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GENERATING A STREAM WITH A STABLE FORMALDEHYDE CONCENTRATION IN THE LABORATORY

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A laboratory-scale bio-trickling filter (BTF) was initialized to evaluate the removal of formaldehyde biologically. However, generating formaldehyde gas in the lab is one of the grand challenges hindering research efforts. Formaldehyde was introduced into the gaseous phase by aerating the required air flowrate through a diluted formaldehyde solution mixed with methanol as a stabilizer by a bubbler. However, achieving stable gaseous influent concentrations of formaldehyde was challenging since it polymerizes while volatilizing. Resulting in paraformaldehyde. The resulting white powder clogged the pipes and generated uneven gaseous concentrations. To solve this problem, sodium hydroxide (NaOH) was added with a phosphate buffer to the aqueous formaldehyde solution to maintain the pH between 7.00-7.20. Additionally, the aqueous solution needed to be heated at 60 °C to eliminate the polymerization. The exhausted formaldehyde by volatilization was replaced by a continuous supply of aqueous diluted formaldehyde solution to keep the volume and mass of the aqueous solution and formaldehyde constant, respectively. Stable gaseous concentration was achieved for extended periods of time and verified by Fourier transform infrared (FTIR) spectroscopy.

Keywords: Biofiltration, Precipitation, Ethanol, Carcinogen.

1 INTRODUCTION

Formaldehyde is an organic compound that is emitted from several industrial processes (Prado *et al*. 2004). Ethanol manufacturing is an industrial process that emits formaldehyde into the atmosphere. Formaldehyde is emitted from both fermenters and the dryers at ethanol plants, where the waste gases from the fermenters are usual at temperatures lower than 35 °C and waste gases from the dryers are at elevated temperatures in the range of 40 to 55 °C (Chen *et al*. 2010). The US Environmental Protection Agency (USEPA) lists 187 pollutants as Hazardous Air Pollutants (HAPs) and formaldehyde is included in that list (USEPA 2020). Formaldehyde could cause adverse health effects and is considered a carcinogen under the International Agency for Research on Cancer (IARC) (IARC 2011). To control the HAPs the U.S EPA have identified the best available control technologies (BACT) (USEPA 2016). The traditional technologies used to control emissions from ethanol plants are regenerative thermal oxidizers (RTOs) and CO_2 scrubbers (USEPA 2019). However, these technologies require huge energy input and can be costly to operate. BTFs are an attractive solution that could replace the BACT used at ethanol plants (Duerschner 2019). BTFs are packed beds where the packing is a biologically active material or an inert material used for biofilm to attach on (Crocker and Schnelle 1998, Gabriel

and Deshusses 2003, Delhoménie and Heitz 2008, Duerschner 2019). As the contaminants move along the BTF, the contaminants get absorbed in the aqueous layer and then it gets biodegraded in the biofilm layer. To ensure microbial growth, a trickling liquid with nutrients and minerals is used along the bed (Gabriel and Deshusses 2003). Several studies have evaluated the biodegradation of formaldehyde and used formalin as a source of influent formaldehyde (Teh and Mahmood 2013, Maldonado-Dias and Arriaga 2015, Rezaei *et al*. 2015), but none of the studies have reported the polymerization of formaldehyde into paraformaldehyde in the gaseous state. For this study, the polymerization of formaldehyde was investigated. Methods for successfully depolymerizing formaldehyde and controlling the influent formaldehyde concentration introduced to the BTF were developed. Two in parallel BTFs were operated at 20 °C called and the other at 60 °C. The influent formaldehyde concentration was increased in a stepwise manner and it was measured during all days of operation.

