Biofiltration of xylene and toluene in pure and mixed forms in a biofilter

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Abstract

Biodegradation of xylene (B) and toluene (T) are significant in vapour contaminant due to discharge of huge quantities in the many chemical and petrochemical industries. In this work, experiments were conducted to estimate the performance of the reactor in treating xylene and toluene. The laboratory scale biofilters was functioned in long term experiments in direction to study the removal of BT in separate biofilter and also as a mixture in another biofilter. The biofilter media consists of a blending of casuarina seeds and berl saddles (50: 50 vol, %). The media was mixed with wastewater sludge attained from the paper industry as inoculum.

The biofilters were functioned at different influent concentrations of VOCs (0.2 to 1.2 $gm^{-3}h^{-1}$) and at a gas velocity of 0.03 m^3/h. Maximum removal efficiency (RE) of more than 95% were obtained with the mixture of xylene 60 % and toluene 40% of inlet concentration. Further rising the toluene concentration caused a drop in the RE. Ottengraf–van den Oever (OVDO) model was tried and fitting confirmed a better agreement between designed and investigational data for pure VOCs.

Keywords: Biofilter, casuarina seeds, EBRT, *Ottengrafmode.*

Introduction

Enormous amount of pungent compounds as pollutants are actuality exhausted into the atmosphere by several industries. Among these pollutants volatile organic and inorganic compounds, is mainly due to industrial happenings including those associated with the process, transport, storage and consumption of fuels. Benzene, toluene and xylene (BTX) set up an important part (30% v/v) of the entire composition in commercial gasoline in India[1,4].

The efficacy and efficiency of long-standing pollution emission control methods such as condensation, absorption, incineration and membrane separation or some of the latest techniques, including biological processes, have therefore been used to manage polluted air. The choice of the selection method depends on the operating conditions like pollutant concentration, stream flow rate, temperature and humidity. Most of the above revealed methods suffer from disadvantages like minor conversions, generation of secondary pollutant, the high operating cost and lesser selectivity.

As in biological wastewater processes, the concept of the air treatment is based on biodegradation activity of the microbial population living in the biological reactor. Some of the provand biological methods has to be an substitute for the treatment of organic compounds[3] and the most widespread and oldest bioreactor configuration is the biofilter. Biofiltration has been used effectively in odor control and for the removal of organic and inorganic pollutants in air from motionless sources. It aids from the capacity that some bacteria, fungi and yeast have to degrade a great variety of pollutants into harmless compounds (H_2O, biomass and CO_2).

Biofilters are more suitable for handling a wide range of gas flow rates with a concentration range of 0 -10 g/m^{33}. Xylene and Toluene are volatile hydrocarbons present in gasoline and are reported to be two common air pollutants released into the environment from refineries, oil wells and storage vessels. Many studies on biological treatment of single air pollutants like ethyl benzene[1], toluene [4], xylene [6] and styrene [5] have been investigated. Studies on mixtures of volatile organics, namely Benzene, Toluene, Ethylbenzene and Xylene (BTEX) as a whole or any combination of the member components are comparatively less and needs more attention as the possibility of the co-existence of two pollutants are high in an industrial environment. In this back ground, the present study is aimed to degrade the xylene – toluene mixture in a biofilter operated in an upflow media with a novel biofilter media.

Among the packing materials used for biofiltration, activated carbon has a great potential for the elimination of VOCs from air. However, the preparation and regeneration costs of activated carbon have encouraged the application of alternative materials[9]. Natural materials existing in enormous amounts from agronomic operations and plant biomass can be used as minimum-cost, broadly accessible and environmentally friendly packaging material[6-9]. Numerous researchers utilized cheaper and effective packing material such as pressmud[9], sugarcane bagasse[7], corn stack[8], wood chips[5] and peat[3] biofiltration process.

Casuarina equisetifolia is a genus of 17 species in the Casuarinaceae family, native to Australia, South East Asia, and West Pacific Ocean islands As it is available more in nature, Casuarina equisetifolia plant seeds are believed to be crop biomass. The aim of this study is therefore to explore

the possible of Casuarina equisetifolia plant seeds as a packaging material for VOC's biofiltration.

