Analysis of Oxygen Interation Kinetics on Toluene Biofiltration

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Abstract- **In this study, the effect of oxygen on the removal of toluene is demonstrated using a biofilter packed with peat media. Experimental results obtained from the peat-biofilter are validated with numerical predictions from an earlier model. There is an acceptable agreement between them. The increase in the level of oxygen increased the removal of toluene; however, the effect was not significant at inlet concentration of 1.5 gm^{-3}. A correlation between removal efficiency of toluene and fraction of oxygen in the inlet airstream is developed. The simulation data showed that at high toluene concentrations, the effect of oxygen was more significant. Although this study is of industrial significance, the results are valid for hydrophobic compounds (i.e., toluene). It is expected that for hydrophilic compounds (i.e., ethanol) the effect of oxygen in the inlet air on biofilter performance will be more prominent.**

Keywords- Oxygen Limitation; Toluene Biofiltration; Peat Biofilter; Model Predictions; Experimental Validation

I. INTRODUCTION

Increasing regulations concerning public health and the environment have resulted in paying more attention to environmental aspects of industrial processes. One of these aspects concerns the treatment of waste gases, which contain volatile organic compounds (VOCs). These compounds directly endanger health depending on their nature or may merely be a source of nuisance. As a result of statutory control of air pollution being enforced in many countries, small factories and industries are in need of simple, inexpensive and reliable waste gas cleaning techniques. Various technologies have been used for years to control the emissions of VOCs discharged from point sources. The most common are incineration, carbon adsorption, chemical scrubbing and biofiltration. Biofiltration utilizes micro- organisms immobilized on porous solid material (e.g., peat, perlite, compost, ceramic particles) to degrade pollutants. Compared to conventional techniques, biofiltration is relatively environmentally friendly and more economical.

The aerobic heterotrophic bacteria present in the biofilter bed require oxygen. Although the amount of oxygen in the inlet air is about 21%, biodegradation of many VOCs at high concentrations are limited by the availability of oxygen (Shareefdeen et al., 1993). The lack of oxygen in the biofilter bed can lead to the development of anaerobic zones. Thus, poor distribution of oxygen will inactivate the microorganisms. Furthermore, the formation of anaerobic zones might start producing foul-smelling emissions. There are claims that the amount of oxygen in the inlet air to the biofilter is sufficient or may even be in excess of what is required (Diks and Ottengraf, 1991; Bohn, 1993); however this is true for hydrophobic compounds (e.g. benzene, toluene etc.) at low inlet concentrations. At high inlet VOC concentrations, oxygen could become process limiting. For the case of hydrophilic compounds, such as methanol, ethanol etc., the effect of oxygen could be very prominent even at low concentrations. Yang et al., (2007), used a bench-scale biofilter to demonstrate the treatability of off-gas containing nitric oxide (NO) under different oxygen levels and reported that the oxygen concentrations in the inlet air would affect NO removal performance significantly. Baquerizoa et al., (2007), presented a dynamic model of ammonia removal by gas-phase biofiltration and considered biodegradation kinetics including inhibitions and oxygen limitation. Alvarez-Hornos, et al., (2009), presented a dynamic model for ethyl acetate and toluene removal by biofiltration. They considered Haldane-type kinetic expressions that include the oxygen limitation, the inhibition effect due to high concentration of substrate, and the cross-inhibition between the substrates. In the work of Zamir et al. (2012) on toluene biofiltration, kinetic of the system is expressed by a Monod relationship assuming that oxygen limitation was negligible.

Although the literature on biofiltration emphasizes the importance of oxygen limitations, experimental studies and theoretical comparison on the influence of oxygen on the removal of contaminants are limited. Therefore, the objective of this work is to present an experimental study on the effect of oxygen on the biofiltration of a volatile organic compound (toluene) along with theoretical analysis.

