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Biotreatment of formaldehyde-contaminated air in a trickle bed bioreactor

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ABSTRACT

A biofilm developed on polyurethane packing in a trickle bed bioreactor was used to effectively remove formaldehyde from contaminated air. Formaldehyde removal depended on the retention time of the gas in the bed as well as on the gas-liquid mass transfer coefficient. Both retention time and the mass transfer coefficient depended on the gas flow rate. At 25±1°C and pH 7, a 99% removal of formaldehyde from air with an initial contamination level of 450 mg L^{-1} was achieved at a hydraulic retention time of 132 s. The degradation rate was likely limited by oxygen mass transfer. The bioreactor could be operated stably over the pH range of 5 to 7 at 25±1°C. Formaldehyde removal in the bioreactor was mathematically modeled to facilitate design and scale up. The model was shown to agree well with the experimental data. Trickle bed bioreactors offer a potentially viable option for cleaning air streams contaminated with formaldehyde.

Keywords: Biofilter; Formaldehyde; Biodegradation; Biofilms; Trickle bed bioreactor

1. Introduction

Environmental pollution is directly and indirectly associated with population growth and industry-related operations [1–5]. Many processes require cleaning of an otherwise innocuous gas contaminated with low levels of highly toxic volatile organic compounds [6–9]. Contaminants such as formaldehyde, volatile organic compounds (VOCs) and carbon dioxide (CO_2) can be removed and/or degraded in various ways including adsorption on solids, absorption into a liquid and oxidation in a catalytic bed [10–17]. One possible method of decontamination is to use a trickling bed bioreactor, or a biofilter, to oxidize the pollutants [9,18,19].

A trickle bed is a highly porous bed made of an inert matrix. The matrix supports a biofilm formed by a consortium of microorganisms that are capable of degrading the organic pollutant contaminating the gas phase. The pollutant laden gas moves up the microbial bed through the interstitial spaces. The pollutant diffuses from the gas phase into the biofilm where it is degraded by microbial action. The cleaned carrier gas leaves the bed at the top. Degradation in a biofilter depends on the nature of the organic pollutant including

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its toxicity, concentration and recalcitrance. Microbial action requires water and various other inorganic nutrients. These are supplied to the biofilm by a nutrient solution that is intermittently sprayed on top of the bed. The solution trickles down the bed to irrigate the biofilm. The loading rate of the sprayed liquid is such that the bed is never flooded and allows free passage of the gas up the bed. Biodegradation in a trickle bed is typically an aerobic process with the necessary oxygen being provided by the air carrying the pollutant.

Formaldehyde (CH_2O) is a highly toxic volatile organic pollutant. Gases containing formaldehyde are generated in numerous industrial processes [20–23]. Formaldehyde is highly water soluble and, therefore, especially amenable to treatment in a biofilter. Formaldehyde is strongly antimicrobial [24]. Therefore, treatment is feasible only if the biofilm has been adapted [24] to withstand and degrade this pollutant and its concentration in the gas stream is kept at a sublethal level. Many microorganisms are able to degrade formaldehyde at low concentrations [25–28]. Gases containing formaldehyde mixed with other organics have been treated in trickle bed biofilters [24]. As formaldehyde does not contain any nitrogen, this essential nutrient must be provided [29] in the inorganic nutrient solution used for irrigating the bed. Models for degradation of various pollutants in trickle bed bioreactors have been published [10,29].

This work reports on elimination of formaldehyde from contaminated air in a trickle bed biofilm reactor using an adapted microbial consortium. The effects of pH and the hydraulic residence time of the gas phase in the bed, on formaldehyde degradation are reported. Formaldehyde removal is mathematically modeled for design and operation of trickle bed bioreactors.

2. Materials and methods

2.1. Experimental set-up

A schematic of the trickle bed biofilm reactor and peripheral equipment is shown in Fig. 1. The packed height of the cylindrical trickle bed column was 0.66 m and the diameter was 0.08 m. The nominal volume of the packed section was 3.32 L. Small pieces of a polyurethane pipe of 1 cm length and 0.5 cm diameter were used as supporting material. The calculated void fraction of the randomly packed bed was 90% [30].

Formaldehyde-contaminated air was produced by bubbling air through a pool of water containing 37% by weight formaldehyde. Some formaldehyde from the aqueous solution was transferred to the gas phase. The contaminated air so produced was injected into the bottom of the trickle bed column at a measured flow rate (Fig. 1).

A nutrient solution from a reservoir located at the base of the packed column was pumped to the top of the column and sprayed on the packed bed (Fig. 1). This solution trickled down the bed by gravity to drain back to the reservoir. This solution provided the microbial film with all the inorganic nutrients. The formaldehyde vapor in the contaminated air was the sole source of carbon. The composition of the aqueous nutrient medium was as follows (g L^{-1}): 0.1×10^{-3} $MgSO_4$, 0.5 KH_2PO_4, 0.01 $CaCl_2{\cdot}2H_2O$, 0.001 $FeSO_4$, 1 NH_4Cl, 1×10^{-6} $MnSO_4$, and 0.5 K_2HPO_4 [31]. This nutrient medium was sprayed on the bed intermittently at a flow rate of 50 L h^{-1}. The spray pump was operated for 15 min each hour to minimize formaldehyde removal in the nutrient medium and ensure its absorption into the