Mathematical modeling: Biofilter models are found by connecting kinetics of substrate and growth of microbes to a reactor model. Assuming a growth model is neglected or constant biomass concentration all over the filter bed Assume, tubular reactor and pseudo order reactions. Biological systems are fundamentally multifaceted as the packing materials (i.e. compost, peat or soil) usually have varied microorganisms, chemical compositions and structures. In order to simplify this, many models have been recognized seeing both the steady-state and the transient state performance of bioreactors. Among them, OVDO model (1983) developed a biofilter model for the elimination of VOC.

Application of the hypothetical model: The outflow concentration of pollutant, in the state of diffusion determining step can be defined by the subsequent equation:

$$\sqrt{C_i} = \sqrt{C_o} - k_1 \frac{V}{Q} \tag{1}$$

The reaction influential stage behavior reached at a close of pollutant load that resembles to a given gas flow velocity and to the critical influent concentration at which the biofilter behavior is in conversion between the diffusion and the reaction determining step. Therefore, the critical concentration of VOC can be assessed from the subsequent relationship:

$$EC = \frac{Q}{V} C_{o,Crit} L\left(1 - \left((1 - k_1 \frac{V}{Q} \frac{1}{\sqrt{C_{o,crit}}}\right)^2\right) = k_o \tag{2}$$

Hence,

$$C_{o,Crit} = \frac{1}{4}\left(\frac{k_o}{k_1} + \frac{k_1 V}{Q}\right)^2 \tag{3}$$

The model is tested for the biofiltration of VOC using Casurriane seed based biofilter.

Improved Ottengraf model: In this model, we consider two phenomena and two equation for describe thesemodel already discussed in above section. The improved Ottengraf model deals with the reaction defining step and diffusion defining step in single equation and established with the investigational data. At low OLR values, diffusion is the rate defining step and, in such situations, the EC is given by the subsequent equation:

$$EC_{dL} = L\left(1 - \left(1 - A_s \sqrt{\frac{k_0 D}{2m}} \sqrt{\frac{V}{QL}}\right)^2\right) \tag{4}$$

where the index dl indicates diffusion determining step. Otherwise, at high OLR, the elimination of the VOC is mainly exaggerated by the organic reaction and the EC is load-independent.

$$EC_{rl} = EC_{max} = A_s k_0 \delta \tag{5}$$

Nevertheless, making the use of a single formula can only link the different expressions of EC_{dl} and EC_{rl} endlessly. The following equation can satisfy this condition:

$$EC = EC_{max} + \frac{(EC_{d1} - EC_{max})}{1 + \left(\frac{L}{L^*}\right)^p} \tag{6}$$

where L* - load at which the evolution between reaction and diffusion defining step occurs. Parameter p was considered by suitable of the investigational data. Its value agrees the rate at which the passage between the two different determining step occurs. The main advantage of the model is compare straight to the RE to the OLR and to the influent concentration. Indeed:

$$\eta = \frac{C_i - C_o}{C_i} = \frac{EC}{L} = \left(EC_{max} + \frac{(EC_{dl} - EC_{max})}{1 + \left(\frac{L}{L^*}\right)^p}\right) / L \tag{7}$$

With some numerical steps and using the explanation of L and EC, it is also likely to write efficiency and C_o as a function of C_i:

$$\eta = \frac{\left(A_s k_o \delta + \frac{\frac{C_i Q}{V}\left(1 - \left(1 - A_s \frac{V}{Q}\sqrt{\frac{k_o D}{2mC_i}}\right)^2\right)}{1 + \left(\frac{C_{g,in}}{C_g^*}\right)^p}\right)}{\frac{C_i Q}{V}} \tag{8}$$

$$C_o = C_i - \left[\frac{Q.A_s k_o \delta}{V} + \frac{C_i\left(1 - \left(1 - A_s \frac{V}{Q}\sqrt{\frac{k_o D}{2mC_i}}\right)^2\right) - A_s k_o \delta}{1 + \left(\frac{C_i}{C^*}\right)^p}\right] \tag{9}$$

where C* - influent concentration at which OLR is identical to the L*, at same flow rate and volume. In the equation (8) and (9) the Ottengraf's model is not purely an algebraically practical to give mathematical continuity equation. Inside the biofilter, diffusion and reaction defining stage simultaneously occur.