II. THEORETICAL BACKGROUND

The mathematical model of Shareefdeen et al. (1997) incorporates possible limitations of oxygen as well as general mixing of gas phase through axial dispersion terms. Model equations are presented here for comparison of experimental data of this study. This model was based on several assumptions.

(a) The thickness of the biofilm is small compared to curvature of the solid particles.

(b) Biofilm does not grow in the pores of the particles. It is formed only on the exterior surface.

(c) The pollutant and oxygen are in equilibrium at biofilm-air interface.

(d) The depth of penetration of pollutant and oxygen is smaller than the actual size of the biofilm.

(e) Diffusivities of the pollutant and oxygen in the biofilm are equal to the diffusivities of the same compounds in water corrected by a factor.

(f) In order to account for oxygen limitations, kinetic expression is modified by incorporating the term $S_O/(k_O + S_O)$.

(g) Biofilm density (X_V) and specific biofilm surface area are constant.

The following equations are mass balances of VOC (j) and oxygen (O_2) in the biofilm:

$$f(X_v)D_{jw}\frac{d^2S_j}{dx^2} - \frac{X_v}{Y_j}\mu(S_j,S_o) = 0 \tag{1}$$

$$f(X_v)D_{ow}\frac{d^2S_o}{dx^2} - \frac{X_v}{Y_{oj}}\mu(S_j,S_o) = 0 \tag{2}$$

where, specific growth rate $\mu(S_j,S_o)$ is given by:

$$\mu(S_j,S_o) = \frac{\mu_j^* S_j S_O}{\left(K_j + S_j + \frac{S_j^2}{K_{Ij}}\right)(K_O + S_O)}$$

Boundary Conditions (3) and (4) indicate equilibrium at the air/biofilm interface and zero flux at the biofilm/solid interface, respectively. In Equations (3) and (4), x refers to the distance in the direction normal to the biofilm surface.

at x = 0,

$$S_j = \frac{C_j}{m_j} \qquad S_o = \frac{C_o}{m_o} \tag{3}$$

at x = d,

$$\frac{dS_j}{dx} = 0 \qquad \frac{dS_o}{dx} = 0 \tag{4}$$

The following equations are mass balances of VOC (j) and oxygen (O_2) in the air phase:

$$\upsilon D\frac{d^2C_j}{dh^2} - U_g\frac{dC_j}{dh} + f(X_v)D_{jw}\frac{dS_j}{dx}\bigg|_{x=0} A_s = 0 \tag{5}$$

$$\upsilon D\frac{d^2C_O}{dh^2} - U_g\frac{dC_O}{dh} + f(X_v)D_{Ow}\frac{dS_O}{dx}\bigg|_{x=0} A_s = 0 \tag{6}$$

Axial dispersion effects at the inlet and exit of the biofilter are described by Danckwert's boundary conditions (Shareefdeen et al. (1997). These boundary conditions are as follows:

at h = 0,

$$\upsilon D\frac{dC_j}{dh} = U_g(C_j\big|_{0^+} - C_j\big|_{0^-}) \tag{7}$$

$$\upsilon D\frac{dC_O}{dh} = U_g(C_O\big|_{0^+} - C_O\big|_{0^-}) \tag{8}$$

at h = H,

$$\frac{dC_j}{dh} = 0 \qquad \frac{dC_o}{dh} = 0 \qquad\qquad (9)$$

Solution of this model is obtained through normalization using several dimensionless variables and groups. Details of the normalized form of the model equations, dimensionless groups, solution procedure and parameters used in solving the model are given elsewhere (Shareefdeen et al., 1997).