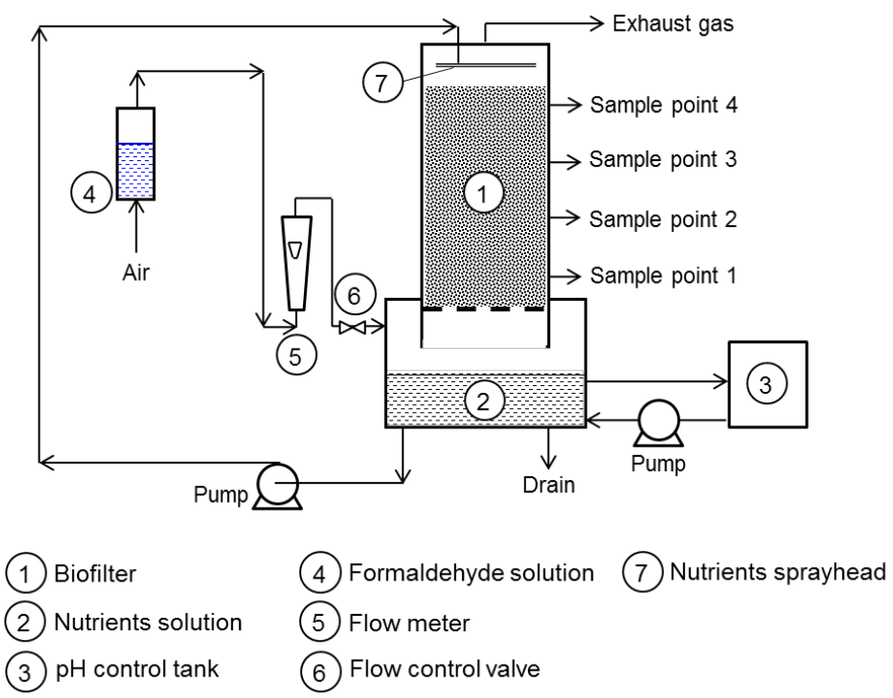

Fig. 1. Schematic of the biofilter and peripheral equipment. Sample points 1–4 were located at heights of 0.05, 0.15, 0.25, and 0.40 m, respectively, from the base of the bed.

biofilm on the surface of the packing. The pH of the nutrient medium was controlled at a specified value by recirculating it through an external tank (LiFlus GX; Biotron, Inc., Puchon, South Korea) where the pH was continuously measured and acid/alkali were added automatically as needed (Fig. 1). The residence time of the nutrient medium in the pH control tank was 24 h. The trickle bed and the peripheral equipment were kept in a room with a controlled temperature of 25°C during experiments. Gas samples could be collected from the trickle bed at the four sampling points shown in Fig. 1.

2.2. Development and adaptation of the microbial biofilm

Prior to any formaldehyde degradation work, a biofilm was developed on the support material in the packed bed. For this, 1 L of activated sludge collected from a municipal wastewater treatment plant was mixed with 2 L of distilled water. Peptone (5 g per g of aqueous activated sludge suspension) was added. This mixture was used as the nutrient broth in the reservoir at the base of the trickle bed (Fig. 1). The sludge suspension was recirculated from the reservoir and sprayed on top of the bed for around 70 d. By this time a biofilm had developed on the packing in the bed. Now the sludge suspension was completely drained and replaced with the above noted solution of inorganic nutrients in reservoir 2 (Fig. 1). The nutrient solution was sprayed on the bed intermittently as explained earlier. The adaptation process was carried out the pH of the collected sludge (≈ 7).

A mixture of formaldehyde and methanol (1 L methanol and 100 mL formaldehyde (37% w/w formaldehyde in water)) was used in reservoir 4 in Fig. 1. Initially, the methanol vapor provided most of the carbon in the gas phase flowing into the bed and the initial concentration of formaldehyde in the gas phase remained low to acclimatize the biofilm to this toxic compound. Over a period of 90 days, the formaldehyde level in reservoir 4 (Fig. 1) was gradually increased and methanol was replaced with water. Thus, by day 90, the reservoir 4 (Fig. 1) contained 1 L of only the 37% w/w aqueous solution of formaldehyde. All carbon in the gas phase was now being provided by formaldehyde vapor. The flow rate of the gas phase entering the bed was 90 L h^{-1} during biofilm development. Other specified flow rates were used in other experiments.

2.3. Determination of biomass in the packed bed

The quantity of the microbial biomass in the biofilm was determined by removing ten pieces of the packing. These were gently rinsed with deionized water, drained and dried for 24 h at 104°C. The dried pieces were weighed. The dried biofilm was then completely removed from support pieces by suspending them in 10% HCl. Once the film had detached, the support pieces were thoroughly washed with deionized water, dried as explained above and weighed. Thus the average quantity of the dry biomass per piece of the packing could be calculated. As the total quantity of the plastic pieces in the packed bed was known, the total dry biomass in the bed could be estimated [32].

2.4. Evaluation of the formaldehyde elimination efficiency

Formaldehyde removal from the gas phase was investigated at flow rates of 90, 291 and 1512 L h^{-1} [30]. These flow rates corresponded to a gas phase retention time in the bed of 132, 41, and 8 s, respectively. Concentration of formaldehyde in the inlet and exhaust gas (Fig. 1) was measured using a formaldehyde meter (Interscan model 4160; Interscan Corp., Simi Valley, CA, USA). The concentration of formaldehyde in the gas entering the bed was always 450 mg L^{-1}. Therefore,the mass loadings of formaldehyde (the mass flow rate of formaldehyde per unit nominal volume of the bed) at volumetric flow rates of 90, 291, and 1512 L h^{-1} were 3.389, 10.95 and 56.94 mg m^{-3} h^{-1}, respectively.