Ingredients and Methods: The packing materials used in this analysis were collected from the district of villupuram, Tamilnadu, India. The seeds were processed and dried for one day in an hot air oven at 90 ° C. The processed packing materials are packed and prepared for use in airtight containers. The biofilter used sludge as inoculum in waste water treatment plant. Activated sludge obtained from paper industry, Sivakasi, India. To increase the growth period, microorganisms in the sludge were acclimatized to VOCs. A liter of activated sludge was placed in an sparkling tank for acclimatization and diluted with 2 L of mineral solution. The composition of mineral solution per liter of distilled water was: K_2HPO_4 – 0.91 g; $Na_2HPO_4.2H_2O$ -2.39 g; $(NH_4)_2SO_4$ – 1.97 g; $FeSO_4$. $2H_2O$ – 0.2 g; $MgSO_4.7H_2O$ – 2.0 g; $MnSO_4$. 7 H_2O – 0.88 g; Na_2MoO_4. 2 H_2O – 1.0 mg; $CaCl_2$– 3.0 mg; $ZnSO_4$. $7H_2O$ – 0.04 g and $CoCl_2.6H_2O$ –0.04 mg.

Biofilter Operation: In this study, the pearl millet stack was used as a packing medium. The packing media was sterilized by autoclave before packing. The height of the column was about 1m cylindrical acrylic column with an ID of 0.05 m and filled to a height of 0.75m with the packing media inoculated with paper industry WWTP sludge as shown in figure 1. In this analysis, through double tanks filled with xylene and toluene respectively, the air is fizzed successively. Through mixing with the saturated pure air stream in the mixing chamber, the air stream occupied with xylene and toluene was calibrated for its concentration and pumped upward into the system. The working limits are unique and the investigational design is described in the table 1.

Flow meters, 2-Xylene tank, 3- Humdifier,4-Mixing tank,5-Toluene tank, 6-Humidifer,7- Mixing Tank, 8- Xylene Tank, 9- Toluene Tank, 10. Mixing Tank,11-Mixed VOC biofilter,12- Toluene biofilter, 13- Xylene biofilter, 14-Peristaltic pump, 15- Nutrient Tank,16- Compressor, 17-Humidifier.

Assay Techniques: The VOC influent and effluent concentration in the Cassurinae seed based biofilter was estimated using a PID detector in gas alert system. The CO_2 influent and effluent concentration was determined using a IR detector system.

Performance estimation: The biofilter performance was given below. The results are stated in terms of organic loading rate, RC and RE obtain in the biofilter.

Table 1
Experimental Plan

Phase	Days of Operation	Pure		Mixed			
		Inlet Concentration					
		Xylene	Toluene	Inlet Concentration		Percentage	
				Xylene	Toluene	Xylene	Toluene
A	1-10	0.2	0.2	0.2	0.2	**Start up period**	
B	11-20	0.2	0.2	1	0.2	90	10
C	21-30	0.4	0.4	0.8	0.4	80	20
D	31-40	0.6	0.6	0.6	0.6	70	30
E	41-50	0.8	0.8	0.4	0.8	60	40
F	51-60	1	1	0.2	1	50	50

