of inlet CS₂ concentration.
showing wide fluctuations in CS₂ concentration, a removal efficiency of at least 75% could be reached for the given residence time tested.

Also, the pilot tests served to confirm available data for scale-up, gave opportunity to optimize operating conditions and to calculate chemical and utility consumption factors. The procurement of this information was also an objective agreed upon for the project since it was necessary to properly design a full scale system and to prepare an economical appraisal of the technology.

LITERATURE CITED
17. Torres, M; Revah, S; Hinojosa, A; Páez, F; Morales, V. (1993), Biological Process for the Elimination of Sulphur Compounds Present in Gas Mixtures, United States Patent No.5236677