Formaldehyde concentration in nutrient solution was measured using the colorimetric method of Nash [33]. The chemical oxygen demand (COD) in the liquid was determined using the standard method [34].

2.5. Effects of pH on formaldehyde removal in the trickle bed

A set of experiments examined the effects of operational pH on the formaldehyde removal performance of the trickle bed. For this, the pH of the nutrient medium was controlled at the specified values (pH 3, 5, 6, 7, and 9) in separate experiments as explained earlier.

2.6. Characterization of the microorganisms in the biofilter

As the biofilm was developed using municipal sewage sludge as the inoculum, many of the microorganisms in the film were expected to be *Enterobacteriaceae*. Therefore, an *Enterobacteriaceae* identification kit (Hi25™ Enterobacteriaceae Identification Kit; www.ridacom.com) was used to identify the key species in the biofilm samples detached from the packing removed from specified locations in the bed.

2.7. Process modeling

2.7.1. A simplified model for the biofilter

Formaldehyde is used to kill microorganisms and at sufficient concentration it completely suppresses microbial growth. Nonetheless, in trace concentrations as typically found in polluted gases, it is biodegradable [16,35,36] especially if the microorganisms being used for degradation have been adapted to it through long-term exposure to sublethal concentrations. Microbial degradation of formaldehyde can occur both under aerobic [28] and anaerobic conditions [27,37]. Only aerobic degradation is relevant in a trickle bed filter supplied continuously with a large volume of oxygen-rich air mixed with traces of the contaminant. In aerobic degradation by bacteria such as Pseudomonas putida, formaldehyde is first converted to methanol and formic acid via the action of the enzyme formaldehyde dismutase [38]. In some aerobic microorganisms, only formic acid is the initial degradation product [39]. Both methanol and formic acid are ultimately oxidized to carbon dioxide and water.

Irrespective of the nature of the degradation kinetics, a mass balance of the reactant (i.e. formaldehyde) on a thin

horizontal differential segment of the packed bed is necessary for assessing the degradation performance. This analysis assumes plug flow of the gas phase in the bed as would normally be the case. A thin differential segment of the packed bed with a thickness dx and a cross sectional area A is shown in Fig. 2. The gas phase flows in and out of the segment at a flow rate Q. The concentration of formaldehyde entering the segment with the gas phase is C and the concentration leaving the segment is $C+dC$ (Fig. 2). The differential volume of the bed (dV_R) corresponding to the thickness dx is $A{\cdot}dx$. The change is concentration (i.e. dC) of formaldehyde as the gas phase moves a distance dx in the bed is due to consumption by the microorganisms. The rate of consumption is r. Therefore, a steady state mass balance of formaldehyde on bed segment in Fig. 2 can be written as follows:

$$\underbrace{QC}_{\substack{Inflow\\ of\ substrate}} - \underbrace{Q(C+dC)}_{\substack{Outflow\\ of\ substrate}} - \underbrace{\tfrac{dC}{dt}(A\,dx)}_{\substack{Substrate\\ consumption\\ by\ reaction}} = 0 \tag{1}$$

But $dc/dt = r$ and, therefore, Eq. (1) can be written as follows:

$$QC - QC - QdC - rAdx = 0 \tag{2}$$

Or,

$$\frac{dC}{dx} = -\frac{A\,r}{Q} \tag{3}$$

Eq. (3) is applicable to any kind of degradation kinetics, but does not consider any mass transfer effects.

In practice, the formaldehyde vapor must diffuse from the gas phase into the liquid film surrounding the microbial layer before it can be degraded by the microorganisms. Therefore, gas-liquid mass transfer effects have the potential to influence the formaldehyde degradation kinetics. Eq. (3) accounting for the mass transfer of formaldehyde, can be written as follows:

$$\frac{dC}{dx} = \frac{A}{Q}\left[K_{La}(C_{in} - C) - r\right] \tag{4}$$

In Eq. (4), K_{La} is the overall volumetric gas-liquid mass transfer coefficient for formaldehyde, C_{in} is the formaldehyde concentration in the gas phase entering the bed and C is the formaldehyde concentration in the gas phase at any location x in the bed.

The kinetics of degradation of a pollutant such as formaldehyde in a biofilter depend on the local concentration of the pollutant in the gas phase. Initially, at a high concentration of pollutant, the kinetics of degradation may be zero-order in concentration and later, as the concentration declines, the degradation may switch to a first-order dependence on concentration [10]. The concentration dependence of the degradation rate r (mg cm^{-3} h^{-1}) can be described using the following equation [10,40]:

$$r(C) = \frac{k_1 C}{1 + k_2 C} \tag{5}$$

where $r(C)$ is the degradation rate at concentration C (mg cm^{-3}) and k_1 (h^{-1}) and k_2 (cm^3 mg^{-1}) are kinetic constants [10].