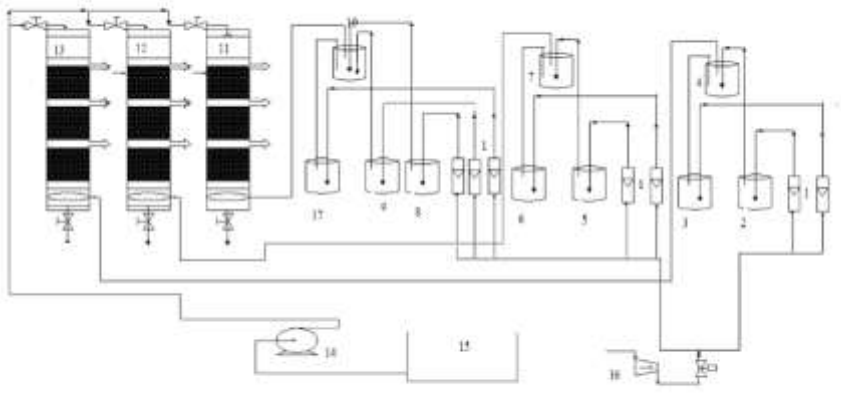

Figure 1: Experimental setup of the biofilter

$$\text{Removal Efficiency} = \frac{C_{in} - C_{out}}{C_{in}} X100 \quad (10)$$

$$\text{Elimination capacity} = \frac{F(C_{in} - C_{out})}{V} \quad (11)$$

$$\text{Organic loading rate} = \frac{F(C_{in})}{V} \quad (12)$$

where C_{in} and C_{out}- influent and effluent VOC (g/m^3), F - flow rate of the air (m^3/h), V -Volume of the packed bed reactor (m^3).

Results and Discussion

The performance of the biofilters in the experiments is given in Fig 2 - 5. For the treatment of pure VOC, the whole experimental period (60 days) was split into six consecutive stages, i.e. I, II, III, IV, V and VI. The results of xylene removal are given in Fig 2. The biofilter's RE was 78 percent on the first day during stage I (inlet pollutant concentration= 0.2 g / m^3), which was a start-up time. Then the efficiency of removal was increased due to biodegradation and the stable state was reached 7 days after the start of the experiment. For stages II, III, IV, V, and VI, the influent pollutant concentration was kept at 0.2 0.4, 0.6, 0.8 and 1 g/m^3, respectively. The experiment for removal of toluene was operated in the same way and the stable state was touched 7 days after the start of the experimentation (Fig. 3). Fig. 2, shows that during stages II, III, IV and V the maximum RE of xylene were 96%, 92%, 88% and 84% respectively. In stage VI (inlet concentration = 1 g/m^3), the RE was decreased to 80 %. The RE was highly influenced by the inlet pollutant concentration. For the removal of toluene, 94% removal was detected on the starting stage of operation and the RE in stages II, III, IV and V were 92%, 88%, 84% and 81 % respectively.

Fig. 3 show that during stages VI, 80 % removal was obtained with the average inlet pollutant concentration of 1 g/m^3. The toluene RE also reduced through stage F due to higher inlet pollutant concentration. Treatment of a mixture of xylene (X) and toluene (T) can be divided into five consecutive stages, i.e. A (X- 90%, T- 10%), B (X- 80%, T- 20%), C (X- 70%, T- 30%), D (X- 60%, T- 40%), and E (X- 50%, T- 50%). For xylene treatment (Fig. 4), the removal efficiencies varied during stage A corresponding to the acclimation period of the microbial population and the influence of the inlet pollutant concentration. The steady state was reached on day 9. This suggests that the start-up period for the treatment of a mixture of xylene and toluene was longer than the start-up periods for pure xylene and pure toluene treatment. Removal efficiencies of xylene and toluene as well as treatment of pure VOC in stages A, B, C, D and E, while the RE of xylene in stages F was unexpectedly reduced to 60 percent due to higher toluene concentrations in the biofilter during stage E. For removal of toluene (Fig. 5), parallel results were obtained.

The maximum RE was found to be 88% at stage C, 84% at stage D, 81% at stage E and 77% at stage F. In the stage E, the RE of xylene decreased as in the occasion of pure xylene. The EC, however, is an imperfect biofilter quality metric because it varies with the concentration of pollutants and the size of biofilters and only represents the specific conditions under which they are measured. The EC allows the results of different biofilter systems to be compared directly because, by definition, volume and flow are normalized.

