Kinetics and Modeling studies of elimination of toluene vapour in a packed column bioreactor

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Abstract
Toluene is a colorless and sweet-smelling greasy fluid used mostly in the petroleum and chemical processing industry and used as the main compound in this work. Continuous experimentation was led in a lab scale bioreactor for controlling toluene as a single contamination. Pearl millet (PM) stacks and berl saddles were used as packing material for association in the growth of microorganism. Toluene was treated successfully, with toluene influent concentrations kept at below 0.4 g m^{-3} and a maximum removal efficiency (RE) of over 96%.

The maximum removal capacity (RC) of the PM stacks based biofilter was 93.8 g $m^{-3}h^{-1}$. The rate of carbon dioxide production (CO_2) and spreading of microorganisms followed toluene RC. The toluene RC and RE were also determined by Ottengraf–van den Oever (OVDO) model. It was detected that at low concentration, the ottengraf model is in better with investigational data. Modified OVDO model was better fits the with both low to high concentration and fits well with experimental values.

Keywords: Biofilter, Pearlmillet, EBRT, Ottengraf model.

Introduction

Many Volatile Organic Compounds (VOC) like benzene, toluene, Xylene, Ethylbenznene etc. are present in the Waste - Water Treatment Plant (WWTP) and discharged in the utility areas[6]. In this VOCs are treated in WWTP and disposed into troposphere owing to these compounds are less volatile. The VOCs emitted from WWTP may show the risky and harmful on human and flora in the closeness of discharge sources [2].

This VOCs emitted from the WWTP origin the chief subject in manufacturing and management authorities in global wise which in turn motivated to all industry to focus on treatment knowledges to reduce these discharges.[3]

The main causes of VOC discharges from all the industry comprise distillation column, pyroloysis, operational process, quick emissions and mainly owing to the leakage from the process equipment and loading tanks to the overall pollution[4]. This colorless liquid toluene has a high-pitched, sweet odor expressive of many food products and acetone. Toluene is manufactured huge scale in industry, and also arises in less quantities in landscape. It is largely used as industrial solvent and best soluble in water. Toluene is an real and common solvent and is present in processes involving many products like nail polish, ion exchange resins, polymer based cellulose acetate and coatings and in vinyl films.

There are numerous techniques present to reduce toluene emitted from the ETP plant. Some of the performances are Oxidation, Adsorption, condensation, burning process and microbial methods. Among these methods biofiltration (Microbial methods) is a inexpensive and current substitute for VOCs elimination.[5] Biofiltration is a development that contains a mixture of different processes mainly adsorption, desorption and biodegradation of waste gas pollutants. Biofilter also required little amount of mineral addition for humidification and growth of microbes without formation of secondary pollutants [1]. Mostly many biofilter reactor having packing material which is used for attachment of biofilm, such as mixed fungi, bacteria and yeast strains. [4]

The packing material is always chosen based on the water holding capacity, large shallow area, less cost efficiency and pore structure for the improving the efficiency. The packing material may be sugarcane bagasse, pressmud, corn cob, compost, peat, perlite and wood chips are under the category of improving the efficiency. The biofilter efficiency is limited by a numeral factors such as influent concentration, gas velocity, pressure drop, Relative humidity, surface area and acidic nature of the packing material.

PM stack is an agricultural residue generated from the separation of PM and stack. This stack mainly used for animal feed and natural fertilizer. Many factories utilized as firewood for the steam boilers, huge amounts are gathered in the factory and making social issues.

Many studies have presented for the high RE in their bench scale packed bed reactors for the removal VOCs under heat sensitive biofilter[3] Using mixed culture the biofiltration of mixture of ethylbenzene - xylene was studied [4] Bakaran et al. 2016 concluded the toluene degradation due to the minerals supply, influent concentration and heat sensitivity in a compost based biofilter.

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 (1983) developed a biofilter model for the removal of VOC.