2 MATERIALS AND METHODS

2.1 Bio-trickling Filter (BTF)

Two BTFs were operated in parallel. In each BTF media consisting of (0.3" - 0.5") pellets of diatomaceous earth (Celite 6mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA), was housed in a three-inch internal diameter glass column. The media has a mean pore diameter of 20 µm, BET surface area of 0.27 m^2/g, and a bed density of 513 kg/m^3. It consists mainly of SiO_2 with a significant fraction of Al_2O_3. One BTF was operated at room temperature of 20°C called the mesophilic BTF. The other BTF was operated at 60°C called the thermophilic BTF. The heated BTF is heated by using a heating tape and controlled via BriskHeat X2-120JTP Single Zone PID Temperature controller. The beds were seeded with microorganisms. The mesophilic BTF bed was submerged overnight in return for activated sludge obtained from the local wastewater treatment plant, while the thermophilic bed was submerged overnight with cooking compost slurry. The compost was taken from yard waste from the center of a windrow, and then it was mixed with water to create the slurry. Two g/L of glucose was added to both BTFs overnight. Afterward, both BTFs were used for the degradation of acetaldehyde (Duerschner 2019). The columns extend for 3 inches (7.6 cm) above the top of the packing material, where the formaldehyde-laden air was introduced at the top to allow uniform mixing. Each BTF is equipped with sampling ports located at packed depths of 4.5 (11.4 cm), 13.5 (34.3 cm), 22.5 (57.2 cm), 31.5 (80.0 cm), and 36 inches (91.4 cm). For the thermophilic BTF, a thermocouple was inserted at bed depth of 22.5 inches (57.2 cm) to better control the temperature; therefore, no samples were taken at that depth. All connections are airtight. Air from any sampling port can be directed for analysis to either a Nicolet IS20 FTIR spectrometer equipped with a gas cell or a 490 µ-GC equipped with a thermal conductivity detector and a two-channel module.

2.2 Gas Delivery System

Figure 1 demonstrates the apparatus used to test the formaldehyde-laden air concentration. House air is filtered through a Parker Filtration 2000 series compressed air and Balston sterile air filter followed by a Parker compressed air gas water separator. The air is filtered to avoid any impurities that affect the volatilization of formaldehyde. Following filtration, the air stream is split, and flowrate is regulated to 8 L/min (empty bed resident time (EBRT)= 32 seconds) by two Aalborg mass flow controllers (Orangeburg, New York). Liquid formalin (37% formaldehyde and 10-15% of methanol by weight) is infused into the air stream through a septum housed in a stainless-steel tee union. A Harvard Apparatus Pump 11 Elite syringe pump (Holliston, MA) and

luer lock tip syringes were used to regulate the infusion. Sodium hydroxide (NaOH) and a phosphate buffer were added to the formalin solution contained in the syringes to pH between 7.2-7.4 and it was heated at 60 °C to minimize polymerization of formalin.

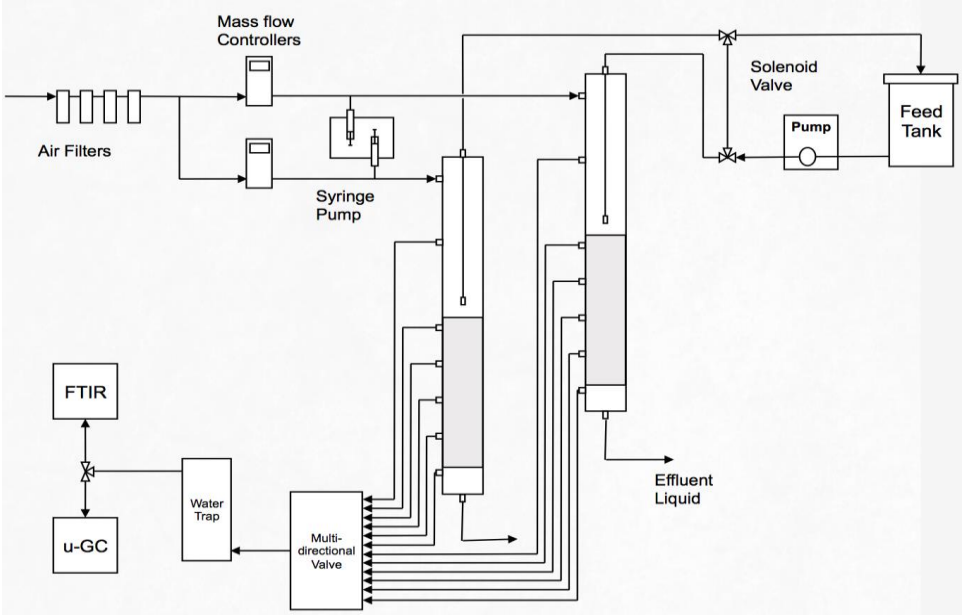


Figure 1. Experimental apparatus of formaldehyde experiment.

2.3 Nutrient Delivery System

Nutrient/buffer solution is delivered to the BTF beds intermittently by a pump and timer-controlled solenoid valves. The nutrient solution, which is used for a once-through flow and was not recycled, consists of essential inorganic salts and vitamins necessary to grow microorganisms. A fresh five-gallon batch of nutrient solution is prepared every five days. A pressure valve and a misting nozzle control the pipe delivering solution to the BTF. The valve is opened for 5 seconds on a 5-minute cycle controlled by the timer, to ensure to have an effluent liquid volume of about 1.5-2.0 L. The composition of the nutrient solution is similar to the one reported by Sorial *et al.* (1997).