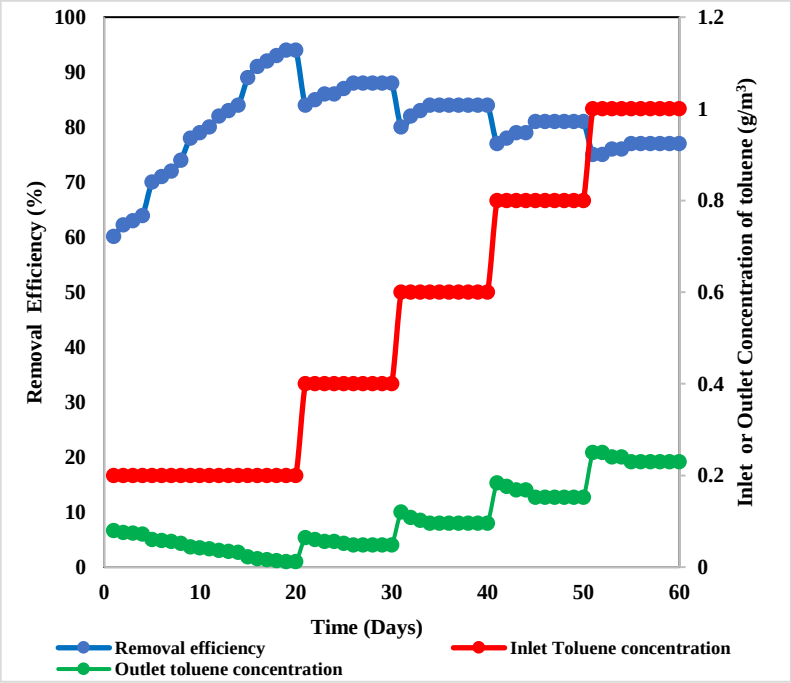

Figure 2: Overall performance of the biofilter for the removal of toluene from air contaminated with pure toluene

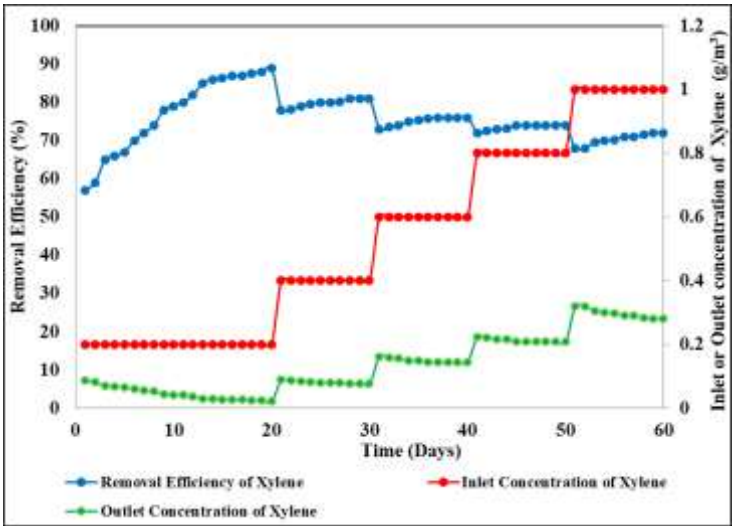

Figure 3: Overall performance of the biofilter for the removal of toluene from air contaminated with pure toluene

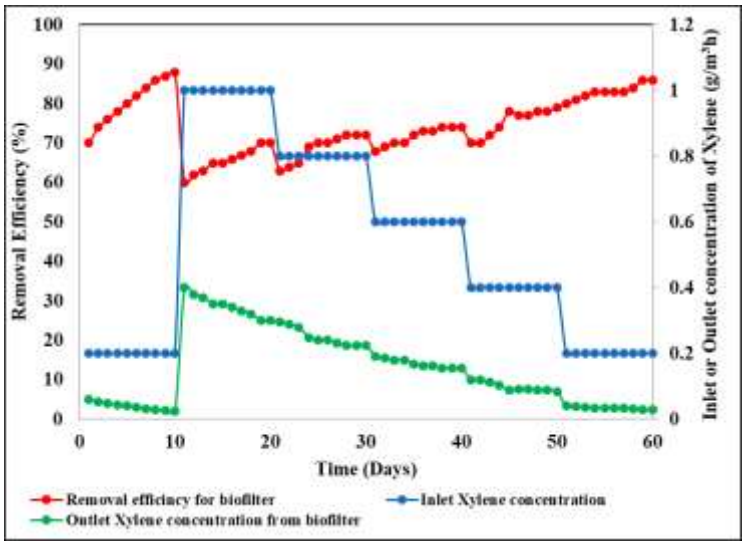

Figure 4: Overall performance of the biofilter for the removal of Xylene from air contaminated with a mixture of Toluene and Xylene