The main study of the work is to examine the presentation of PM stacks based biofilter mixing with berl saddles. The RC and RE were detected under various working situations. To develop a model for above experimental result.

Ingredients and Methods

Culture Media used for Microorganism: Table 1. shows the mineral salt medium for the mixed microbial culture obtained from a paper industry WWTP, sivakasi, Tamilnadu, India The pH of the medium was adjusted near to neutral and the medium were grownup under human environment in a orbital shaker.

Table 1
Shows the mineral medium

S.N.	Mineral	Weight (g/l)
1	K_2HPO_4	0.5
2	KH_2PO_4	9.0
3	$MgSO_4\,7H_2O$	0.21
4	NH_4Cl	2.0

Packing Material: In this work, the PM stacks was main constitute in the biofilter as packing material. The hole grains of PM stack about 13 to 15 cm in length which can pale yellow, grey colour. The PM stack used in the biofilter for removal of waste gas containing toluene

Toluene: Toluene is a colorless liquid mostly present in the petrochemical, paper and polymer-processing industries, it is main pollutant contributes to the atmospheric.

Biofilter system: In this study, the PM stack was used as a packing medium. The packing material was autoclaved prior to packing in the column. The height of the column was about 1m cylindrical acrylic pipe with an ID of 0.05 m and packed at a height of 0.75m of mixed consortium from paper industry WWTP sludge as exposed in figure 1.

The air from the compressor was passed into the air filtered was divided into twofold air portions. The main percentage of flow was moistened using humidifier to make the air RH was nearly 100%. The other segment of air was permitted to toluene flask to create the pollutant. Then these streams of air were mixed in an air mixing tank and send in bottom of the biofilters in counter current to the mineral solution. The flow velocity were maintained by rotometers to attain the desired toluene loading rate and gas velocity in the biofilter. The mineral solution was sprinkled continuously at the upper section of the reactor for 40 min in every day to maintain desired conditions of water content and supply of minerals to microbes.

Biofilter Procedure: Experiments were achieved for 200 days. The experimental procedure was separated into four units (I, II, III and IV) according to EBRT of gas velocity and inlet toluene concentrations. The working conditions of each sections were briefed in table 2.

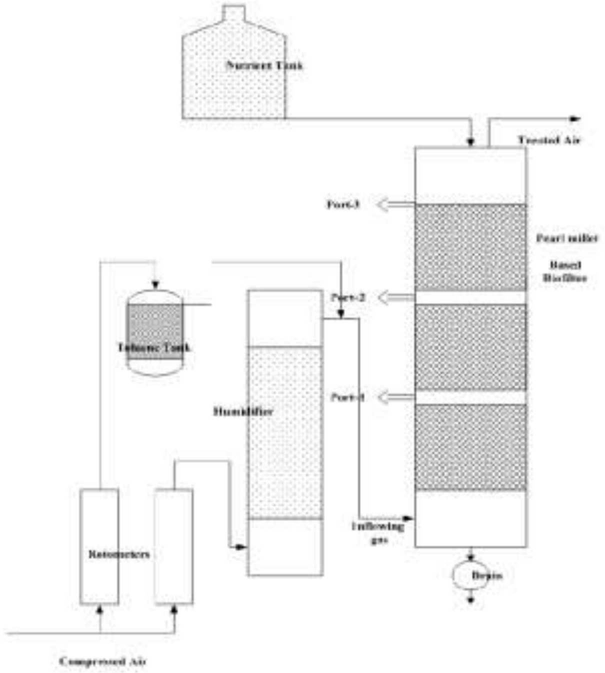

Figure 1: Experimental View for PM stacks based biofilter

Table 2
Shows the experimental plan

Stages	Days of operation	Gas Velocity	Inlet Toluene Concentration
I	1- 10	0.03	0.2
	11-20		0.2
	21-30		04
	31-40		0.6
	41-50		0.8
	51-60		1.0
II	61-70	0.06	0.2
	71-80		04
	81-90		0.6
	91-100		0.8
	101-110		1.0
III	111- 120	0.09	0.2
	121-130		04
	131- 140		0.6
	141-150		0.8
	151-160		1.0
IV	161-170	0.12	0.2
	171-180		04
	181-190		0.6
	191-200		0.8
	201-210		1.0

Assay Techniques: The VOC inflow and outflow concentration in the PM stacks based biofilter was estimated using a PI detector in gas alert system. The CO_2 inflow and outflow concentration was estimated using a IR detector system.