2.4 Sampling Setup

To detect the formaldehyde gas concentrations, a Nicolet IS20 FTIR spectrometer (Thermo Fischer, MA) was used. The FTIR was equipped with a 2-meter gas cell. The gas cell volume is 200 mL and was kept at a temperature of 161°C to avoid condensation in the walls. Nitrogen gas was used to keep the instrument at constant purge to eliminate any condensation in the instrument or in the gas cell. The resolution of 0.5 cm^{-1} was chosen to provide a high measurement resolution. A 64 scans procedure was chosen to ensure high sensitivity and eliminate noise associated with sample spectrum since peaks tend to be hard to analyze and quantify at lower scan numbers. The sample was allowed about 10 minutes to fill the 200 mL gas cell flowing at 1 L/min. Then the inlet and outlet valves of the gas cell were closed for 5 minutes to stabilize sample temperature. The wavelength range used for the detection of the formaldehyde spectrum was determined to be between 2657.0 and 2784.0 cm^{-1}.

3 RESULTS AND DISCUSSION

3.1 Depolymerization of Formaldehyde

Formalin was used to create the formaldehyde vapors. The solution contains 37% and 10-15% by volume of formaldehyde and methanol, respectively. It was challenging to create the formaldehyde vapors at a higher concentration due to the polymerization phenomena. Longer chain paraformaldehyde of up to 100monomer units is insoluble and exists as a white waxy powder (Kiernan 2000). The polymerization inhibits the infusion of stable influent formaldehyde concentrations to the BTF. As a result, the polymerization needed to be successfully reduced.

Previous studies have used the formalin solution to create formaldehyde vapors (Prado *et al*. 2004, Chen *et al*. 2010, Teh and Mahmood 2013, Rezaei *et al*. 2015, Talaiekhozani *et al*. 2016). None of these studies reported the occurrence of any polymerization. To eliminate the polymerization of formaldehyde, a study by (Kiernan 2000) indicated that adding a hydroxide source (such as NaOH) with buffering the paraformaldehyde to a pH between 7.00-7.40 and heating the solution to 60°C can help reduce the polymerization (Kiernan 2000). This procedure was implemented herein. A solution of 1 M NaOH was used as the hydroxide source. Phosphate buffer was used to help maintain the pH levels in the formalin solution between 7.00-7.40. The solution was heated prior to usage in a water bath at 60°C.

3.2 Detection of Formaldehyde

For proof of the depolymerization of formaldehyde, first formaldehyde concentrations in the BTF were analyzed by an external laboratory. The samples were detected by Atmospheric Analysis and Consulting (AAC) Laboratories. The AAC labs have provided cartridges for the adsorption of the formaldehyde gas in the BTF. Samples were obtained from ports 1, 3, and 6 from the mesophilic BTF. The BTF was operated at an influent formaldehyde concentration of 20 ppm_v. Figure 2 illustrates the relation of the formaldehyde concentration with the EBRT of the BTF. The influent formaldehyde concentration detected by the AAC labs was 21.9 ppm_v. The difference between the target influent formaldehyde concentration of 20 ppm_v and the calculated one of 21.9 ppm_v was around 7.0%. This indicated the successful depolymerization of formaldehyde and the ability to introduce the formaldehyde vapors to the BTF successfully. Figure 2 illustrates the concentration of formaldehyde in relation to EBRT that was detected in the AAC laboratories.