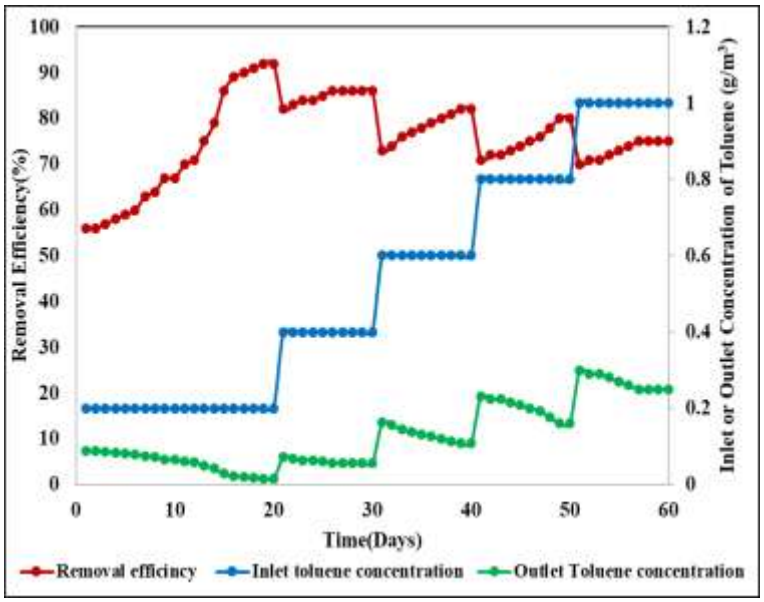

Figure 5: Overall performance of the biofilter for the removal of Toluene from air contaminated with a mixture of Toluene and Xylene

Relationship between EC and OLR: The OLR which represents the pollutant loading on the biofilter per unit time is examined for its effect on the RE of the biofilter. The total OLR is calculated by adding up the distinct OLR of pollutant and plotted against the total EC which represents the joint EC of the two compounds, BT. Fig. 6 and 7 shows the relation between total OLR and total EC. Two different sections were observed. First a nearly linear and then followed by non-linear second region. Fig. 6 shows the EC and OLR curve. The critical EC and the maximum RE for xylene were higher than those found for the biofiltration of toluene. During the biofiltration of mixture of XT, the critical EC for xylene removal was low as observed for pure xylene removal while the maximum EC was developed. On the other hand, the maximum EC for toluene removal from mixtures was same as the maximum EC for removal of pure toluene and the critical EC for toluene removal from mixtures was observed same as mixed toluene.

The results show that toluene elimination was not strongly affected by the presence of xylene, whereas the presence of toluene was significantly affected by the removal of xylene. Perhaps this can be explained by the phenomenon of competition and its solubility and bioavailability.

Ottengraf Model: The values of ottengraf model parameters, kinetic constants and maximum removal capacity for at various operating conditions obtained were tabulated in table 2.