Isolation of strains: Microbial cell counts are find out at each surface of the reactor by taking 1 g of sample from three different place. Microbial media population was counted using culture method to estimate the counts of microbes present and growth during biofilter activity. For this reason, 1 g of packed bed was combined with a NaCl solution of 9 mL (0.9% w / v sodium chloride). The NaCl solution was mixed for 3 minutes and consecutively diluted to 10:10 dilution. Then 0.1 ml of these dilutions was spread over the plates of the agar. For cultivating bacteria and fungi, respectively, nutrient agar and maize meal agar were used. Then all the plates were incubated at a temperature of 28–30°C for 5–7 days and the number of grown colonies was counted by and noted as dry media colony forming unit (CFU) g^{-1}.

Performance estimation: The performance of the PM stack based biofilter performance was shown in table 3. The results are stated in terms of organic loading rate, RC and RE obtain in the biofilter.

Table 3
Performance calculation of PM based biofilter

S.N.	Term	Equation	Unit
1	RE	$\frac{C_{in} - C_{Out}}{C_{in}} X100$	%
2	Inlet Loading rate	$\frac{FC_{in}}{V}$	g/m^3h
3	RC	$\frac{F(C_{in} - C_{Out})}{V}$	g/m^3h
4	EBRT	$\frac{V}{Q}$	Mins

Results and Discussion

Reactor study: Biofiltration of toluene-containing air stream was achieved over a range of 200 days under various operating conditions in a biofilter up-flow mode using PM stack as packing material. Biofilter performance was a collective result of the concentration of pollutant inlets and the rate of gas flow investigated in four different phases as shown in figure 2. Figure 2 displays the toluene removal experimental results of continuous study. The concentration of the toluene in the inlet gases was between 0.2 and 1.2 g m^3. For the first stage of biofilter activity, the gas flow level in the biofilter was 0.03 m^3h^{-1}. Every experimentation was run at a various toluene IC and gas velocity over a range of 10 days. The duration of the initial study for the growth of flora or fauna in the packing material[4].

The first series of tests were performed to avoid an external surface shock to the microflora, working at the lowest gas flow level ($0.03m^3h^{-1}$) and at the lowest toluene concentration($0.2gm^{-3}$). Figure 3 shows the behavior of toluene RC versus toluene Inlet Organic Loading rate (IOLR) and corresponding RE, which was changed consecutively varying gas velocity and influent toluene concentration. This parameter increased frequently with organic toluene loading up to the maximum levels above which it decreased, probably owing to some inhibition of microbial activity by surplus toluene. The maximum values of RC was 4.82 $gm^{-3} h^{-1}$, operating at the same gas velocity ($0.2m^3 h^{-1}$). It is noteworthy that there was scarce relevance whether the EC variations observed with biofilter due to an decrease EBRT or increase in gas velocity. In contrast, a certain deteriorating of performances was evident with progressively decreasing gas velocity at a given organic rate loading value.