III. EXPERIMENTAL METHOD

The experimental setup (Fig. 1) used in the study was made of Plexiglas with an inner diameter of 5 cm and a height of 68 cm. The length of biofilter bed packing was 64 cm. At the bottom of the column a fine ceramic disperser was attached to obtain a uniform distribution of the air entering the biofilter. The packing material used was peat and the biofilter bed was supplied with a humidified air containing toluene vapour. A peristaltic pump was used to pump air at a low flow rate through a closed toluene tank. Both air and toluene streams were mixed before supplying to the biofilter.
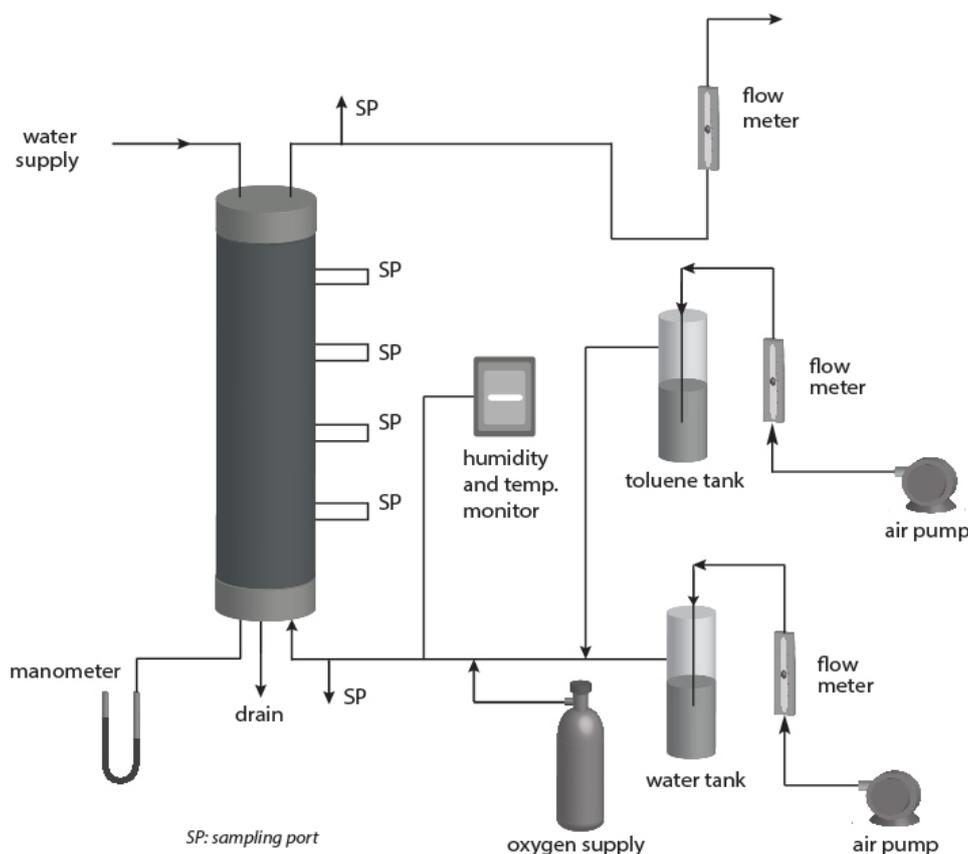

Fig. 1 Schematic of the experimental setup used in this study

The oxygen content in the inlet air was maintained by mixing air with pure oxygen from a compressed oxygen gas cylinder. Oxygen concentrations were analyzed by an oxygen analyzer (Servomex, Oxygen Analyzer) and gas chromatograph (Gow Mac Instrument Co.). The specification of the column was 6"/8" SS Chrom. The operating conditions set were: injector 140^oC, detector 200^oC and column 110^oC. Toluene concentrations were determined using a Perkin Elmer's Autosystem gas chromatograph. The GC was equipped with a stainless steel column and a flame ionization detector. The operating conditions set were: injector 200^oC, column 100^oC, and detector 250^oC. The carrier gas was helium at a flow rate of 21 ml/min. The retention time of toluene in the GC column under these conditions was around 3 min. Different sets of experiments were carried out by changing the inlet concentration of toluene and oxygen entering the biofilter.