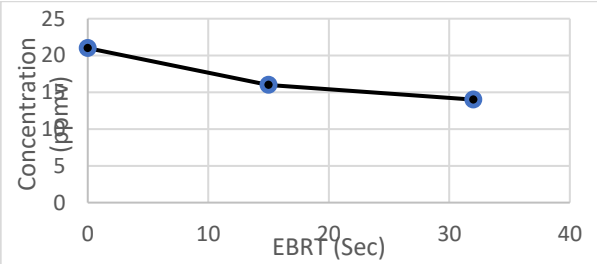
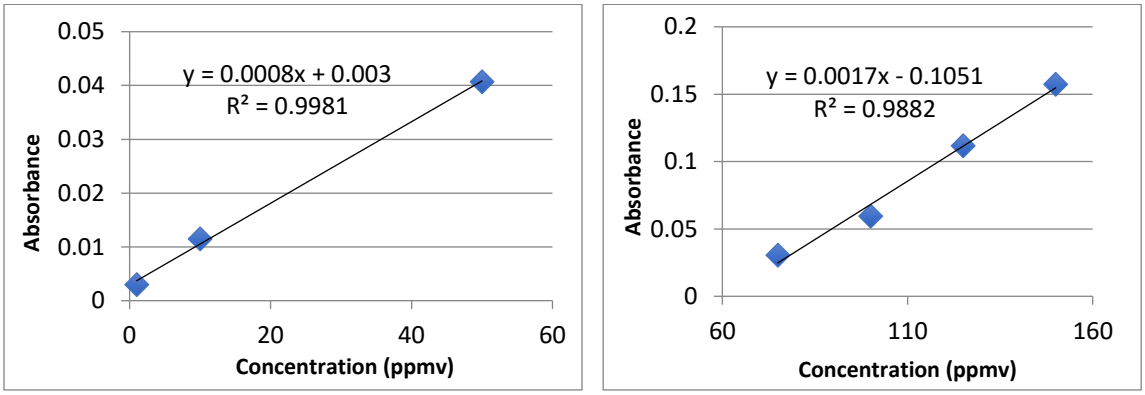


Figure 2. Formaldehyde concentration versus EBRT.

Two calibration curves were established for formaldehyde using the FTIR. The first calibration curve shown in Figure 3a illustrates the calibration curve between 1 ppm_v-50 ppm_v with R-squared value equals 0.9981. The second calibration shown in Figure 3b shows the calibration curve for formaldehyde concentrations between 75-150 ppm_v with R-squared value

equal 0.9982. A strong correlation between the concentration of formaldehyde and the absorbance response measured from the FTIR was observed in both curves. However, at higher concentrations (>150 ppm_v) the calibration data did not exhibit similar trends. This is due to the conversion of formaldehyde to paraformaldehyde (creating a white powder) that creates uneven formaldehyde gaseous concentrations.



a) 1-50 ppm_v b) 75-150 ppm_v

Figure 3. Formaldehyde calibration curve between a) 1-50 ppm_v and b) 75-150 ppm_v.

Each BTF was then operated at a constant formaldehyde influent concentration that was increased in a stepwise manner. A total of three phases were investigated corresponding to influent concentrations of 20, 50, and 100 ppm_v. Table 1 lists the duration of operation target influent concentration, and the measured influent concentration for both BTFs. Variability of the influent concentration was observed due to partial polymerization of formaldehyde to form paraformaldehyde, especially at higher concentrations. The actual measured concentrations for the mesophilic BTF were 14.0±6.1, 34.5±20.2, and 92.5±5.6 ppm_v at Phases I, II, and III, respectively. Similarly, for the thermophilic BTF, the actual measured concentrations in ppm_v were 16.0±9.1, 36.6±21.1, and 100.2±8.9 at Phases I, II, and III, respectively. The measured concentrations are an average of three samples taken each day of the operating days.

Table 1. Different phases of operation including duration, target influent concentration, and target influent concentration for both mesophilic and thermophilic BTFs. Error ranges represent one standard deviation.

Phase	Operating days	Target influent conc. (ppm_v)	Average influent conc. (ppm_v)
Mesophilic BTF			
I	16	20	14.0±6.1
II	18	50	34.5±20.2
III	12	100	92.5±5.6
Thermophilic BTF			
I	16	20	16.0±9.1
II	18	50	36.6±21.1
III	12	100	100.2±8.9

4 CONCLUSION

Formaldehyde was found to polymerize and turn into paraformaldehyde. The precipitation clogs the pipes in the BTFs and makes it difficult to control the influent formaldehyde concentrations. A technique for the depolymerization of formaldehyde was successfully implemented by adding

NaOH to the formalin solution to pH levels between 7.00-7.40 with heating the solution to 60°C. Two successful calibration curves were established for formaldehyde. One calibration curve was for formaldehyde concentrations between 1-50 ppm_v and the second was at concentrations between 75-150 ppm_v. Depolymerization still occurred at higher formaldehyde concentrations.

Acknowledgments

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NOMENCLATURE

Al_2O_3 – Aluminum Oxide; ppm_v – parts per million by volume; SiO_2 – Silicon Dioxide

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