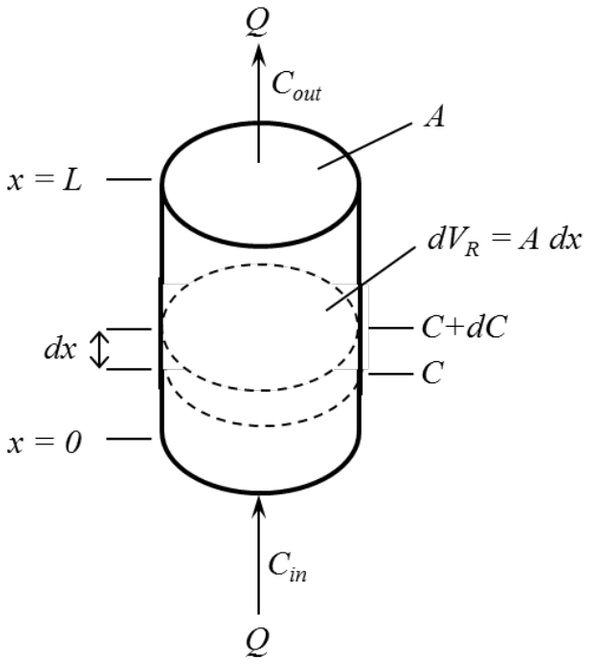

Fig. 2. Mass balance of formaldehyde on a horizontal segment (dashed lines) of the trickle bed. A is cross-sectional area (cm^2); C (g cm^{-3}) is the concentration of formaldehyde in the gas entering the differential segment; $C+dC$ (g cm^{-3}) is the concentration of formaldehyde in the gas leaving the differential segment; C_{in} (g cm^{-3}) is the concentration of formaldehyde in the gas entering the bed; C_{out} (g cm^{-3}) is the concentration of formaldehyde in the gas exiting the bed; dV_R is volume (cm^3) of the bed segment with a differential height dx (cm); Q is volume flow rate of the gas entering and leaving the bed (cm^3 h^{-1}); x (cm) is the distance measured in the direction of flow of the gas phase; and L (cm) is the total height of the bed.

If degradation obeys first-order kinetics at all concentrations, $k_2 = 0$ and, therefore, Eq. (5) reduces to the following:

$$r = k_1 C \tag{6}$$

In this work, both Eq. (5) and Eq. (6) were initially used in Eq. (3) to fit the experimentally observed concentration profiles in the bed. Eq. (6) was always found to produce a better fit and, therefore, a first-order degradation assumption was subsequently used. Eq. (4) written for first-order kinetics (Eq. (6)) is as follows:

$$\frac{dC}{dx} = \frac{A}{Q}\left[K_{La}(C_{in} - C) - k_1 C\right] \tag{7}$$

An alternative to Eq. (5) and Eq. (6) is the use of Michaelis-Menten kinetics to describe the degradation process. If Michaelis-Menten kinetics are obeyed, the degradation rate r should depend on formaldehyde concentration C, as follows [41]:

$$r = \frac{r_{max} C}{K_m + C} \tag{8}$$

In Eq. (8) r_{max} (g m^{-3} h^{-1}), is the maximum rate of the degradation reaction (a constant) and K_m (g m^{-3}) is Michaelis-Menten constant.

Depending of the relative magnitudes of C and K_m, Michaelis-Menten kinetics may effectively reduce to first-order kinetics. Thus, if $C<<K_m$, the denominator in Eq. (8) approximates to K_m and the equation becomes:

$$r = \frac{r_{\max} C}{K_m} \tag{9}$$

Or,

$$r = k_3 C \tag{10}$$

where the rate constant $k_3 = r_{max}/K_m$.

Eqs. (8)–(10) assume that the concentration in the gas phase is a direct reflection of the concentration in the liquid phase surrounding the microbial film and, therefore, r_{max} and K_m are apparent values that include any mass transfer effects.

2.7.2. Determination of kinetic constants

For any steady state operation, depending on the prevailing degradation behavior, the kinetic constants (i.e. either k_1, or r_{max} and K_m) needed to be determined. For first-order degradation, the measured axial concentration profiles in the bed were fitted to profiles generated using Eq. (3) (no mass transfer effects) and Eq. (7) (accounting for mass transfer effects). The fitting parameters were k_1 in the first case and k_1 and K_{La} in the second case.

For estimation of the apparent values of the Michaelis-Menten constants, the volume averaged degradation rate r_a, or elimination capacity of the bed for formaldehyde, was calculated using the measured values of the concentrations in the gas phase [10], as follows:

$$r_a = \frac{(C_{in} - C_{out})Q}{V} \tag{11}$$

where Q (m^3 h^{-1}) was the volume flow rate of gas phase and V (m^3) (= $A \times L$) was the nominal volume of the bed. Similarly, the bed-height averaged concentration C_g of formaldehyde in the gas phase was calculated as the log mean value [10]; thus:

$$C_g = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{in}}{C_{out}}\right)} \tag{12}$$

Eq. (8) written in terms of r_a and C_g is as follows:

$$r_a = \frac{r_{\max} C_g}{K_m + C_g} \tag{13}$$

The above equation could be linearized to the following form:

$$\frac{1}{r_a} = \frac{K_m}{r_{\max}} \frac{1}{C_g} + \frac{1}{r_{\max}} \tag{14}$$

A plot of $1/r_a$ against $1/C_g$ was then used to obtain K_m/r_{max} as the slope and $1/r_{max}$ as the y-intercept. These values were used to calculate the apparent kinetic constants r_{max} and K_m.