IV. RESULTS AND DISCUSSIONS

Removal efficiencies are calculated from the concentration data obtained along the column height. Fig. 2 shows that percent removal increases along the column as expected for an inlet toluene concentration of 1.5 gm^{-3}. The oxygen level in the ambient air is about 21%. By enriching the air with pure oxygen one can increase the oxygen content in the inlet air to the biofilter. When oxygen content in the air is increased from 21% to 33% and 53%, removal efficiency also increased. However, Fig. 2 shows that the increase in the removal efficiency is not significant.
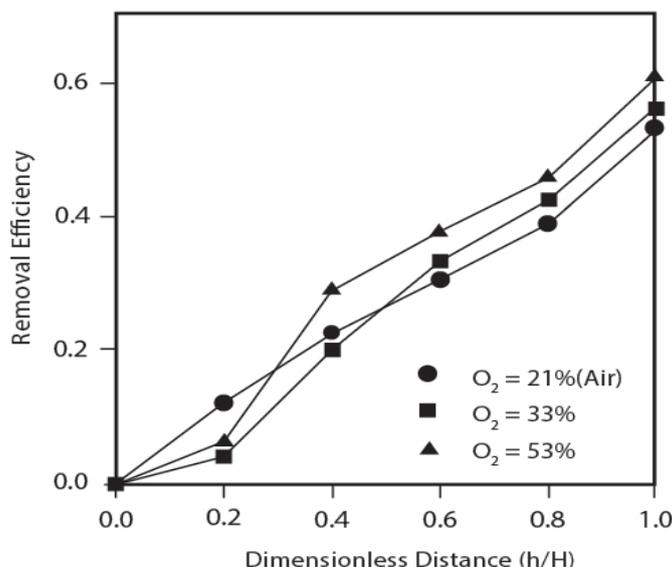
Fig. 2 Removal efficiencies at different oxygen contents (21%, 33%, and 53%) andfor toluene concentration of 1.5 gm^{-3}

Table 1 lists experimental conditions, oxygen content in the air, toluene concentration, residence time, removal efficiency and comparison of removal efficiencies with respect to air (21% oxygen level). The table shows, when oxygen content is increased from 21% to 53%, percent removal increases by only +20.2 with respect to air. One may expect the removal efficiency to reach 99% when the oxygen level is doubled. However, the Table 1 shows that the change in removal efficiency is small for the inlet toluene concentration of $C_{Ti} = 1.5$ gm^{-3}. Using the experimental data in Table 1, a correlation [$RE\% = 70.4 f_{O2} / (0.078 + f_{O2})$] between removal efficiency (RE%) and fraction of O_2 (f_{O2}) is obtained.

TABLE I COMPARISON OF REMOVAL EFFICIENCIES AT DIFFERENT OXYGEN LEVELS IN THE INLET AIR

O_2 (fraction)	C_T (inlet) (gm^{-3})	Residence time (min.)	C_T (outlet) (g m^{-3})	(RE)%	% increase (with respect to air)
0.21 (air)	1.5	2.03	0.73	51.5	0.0
0.33	1.5	2.03	0.66	56.0	+8.77
0.53	1.5	2.03	0.57	62.0	+20.2

The model is used to predict the dimensionless concentration profiles along the biofilter height for different oxygen levels. Fig. 3 shows biodegradation of toluene at low concentration (1.5 gm^{-3}) is not totally limited by oxygen. As seen from the Fig. 3, the comparison between model predicted and experimental values of both toluene and oxygen concentration is in good agreement. Since Danckwert's boundary conditions (Shareefdeen et al. (1997), described by Equations (7) and (8) which account for dispersion in the biofilter at the entrance region, the entrance dimensionless concentration is less than one.
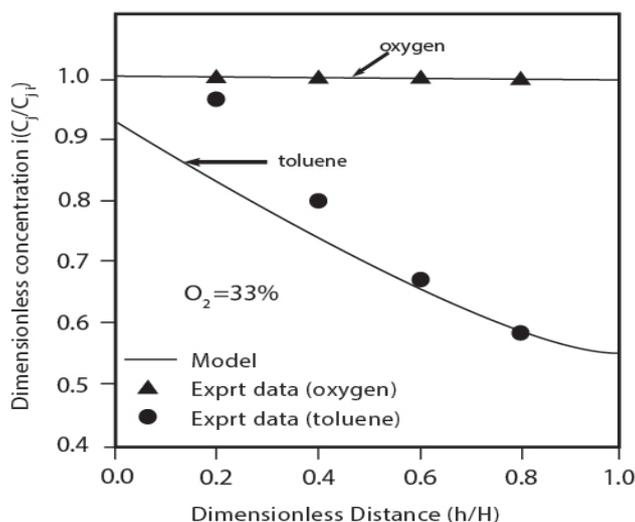
Fig. 3 Comparison between model-predicted gas phase toluene concentration and experimental data along the biofilter [oxygen content = 33% and $C_{Ti} = 1.5$ gm^{-3}]