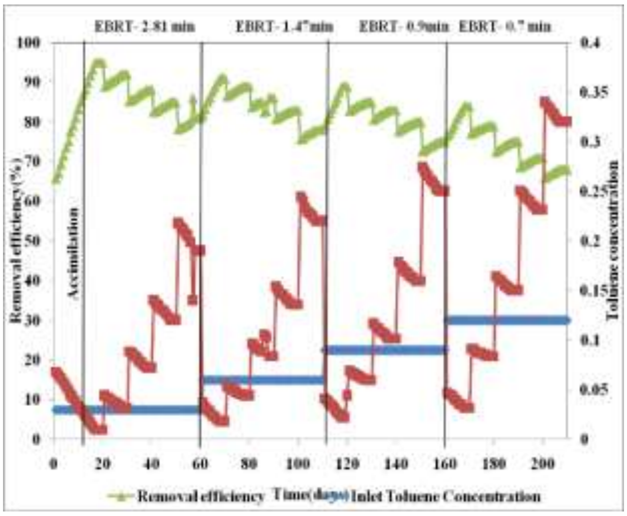

Figure 2: RE toluene by varying different inlet concentration and different EBRTs for PM based biofilter

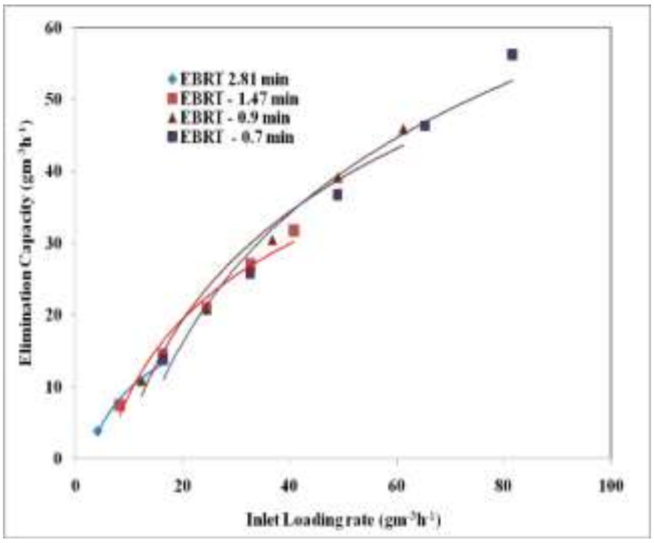

Figure 3: RC vs toluene loading rate for different gas velocity

Profile of bed height: The profiles of toluene with the length of the reactor for various influent concentrations and EBRTs was exposed in Figure 4 to 7. Figure 4 dissipated the RE verses profile of bed height at end of each units in stage 1 20^{th},30^{th}, 40^{th}, 50^{th} and 60^{th} day of biofilter operation. Figure 5 represents the, first phase (EBRT 2.81 min), nearly 61% of the inflow toluene was eliminated in the bottom 0.25 m of the PM stacks based biofilter, 25 % at 0.5 m and remaining at 0.75m of the PM stacks based biofilter for different influent toluene concentration (0.2 to 1 g m^{-3}). Figure 6 shows normalized concentration verses profile of bed height at end of each phase in stage 2 (70^{th},80^{th} 90^{th}, 100^{th} and 110^{th} day) of biofilter operation at an EBRT of 1.47 min.

Similar trend was observed throughout the biofilter cycle. This could be clarified by the existence in parts near the filter bed inlet of more carbon source (toluene), which triggers a higher metabolic reaction[5]. According to the upflow mode of the PM stacks based biofilter, the highest toluene concentration was at the first segment (0-25 cm) of the bed and the minimum toluene concentration was at the upper section of the pearl milled based biofilter (50 -75 cm).