3. Results and discussion

3.1. Loading results

Formaldehyde removal in the packed bed was evaluated at gas volumetric flow rates of 90, 291, and 1512 L h^{-1}. These flow rates in combination with sampling at locations 1–4 (Fig. 1) provided gas-phase hydraulic retention times in the range of 3 to 132 s [30]. All experiments in this section were conducted at a pH of 7.The temperature was always 25°C. For each retention time, the formaldehyde removal efficiency (η, %) of the biofilter was calculated using the following equation [10]:

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \tag{15}$$

where C_{in} (mg L^{-1}) was the concentration of formaldehyde in the inlet gas and C_{out} (mg L^{-1}) was the concentration in the gasphase at a given sample point, or in the outlet of the bed at the top (Fig. 1).

The removal efficiency depended on both the retention time and the volume flow rate of the gas phase as shown in Fig. 3 [42]. A removal efficiency of 99% was obtained at a residence time of 132 s at the gas flow rate of 90 L h^{-1}. At all gas flow rates, the removal efficiency increased as the retention time was increased (Fig. 3) because an increased retention time allowed a greater removal of formaldehyde from the gas phase into the liquid phase surrounding the microbial film and consumption by the microorganisms. At a fixed residence time, an increased gas flow rate greatly improved removal efficiency (Fig. 3). This was because an increased flow rate increased the mass transfer rates of formaldehyde and oxygen from the gas phase to the liquid film surrounding the microbial film. The results in Fig. 3 suggest the formaldehyde removal process was limited by gas-liquid mass transfer.

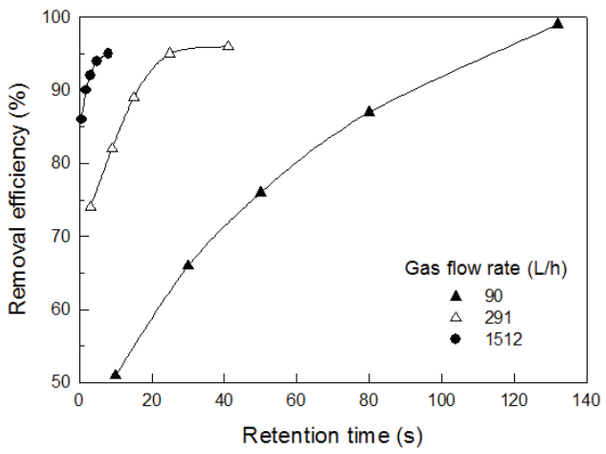

Fig. 3. Formaldehyde removal efficiency versus gas phase retention time in the whole bed or its sections (all measurements were at pH 7).

Although only mass transfer of formaldehyde was considered, mass transfer of oxygen may have been another limiting factor. At room temperature, formaldehyde is highly soluble in water with a saturation concentration of around 400 g L^{-1}. In comparison, oxygen solubility in water in equilibrium with air at 25°C is only around 8×10^{-3} g L^{-1}. Therefore, the concentration difference driving force for diffusive mass transfer from the gas phase to the liquid phase is much higher for formaldehyde compared to the driving force of oxygen. Furthermore, the oxygen diffusivity in water at 25°C is 2.1×10^{-9} m^2 s^{-1} and for formaldehyde the diffusivity value is quite similar ($\approx 2.0\times10^{-9}$ m^2 s^{-1}). In view of these values, the liquid film mass transfer coefficients (approximated as D/δ where D is the diffusivity and δ is the thickness of the stagnant liquid film) for oxygen and formaldehyde for a given set of hydrodynamic conditions in the bed are likely to be quite similar. Overall, because of the much higher driving force, the diffusive mass transfer of formaldehyde is likely to be much faster compared to diffusive mass transfer of oxygen.

In view of the results in Fig. 3, the packed bed system was quite capable of effectively removing formaldehyde from the gas phase so long as the residence time and the gas flow rate were carefully selected. High flow rates of the contaminated gas could be effectively treated within a short residence time. For example, a removal efficiency of >95% was feasible with a residence time of ≤20 s at high gas flow rates (≥291 L h^{-1}) that minimized mass transfer effects. A 100% removal of formaldehyde was reported by Prado et al. [24] in a trickle bed bioreactor treating a gas mixture containing formaldehyde, methanol, dimethyl ether and carbon monoxide. A hydraulic retention time of 60 s was required to achieve a complete removal of formaldehyde [24]. Measurements at different sampling points (Fig. 1) revealed that around 50% of formaldehyde entering the bed was removed within the first quarter of the total depth of the bed.

Operation at short residence times in combination with high flow rates dramatically reduced biomass growth in the bed compared to operation at lower flow rates and longer residence times. This suggested an almost quantitative oxidation of formaldehyde to carbon dioxide and water under conditions supporting a rapid gas-liquid mass transfer. Minimized microbial growth actually improved formaldehyde removal compared to operation under conditions that favored growth. Minimizing biofilm growth in a trickle bed is essential for stable long-term operation. Growth results in an increasing thickness of the microbial film,a constriction of the flow channels and a consequent increase in pressure drop through the bed [43,44]. Once the interstitial spaces are sufficiently constricted, the flow begins to slough off the biomass from the support material.