Figs. 4 and 5 which show model predicted biofilm concentration profiles for both cases of 21% and 100% oxygen contents, respectively for an inlet concentration of 10.0 gm^{-3}. Numerical solutions gave biofilm concentration profiles at every height of the column; however these figures are for the middle point ($h/H = 0.5$) of the biofilter but the trend was similar throughout the biofilter column. Fig. 4 shows that when oxygen concentration is at 21%, oxygen gets completely consumed in a fraction of the biofilm while the drop in toluene concentration is insignificant. However, when oxygen concentration is increased to 100%, the trend is totally reversed as we can see from Fig. 5. Thus for high level of toluene loading, biofilter column will be saturated with toluene in the absence of oxygen and removal efficiency will be significantly reduced. These numerical results suggest that at low concentration of oxygen, the process is limited by mass transfer of oxygen into the biofilm and biological oxidation of toluene. When oxygen concentration in the inlet air to the biofilter is increased, mass transfer of oxygen will increase which results in a higher percentage removal. Thus, practically unchanging profiles of oxygen concentration along the biofilter is due to mass transfer effects.
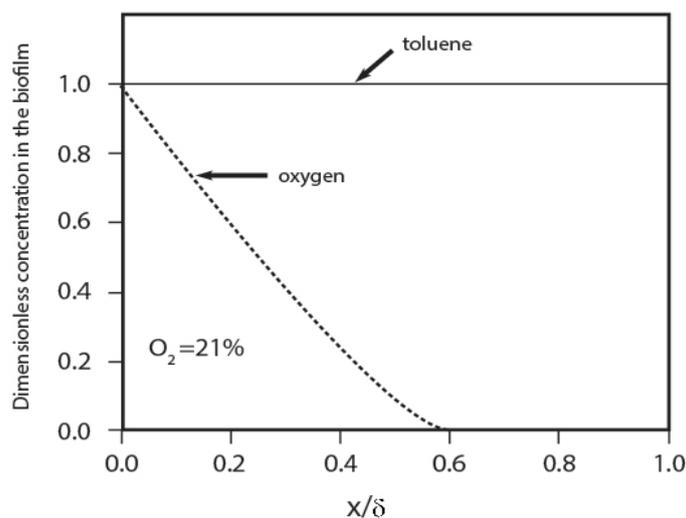

Fig. 4 Model predicted concentration profiles of oxygen and toluene in the biofilm at the middle point of the biofilter for inlet toluene concentration of 10.0 gm^{-3} and 21% oxygen
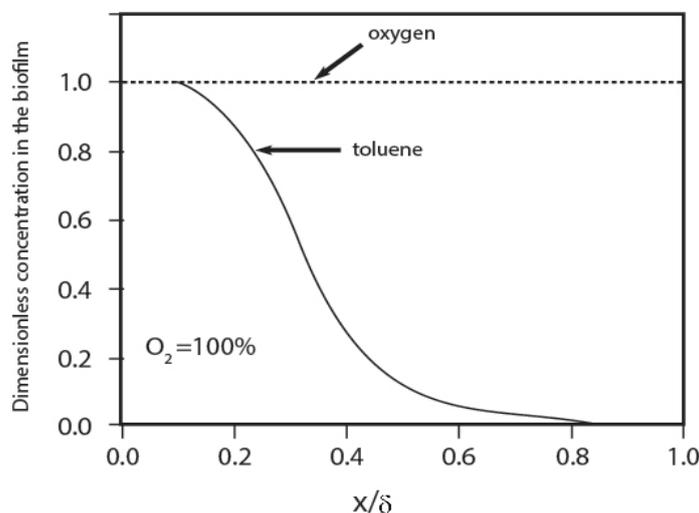