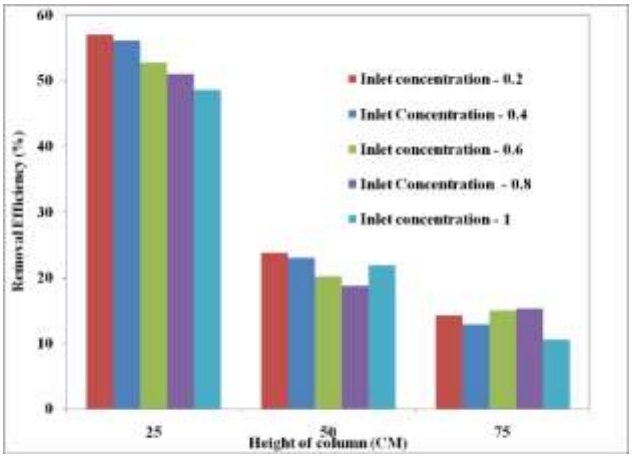

Figure 4: Bed height for the RE of toluene at the EBRT of 2.81min

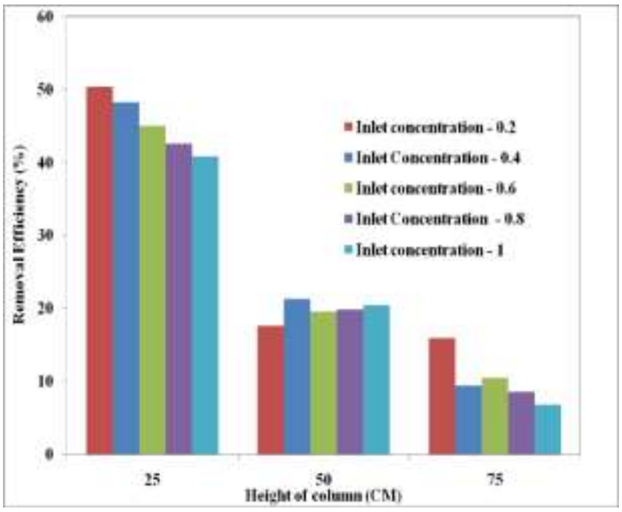

Figure 5: Bed height for the RE of toluene at the EBRT of 1.47min

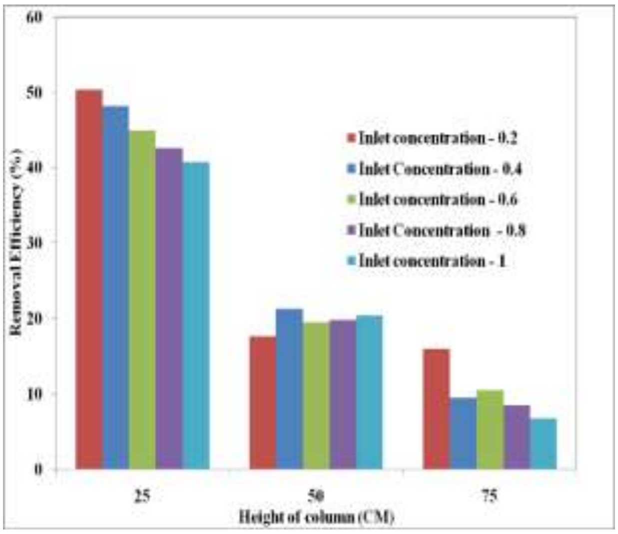

Figure 6: Bed height for the RE of toluene at the EBRT of 0.9 min

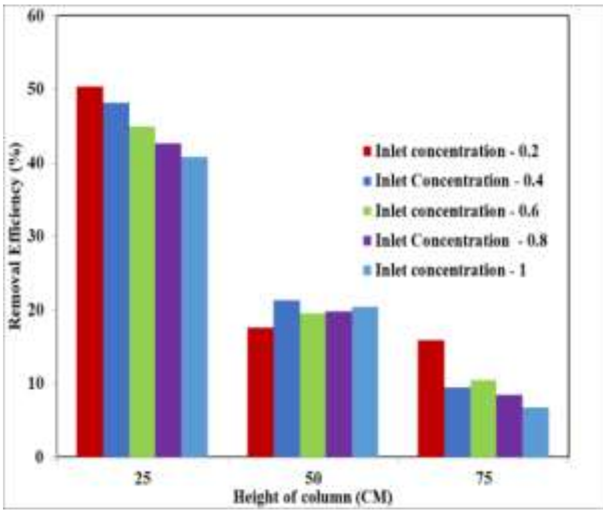

Figure 7: Bed height for the RE of toluene at the EBRT of 0.7min

Carbondioxide Evolution: The production of carbon dioxide PCO_2 in the biofiltration process is an vital limitation demonstrating the step of VOC degradation because VOCs are biodegraded with presents of air into H_2O, CO_2 and made as main source for growth of microorganisms.[5] The weight ratio of PCO_2 to toluene degraded must be 3.08 for the broad oxidation of toluene to H_2O and CO_2, conferring to the subsequent chemical reaction.:

$$C_7H_8 + O_2 \text{---------} 7CO_2 + H_2O \quad (1)$$

The rate of PCO_2 as a function of the toluene RC is given in Figure 8. The data structure states that the amount of CO_2 emitted is strongly associated with the amount of toluene degraded and that the linear correlation is given by the following formula.

$$PCO_2 = 1.907\ CO_2 + 18.3 \quad (2)$$

From the equation, the slope was found in equation [2] displays that around 65% of the degraded toluene was transformed to CO_2. Saravanan et al., 2015 reported similar results for the biofiltration of xylene and p xylene respectively. Biomass output may explain the inconsistency observed in PCO_2 in assessment with the event of peak toluene oxidation.

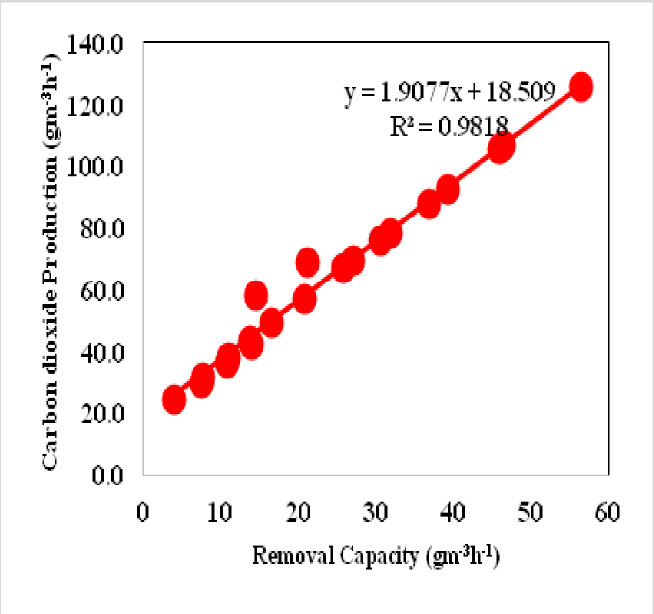

Figure 8: Carbon dioxide production rate and removal capacities of toluene.

Microbial isolation and identification: Clusters of colonies were formed with toluene, respectively, by repetitive subculturing and plating on the Nutrient Agar plate (NA). Two isolates were found to have developed profusely through this process. The isolated strain was maintained by periodic transfer to the nutrient agar slant and processed at $4^{O}C$ for this analysis. Several biochemical tests, including gram staining, were led to classify the two isolated strains. The results exhibited that isolates 1 have a gram-negative and rod-shaped bacteria. The organism was also found to be neutral but negative in the synthesis of indole and hydrogen sulphide and urease tests in oxidase, catalase and lipase (Table 4). All these results are dependable with Pseudomonas and Bacillus species ' various phenotypic characteristics.

Microscopic View: Figure 10 a show the SEM image of PM stack which exposed that very porous and raw exterior with big openings, which allowed the microbial attachment. Furthermore, at the end of the operating cycle, a sample was analyzed using SEM. The surface of the PM stack was bound by a thick biofilm and extended to pores (Figure 10b). Although it is hard to observe the morphology, some coccoid and rod-shaped bacteria are embedded in a matrix. While such dense biofilm restricts pollutant diffusion toward the internal particles, it may increase microorganism tolerance to high toluene concentrations.