Operational factors such as temperature and pH can also be used to limit microbial growth in a bed without affecting its pollutant removal capacity. Microorganisms capable of rapidly consuming an organic compound, but having a minimal growth capacity have been investigated [45]. Certain acidophilic bacteria thrive at low pH values with minimal growth while consuming an organic carbon source [45]. Similarly, thermophilic bacteria grow slowly in a biofilter, but effectively degrade a pollutant vapor [46]. Therefore, operation at a reduced pH, or elevated temperature, provide options for controlling growth while achieving degradation. In view of this, the effects of pH on formaldehyde removal were investigated as described in the next section.

3.2. Effects of pH

Microbial processes generally function best close to a pH value of 7, but microorganisms capable of functioning effectively at extreme acidic and alkaline pHs are known. Furthermore, microbes that typically function effectively around neutral pHs can be adapted to thrive at higher and lower pH values. To examine the effects of pH on degradation of formaldehyde, the packed bed bioreactor was operated at controlled pH values of 3, 5, 6, 7, and 9 in separate experiments. The temperature was always 25°C and the volumetric flow rate of the gas was fixed at 90 L h^{-1}. The formaldehyde removal efficiency was determined as a function of time in the degradation process. The data are shown in Fig. 4.

Consistently high and stable removal efficiencies of 80–95% were seen at pH 7 (Fig. 4a). Relative to operation at pH 7, the removal efficiencies were reduced a little by operating at slightly lower pH values of 5 and 6 (Fig. 4a). If the operational pH was highly acidic (pH 3, Fig. 4) or highly alkaline (pH 9, Fig. 4a), the removal efficiency was dramatically reduced during the first 5-days of operation to around 10% or lower. Subsequently, the removal efficiency gradually recovered as the microorganisms adapted, but after 37 days of operation the maximum removal efficiency was ≤45% (Fig. 4a). A plot of the average removal efficiency over the entire operational period versus the pH is shown in Fig. 4b. Clearly, the optimal pH of operation was around 7, but high levels (≥80%) of degradation could be achieved by operating within the pH range of 5 to 7. Effective degradation was not feasible outside this range (Fig. 4a). The above observations are consistent with other reports. For example, Prado et al. [24] reported a markedly reduced removal efficiency at pH values of <4.2.

In the present work, microscopic observations of biomass samples suggested a dramatic reduction of bacterial population after prolonged operation at extreme pH values (pH 3 and pH 9) and a proliferation of fungi. The total biomass in the microbial film was not affected by operating at extreme pH values. In the pH range of 3–9, the effect of pH on the average formaldehyde removal efficiency (η, %) could the modelled (Fig. 4b) using the following equation:

$$\eta(\%) = -7.1643\text{pH}^2 + 86.837\text{pH} - 174.42 \quad (16)$$

The correlation coefficient for the above equation was 0.97.

3.3. Contribution of the nutrient reservoir to degradation

A portion of the formaldehyde entering the packed bed was absorbed by the biofilm and degraded. A second portion left the bed untreated in the exhaust gas and a third portion drained out of the bed dissolved in the nutrient broth that was intermittently sprayed on the bed. This last portion was minimized by using the nutrient spray intermittently for 15 min in each hour of operation. Nonetheless, some organic carbon reached the nutrient reservoir (2

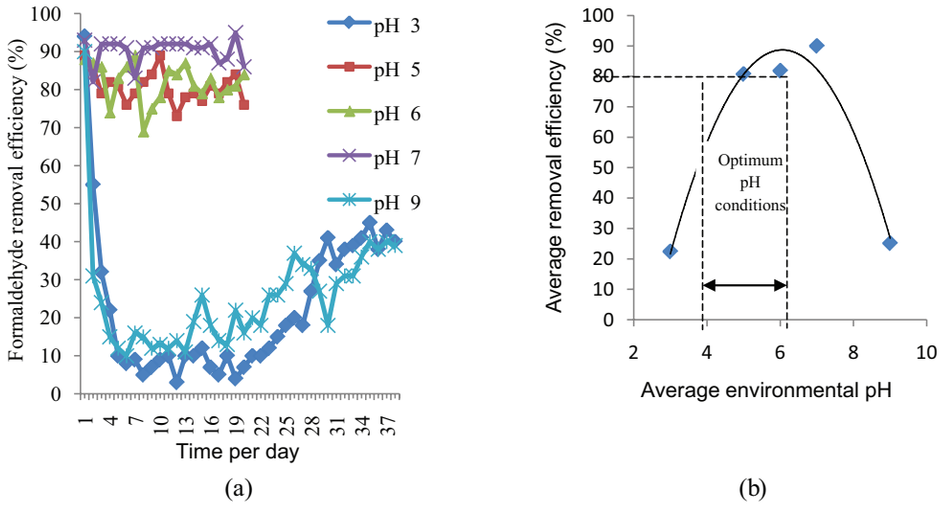

Fig. 4. Formaldehyde removal efficiency during operation at different pH values of the nutrient solution (a). Time averaged removal efficiency versus operational pH (b).

in Fig. 1) as formaldehyde. The amount of organic carbon accumulation in the nutrient reservoir was measured as the chemical oxygen demand (COD) of the nutrient solution.

At all operational pH values, the COD of the nutrient medium in the reservoir increased with time of operation until a steady state was achieved (Fig. 5). Under the conditions that maximized degradation of formaldehyde in the bed (pH = 7, gas flow rate = 90 L h^{-1} and temperature = 25°C), the COD of the nutrient solution in the reservoir stabilized at around 20000 mg L^{-1}(Fig. 5).