Fig. 5 Model predicted concentration profiles of oxygen and toluene in the biofilm at the middle point of the biofilter for inlet toluene concentration of 10.0 gm^{-3} and 100% oxygen

V. CONCLUSIONS

In this study, the effect of oxygen on the percent removal of toluene is demonstrated. Experimental results are validated with the model predictions with an acceptable agreement between them. A correlation between removal efficiency of toluene and fraction of oxygen is developed. It was observed that increase in the oxygen concentration increases the removal of the toluene. Although the oxygen effect is not significant at low inlet toluene concentrations, there is a considerable effect at high level of toluene. The results reported in this study are valid for hydrophobic compounds such as toluene, however, it is expected that for hydrophilic compounds such as ethanol the effect will be more prominent. Further experimental research is needed to verify the effect of oxygen kinetic interaction on the removal of hydrophilic compounds.

NOMENCLATURE

A_s :biofilm surface area per unit volume of the reactor (m^{-1}).

C_j : concentration of substance j in the air at a position h along the biofilter ($g\ m^{-3}$)

C_{ji} : value of c_j at h = 0 ($g\ m^{-3}$)

C_o :oxygen concentration in the air at a position h along the biofilter ($g\ m^{-3}$)

C_{oi} :oxygen concentration in the air at the inlet of the biofilter ($g\ m^{-3}$)

D :dispersion coefficient in the vessel ($m^2 h^{-1}$)

D_{jw} : diffusion coefficient of pollutant j in water ($m^2\ h^{-1}$)

D_o : dispersion coefficient of oxygen in air ($m^2\ h^{-1}$)

D_{ow} :diffusion coefficient of oxygen in water ($m^2\ h^{-1}$)

$f(X_v)$: ratio of diffusivity of a compound in the biofilm to that in water

h :position in the column (m) ; h = 0 at the entrance, h = H at the exit

H : total height of the biofilter bed (m)

Kj :constant in the specific growth rate expression of a culture growing on

        compound j (g m-3)

K_{Ij} :inhibition constant in the specific growth rate expression of a culture growing on compound j ($g\ m^{-3}$)

K_o :constant in the specific growth rate expression of a culture,

        expressing the effect of oxygen (g m-3)

m^j : distribution coefficient for the substance j/water system

m_o :distribution coefficient for the oxygen-in-air/water system

Pe :Peclet number for the reactor, defined as ($UgH/D\upsilon$)

S_j : concentration of pollutant j at a position x in the biofilm at a point h along the column ($g\ m^{-3}$)

S_o : oxygen concentration at a position x in the biofilm, at a point h along the column ($g\ m^{-3}$)

U_g :superficial air velocity in the biofilter; ($m\ h^{-1}$)

X_v : biofilm density (g-dry cells m^{-3})

x : position in the biofilm (m)

Y_j :yield coefficient of a culture on VOC j (g-biomass g^{-1}-compound j)

Y_{oj} :yield coefficient of a culture on oxygen (g-biomass g^{-1}-oxygen) when VOC j is the carbon source

Z :dimensionless position in the biofilter (z = h/H)

GREEK SYMBOLS

δ : effective biofilm thickness (m)

μ : specific growth rate (h^{-1})

μ_j^* : constant in the specific growth rate expression (h^{-1})

υ : porosity of the biofilter bed

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