Table 4
Biological Characteristics of isolated Strains

Characteristics	Isolated -I	Isolated -II
Morphology		
Cell type (Shape)	Rod	Slender, rod shape
Colour	Yellowish White	**Greyish white**
Size	0.4 -0.5 X 1.55 -2.7 µm	1.5–3 mm × 0.5 mm
Arrangement	Isolated	singly or in pairs
Surface	Smooth	**Smooth**
Density	Opaque	**Translucent – Opaque**
Motility	Positive	**Positive**
Biochemical Test		
Gram,s reaction	+	-
Catalase Test	+	+
Spore	+ **central**	-
Indole Production	-	-
Starch hydrolysis	+	+
Citrate utilization	+	-
Methyl red	+	+
Vogas – Proskauer	+	-
Citrate	-	-
H2S Production	-	+
Urease	+	+
Sugar Fermentation		
Glucose	+	+
Fructose	+	+
Maltose	-	+
Lactose	-	-
Sucrose	-	+
Mannitol	+	+
Xylose	-	-
Probable Strain	**Bacillus Sp**	**Pseudomonas Sp.**

Mathematical Modelling: A mathematical model (OVDO) developed for VOC biodegradation in a biofilter assuming tubular flow and removal is represented by Monod model with zero or first order kinetics. For biofilter operations, the two region are clearly seen one is diffusion limitation and other one is region of reaction limitation of substrate inhibition.

Diffusion Limitation

$$EC = \frac{Q}{V} C_{o,Crit} L \left(1 - \left((1 - k_1 \frac{V}{Q} \frac{1}{\sqrt{C_{o,crit}}} \right)^2 \right) = k_o \quad (3)$$

Hence,

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

Reaction Limitation

$$EC_{max} = A_s k_0 \delta \quad (5)$$

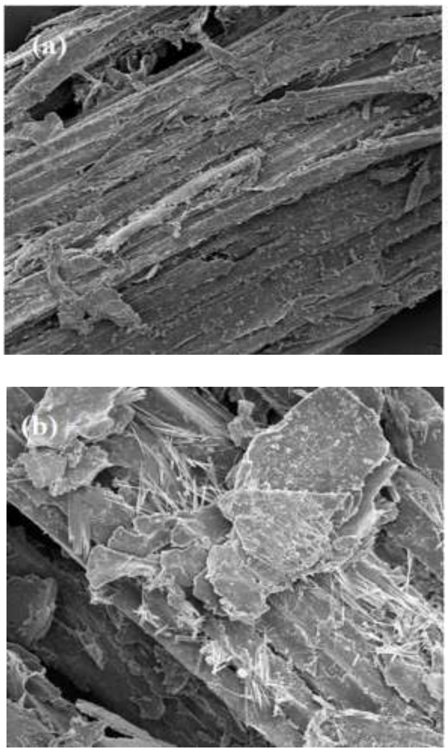

Figure 9: SEM of the filter media (a) before and (b) after biofiltration.

Modified OVDO model: OVDO proposed a new model using the conversion between the two conditions (diffusion limitation and the reaction limitation) is governed by the Thiele number. The new model gives the two OVDO equations a mathematical consistency. It allows for simultaneous analysis of the influence of both phenomena. The revised model was tested in this analysis using experimental data. The revised OVDO model has also been used in this analysis. The new model addresses the drawbacks of diffusion and reaction as a single equation.

$$\eta = \frac{C_i - C_o}{C_i} = \frac{EC}{L} = \left(EC_{max} + \frac{\left(EC_{dl} - EC_{max}\right)}{1 + \left(\frac{L}{L^*}\right)^p} \right) / L \quad (6)$$

$$EC = A_s k_0 \delta + \left[\frac{L\left(1 - \left(1 - A_s\sqrt{\frac{k_0 D}{2m}}\sqrt{\frac{V}{QL}}\right)^2\right) - A_s k_0 \delta}{1 + \left(\frac{L}{L^*}\right)^p} \right] \quad (7)$$