At extreme pH values (pH 3 and 9, Fig. 5), the degradation in the bed was poor and therefore the washout in the nutrient fluid was high and the steady state COD value of the nutrient fluid in the reservoir stabilized at nearly 71000 mg L^{-1}. There was microbial degradation of formaldehyde in the nutrient reservoir as a consequence of the microorganisms washed from the bed into the reservoir and subsequent growth. Thus, once the bed operation ceased, the COD level in the reservoir was found to drop. For example, at pH 7, the COD value fell from 20000 mg L^{-1} to 1780 mg L^{-1} in 36 h. Therefore, in terms of COD, the rate of formaldehyde consumption under optimal conditions within the nutrient reservoir was 506 mg h^{-1} at 25°C.

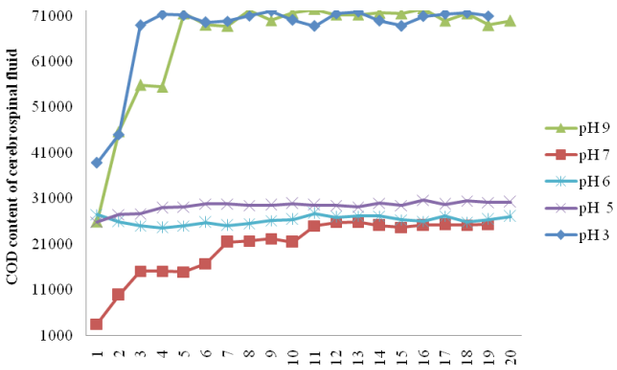

Fig. 5. COD content of the nutrient solution in the reservoir.

3.4. Modeling of packed bed biofilter

For first-order degradation kinetics, the formaldehyde removal efficiency was calculated at any depth of the bed using the model predicted concentration at that depth. Calculations were done with accounting for mass transfer effects (Eq. (7)) and without considering these effects (Eq. (7) with K_{La} = 0). Model equations were solved using the MATLAB software (www.mathworks.com). The mass transfer coefficient K_{La} and the rate constant k_1 were used as fitting parameters to minimize the difference between the calculated axial concentration of formaldehyde and the measured data. The best fit k_1 value was required to be the same for the models with and without mass transfer accounting. The predicted and the measured removal efficiencies are shown in Fig. 6 as functions of bed height, i.e. the distance measured along vertical axis of the bed from the point of entry of the contaminated gas).

The removal efficiency profiles predicted with accounting for the mass transfer effects showed a generally better agreement with the measured data (Fig. 6) compared to the profiles predicted without accounting for mass transfer. The modelled profile accounting for mass transfer was within 12% of measured data whereas the modelled profile disregarding the mass transfer effects was within 16% of the measured data (Fig. 6). The shapes of both the modeled profiles were consistent with the shape of the measured profile (Fig. 6). The mass transfer coefficient value that minimized the difference between the modelled and the measured profiles was 11 h^{-1} and the rate constant k_1 was 180 h^{-1}.

As shown in Fig. 7, the axial variation of the gas-phase concentration of formaldehyde in the packed bed agreed closely with the measured concentrations. The model used (K_{La} = 11 h^{-1}, k_1 = 180 h^{-1}) in the predictions in Fig. 7 accounted for the mass transfer effects. In view of the excel-

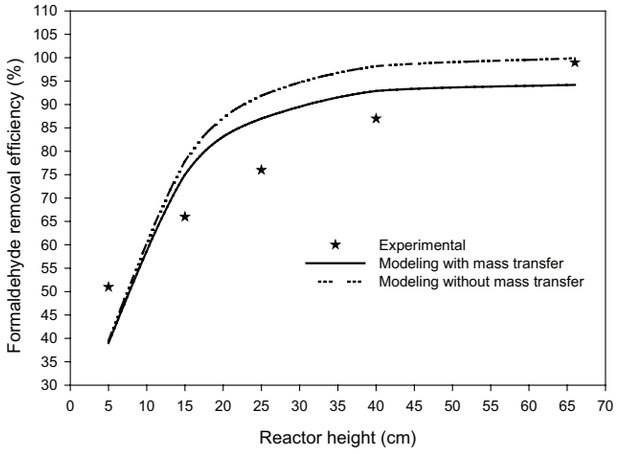

Fig. 6. Experimental and model-predicted removal efficiency of formaldehyde versus height of the packed bed. The gas phase flow rate was 90 L h^{-1}.

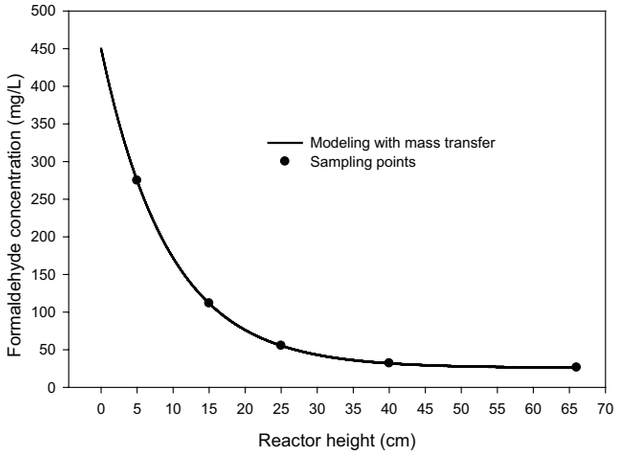

Fig. 7. Comparison of the model predicted and the measured concentrations of formaldehyde in the gas phase at different axial locations in the packed bed. The profiles are shown for a gas flow rate of 90 L h^{-1} and a formaldehyde concentration of 450 mg L^{-1} in the gas phase at the inlet of the bed.

lent agreement between the measured and the predicted concentration profiles (Fig. 7), the first-order degradation kinetics corrected for gas-liquid mass transfer may be quite satisfactory of design and scale-up of packed bed biofilm reactors.