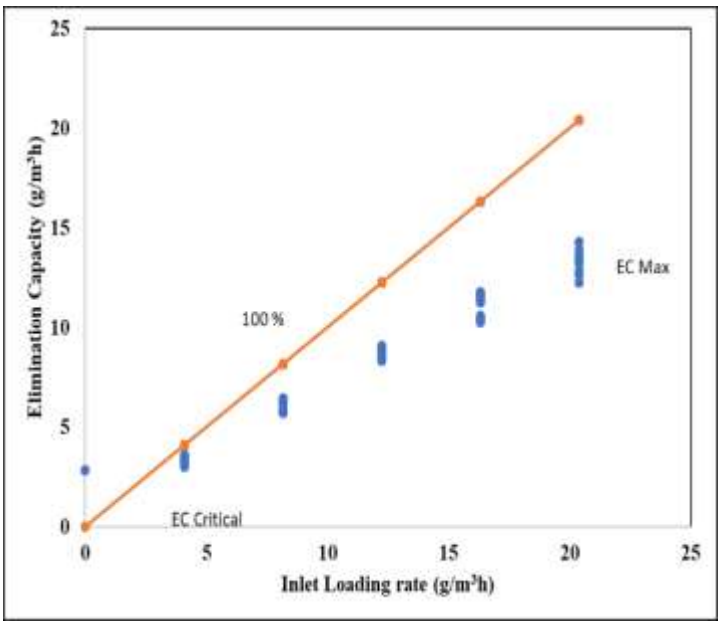

Figure 6: Elimination capacity Vs inlet load for removal of Xylene from air contaminated with mixed Toluene and Xylene

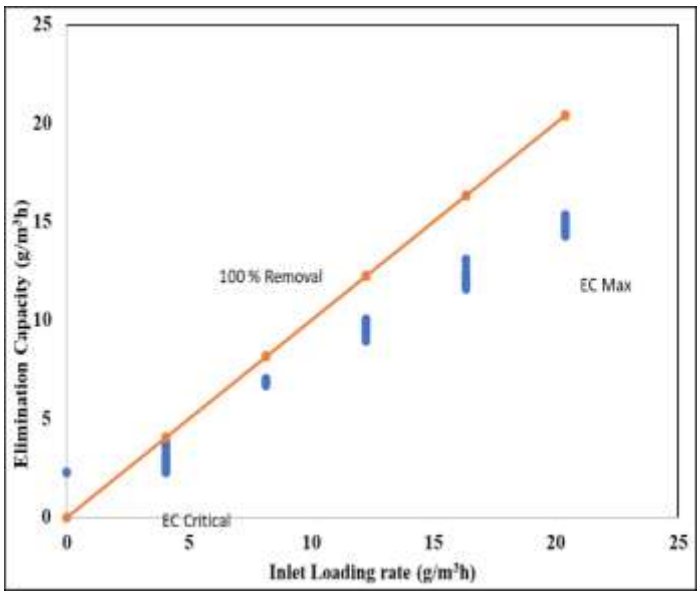

Figure 7: Elimination capacity Vs inlet load for removal of Toluene from air contaminated with mixed Toluene and Xylene

Improved Ottengraf's model: Using equation 13, 14 and from the experimental date the fig 7 and 8 were plotted. The figures indicates the comparison of Ottengraf's model and the improved model. This model relates the EC and the IOLR by the following equation.

$$EC = A_S k_0 \delta + \left[\frac{L\left(1-\left(1-A_S\sqrt{\frac{k_0 D}{2m}}\sqrt{\frac{V}{QL}}\right)^2\right) - A_S k_0 \delta}{1+\left(\frac{L}{L^*}\right)^p} \right] \quad (13)$$

and the calculation of the RE can be easily obtained by using the definitions of EC and L:

$$RE = \frac{C_i - C_o}{C_i} X100 = \frac{EC}{L} X100 \quad (14)$$

EC and L data used for data fitting are obtained during the test to assess EC_{max}. Fixed and calculated parameters were reported in Table 2. The value of L* for the initial set was calculated using Ottengraf's description of the essential Thiele module.

$$\phi_{cr} = \delta\sqrt{\frac{k_o m}{DC^*}} = \sqrt{2} \quad (15)$$

Indeed, as previously described, the transition between the reaction and the diffusion determining step area occurs at $\Phi_{cr} = \Phi$ or at $C_i = C^*$.Using the definition of mass loading rate, L*can be thus expressed as follows:

$$L^* = \frac{C^* Q}{V} = \frac{\delta^2 k_o Q}{2DV} \quad (16)$$

Figure 7 shows the graph between inlet loading rate versus EC, from the figure inferred that Ottengraf and improved Ottengraf model fits very well with data, Similarly, figure 8 shows the inlet loading rate versus RE are well fitted with improved Ottengraf's and Ottengraf model. The figures 8 and 9 shows a good agreement between experimental and calculated data. The change value between diffusion and reaction determining step were presented in Table 2. From the results, it was observed that, the new model found to fit the experimental data well.