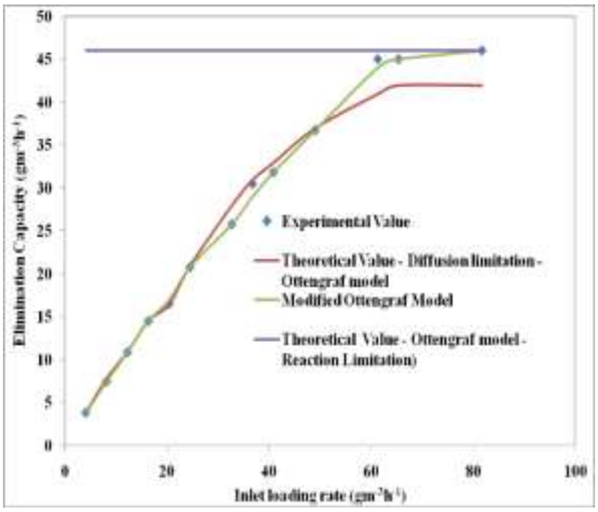

Figure 10: Comparison of new model and ottengraf model for toluene removal in a PM stacks based biofilter.

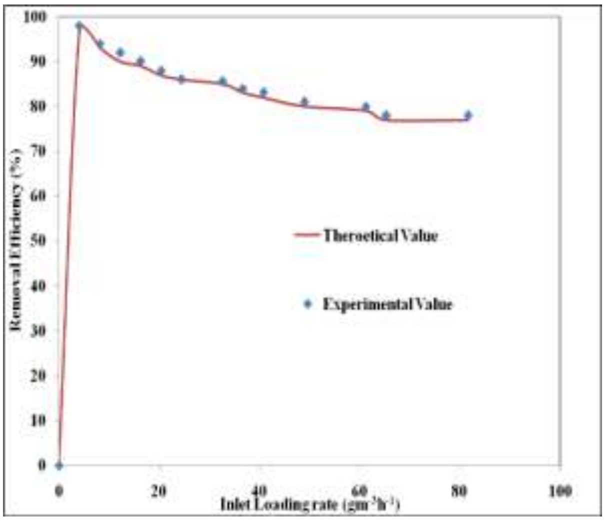

Figure 11: Comparison of investigational data versus predicated value of new model developed for RE of toluene using PM stack based biofilter.

Figure 10 shows the inlet loading rate versus maximum RC for both the models. The test constraint was used consecutively to measure the inlet loading rate necessity of the removal output. Figure. 11, displays the fitting of the biofilter's RE versus inlet load speed. From the figure 11 demonstrated between experimental value and predicated value are fit well. The changeover value among diffusion and reaction limitations were shown in table 5. The new model was a better agreement with the investigational data, given all the shortcomings found and addressed.

Conclusion

The PM stack based biofilter was appraised for the biofiltration of toluene vapours. This packing material has established by the ideal biofilter material, with satisfactory RE laterally the height of beds. High value of toluene concentration up to 1.2 g m^{-3} have been adequately treated, with a extreme RC of 95 g m^{-3} h^{-1} was reached.

Table 5
Kinetic constant for the PM stacks based biofilter

C_{in} (gm^{-3})	GF (m^3h^{-1})	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})	δ (μm)
0.2 - 1.2	0.03	4.16 -25.02	0.771	0.292	17.21	0.945	23	272
	0.06	12.48-50.04	0.745	0.345	31.45	0.942	42	300
	0.09	18.72-75.06	0.731	0.281	69.2	0.91	69	321
	0.12	24.96-100.08	0.727	0.291	72.9	0.9	80	399

The PM stack based biofilters displayed a good performance in terms of RC and long-term constancy. OVDO model was tested and fitting confirmed a better agreement between predicated and experimental value. The model showed a better agreement among the measured data and the process physics so it could provide a reasonable numerical mean for the preliminary design of the system.

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