3.4.1. Michaelis-Menten kinetics

As noted earlier, sometimes the Michaelis-Menten kinetics approximate to first-order degradation kinetics. In view of this, the average reaction rate (Eq. (11)) and the average formaldehyde concentration in the gas-phase in the packed bed (Eq. (12)) were plotted in accordance with Eq. (14) to obtain the apparent values of r_{max} and K_m. The plot of $1/r_a$ versus $1/C_g$ was linear in keeping with expectations (Fig. 8). From the plot shown (Fig. 8), the apparent r_{max} value was 90.09 g m^{-3} h^{-1} and the apparent K_m was 2215.135 g m^{-3}. Therefore, the constant k_3 (Eq. (10)) was 40.7×10^{-3} h^{-1}. As the maximum formaldehyde concentration at the entrance of the bed was always 450 mg L^{-1}, the average C_g value never exceeded 20% of K_m.

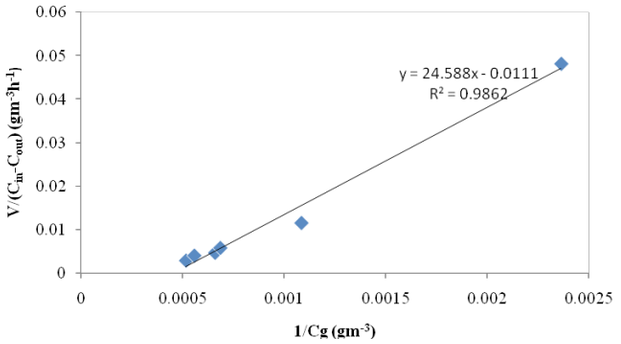

Fig. 8. A plot of $1/r_a$ versus $1/C_g$ for obtaining the apparent values of Michaelis-Menten parameters r_{max} and K_m. The regression coefficient value for the best fit line shown was 0.9862.

3.5. Bed microbiology

During operation at peak removal efficiencies, the microbial population in the bed consisted of mostly bacteria. In steady state operation at a gas-phase residence time of 132 s, the dry biomass concentration in the bed was 210 mg per g of dry packing. Samples of the biofilm collected from the surface of the packing were dispersed in a nutrient medium, diluted with water and grown on nutrient agar plates at 35°C for 24 h. The various colonies formed were identified using the *Enterobacteriaceae* identification kit and the standard biochemical tests. All isolates were rod-shaped, motile, gram-negative and catalase positive. The following bacteria were identified: *Salmonella bongori*, *Salmonella enterica* (formerly *Salmonella choleraesuis*), *Salmonella typhimurium*, *Serratiaentomophila*and *Serratiaficaria*. Several of these bacteria are human pathogens. They occurred in the biofilm likely because the original inoculum came from a municipal wastewater treatment plant. They thrived in the packed bed likely because they were already exposed to formaldehyde in places of origin of the sewage. For example, formaldehyde is commonly used as a disinfectant in hospitals and sewage from such a source is highly likely to contain potentially pathogenic *Enterobacteriaceae* acclimated to formaldehyde.

Studies of the microbiological samples taken from the packing located close to sample points 1–4 (Fig. 1) revealed that *S. bongori* was dominant at sample point 1. Thus it was likely the most tolerant of a high concentration of formaldehyde. *S. choleraesuis* was dominant at sample point 2 (Fig. 1), suggesting a good tolerance for formaldehyde, but not as good as *S. bongori*. Samples from locations 3 and 4 (Fig. 1) contained *S. typhimurium*, *S. entomophila*and *S. ficaria* as the dominant species. Therefore, these species were relatively poorly adapted to high concentrations of formaldehyde. Moreover, approximately 50% of the formaldehyde entering the bed was eliminated in the first 25% length of

the bed, therefore, *S. bongori* was a major contributor to degradation of formaldehyde. Bacteria such as *Pseudomonas* sp. [38] and some yeasts [26] are known to degrade formaldehyde, but these were not found in the biofilm in this work.

4. Conclusions

A trickle bed bioreactor containing an acclimatized microbial biofilm effectively eliminated (99% elimination) formaldehyde from air containing an initial formaldehyde concentration of 450 mg L^{-1}. The optimal treatment conditions were a gas phase residence time of 132 s, pH 7 and a temperature of 25°C. At these conditions the formaldehyde loading of the bed was 3.389 mg m^{-3} h^{-1}. The formaldehyde removal efficiency was adversely affected at pH values outside the range of 5 to 7. Bacteria of the genera *Salmonella* and *Serratia* were the main contributors to biodegradation. Both first order kinetics and modified Michaelis-Menten kinetics could be used to model the degradation process, but the effects of gas-liquid mass transfer needed to be considered.

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