Table 2
Model parameters and kinetic constants at various operating conditions

Pollutant	IL ($gm^{-3}h^{-1}$)	K_1 ($gm^{-3}h^{-1}$)	K_d ($gm^{-3}h^{-1}$)	K_0 ($gm^{-3}h^{-1}$)	$C_{critical}$ (gm^{-3})	$IL_{critical}$ (gm^{-3})	$^{\delta}$ (µm)
Xylene	4.16 -25.02	0.771	0.292	17.21	0.945	23	272
Toluene	4.16 -25.02	0.771	0.292	17.21	0.945	23	272
Xylene: Toluene	4.16 -25.02	0.771	0.292	17.21	0.945	23	272

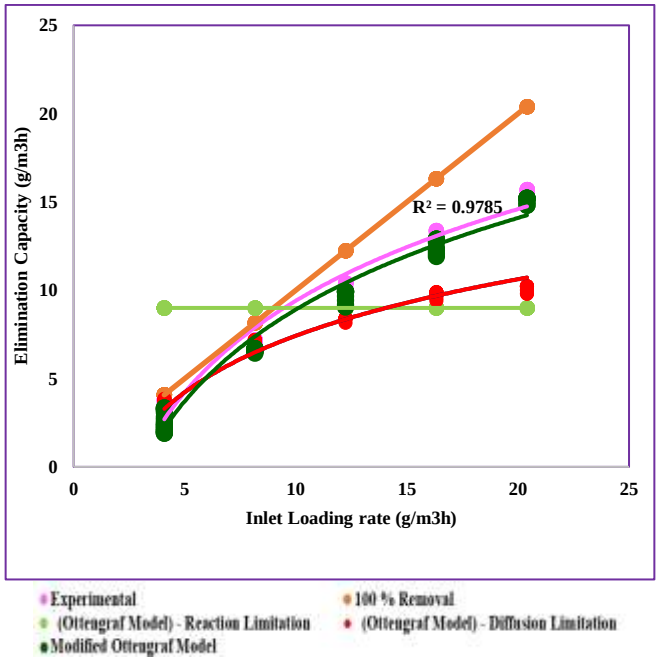

Figure 8: Comparison of experimental and model predicted values for EC of pure Toluene

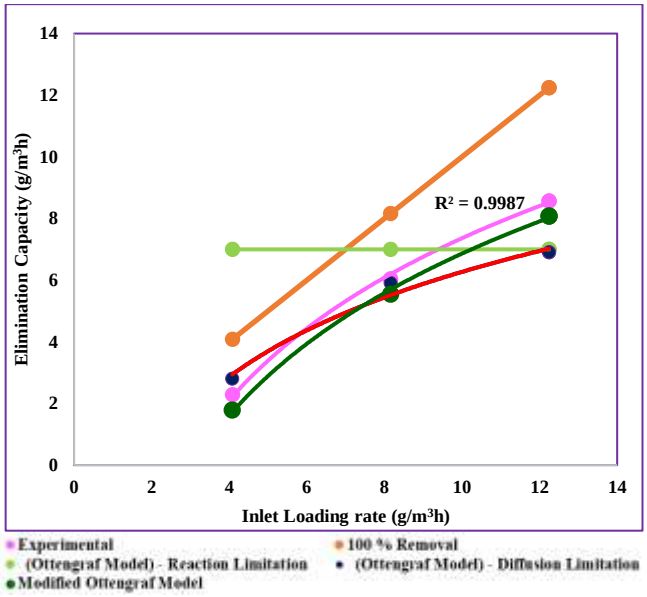

Figure 9: Comparison of experimental and model predicted values for EC of pure Xylene

Conclusion

Xylene and toluene, hydrophobic compounds, were successfully treated in biofilters consisted of a mixture of casuarina seeds and a berl saddles as the filter bed media. The sludge obtained from paper industry wastewater treatment plant was used as inoculum. The presence of toluene in the system significantly decreased the removal rate of xylene while the removal of toluene was not affected by the presence of xylene.

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