4. Biodegradation of Benzene, Toluene and Xylene (BTX) from Air Using Modified Compost Beads as Biofilter Media

As discussed in the previous sections the compost is most widely used media for biofiltration ofVOCs.Compost itself has most of the desirable properties and inherently contains many nutrients essential for growth and sustainability of microorganism. Therefore compost was selected as base material for preparation of biofilter media in the first experiment.

4.1 Preparation Method of PVA/compost/KNO_3Composite beads

The methods of preparation of composite beads are similar to themethod adopted by Chan and Lin (2006). Compost (200 g) was added to an aqueous solution (800 ml water mixed with 128 g KNO_3) in a 2000 ml bucket. The mixture was sealed and kept for approximately 24 h for compost to adsorb KNO_3 and water. Now, an aqueous solution using 2000 ml water mixed with 128 g $KNO_3$was prepared and 200g of PVA powder is added to it and the final mixture was heated to 90°C for dissolution. The Compost/KNO_3 mixture was slowly added to the PVA/KNO_3 mixture at 90°C and stirred for 1.5 h maintaining thesame temperature and then cooled to 40°C. The final cooled mixture was slowly dripped into a 6% boric acid aqueous solution (1500 ml) for 60 min leading to the formation of beads. The beads were transferred into the phosphate aqueous solution (150 g $NaH_2PO_4.2H_2O$ and 335 g $Na_2HPO_4.12H_2O$ in 450 ml water) and stirred for 30 min, and then immersed in the 0.384M KNO_3 solution because some amount of water soluble nitrogen was dissolved out in boric acid solution. Finally, beads were dried and stored in a desiccator at room temperature for use. Bed porosity, dry weight, moisture retention capacity and pH of the composite beads were estimated using theconventional method of analysis.CHN content of composite bead was measured using CHN analyzer (Perkin Elmer).

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4.2 Result and Discussions

4.2.1 Physico-chemical Characterization Results

Physico-chemical characterization results of modified biofilter media were shown in Table 4.1. The characterization results show that the modified media has neutral pH, high bed porosity and high moisture retention capacity.

Table 4.1: Initial characteristics of PVA/Compost /KNO_3 composite beads**.**

Sl. No.	Parameters	Composite bead	Compost Beads (Mathur et al;2007)
1.	Particle size(mm)	6-8	
2.	pH at 26^{0}C	7.1	-
3.	Bed porosity,%	81	-
4.	Moisture retention capacity, %	68.3	69.2
5.	Dry weight,%	0.67	-
6.	C H N Content % C H N	 28.69 1.83 3.2	 7.58 3.58 0.065

4.2.2 Performanceof biofilter under individual loading rates of Benzene, Toluene and Xylene

The continuous biodegradation studies of Benzene, Toluene and Xylene (BTX) vapours in air were carried out for a period of 57 days in three distinct phases as shown in Tables 4.2. The objective of this experiment was to test the modified media for varying condition At the start of the operation, the biofilter was operated for 18 days with a high EBRT of 57.9 sec and low inlet concentration ranging from 0.3317 to 1.1275, 0.1221 to 0.8565 gm^{-3} 0.055 to 0.4912 respectively for benzene, toluene and xylene with aim to acclimate the biofilter unit.Removal efficiencies of 90.60, 92.50 and 87.40 % were achieved for benzene, toluene and xylene respectively at steady state (on the18th day of operation) in this phase. The acclimation phase was confirmed by almost constant RE during the last period of this phase (Fig. 4.1). During phase I, theflow rate was increased to 0.12 m^3h^{-1} with corresponding EBRT of 28.4 sec. The inlet concentrations of benzene, toluene, and xylene vapourincreased and were varied in the range of 1.5411- 2.61124, 1.0555- 2.3611 and 0.6931- 2.1323 g m^{-3} respectively and the removal efficiencies were observed in the range of 90 to 96%, 89 to 93%and 85 to 94%. The maximum removal efficiencies of 96.80, 97.50 and 94.5%were achieved on the29th day of operation for benzene and toluene and on 27thday of the operation for xylene. Further increase in inlet concentrations, a reduction in RE wasobserved. At theend of this phase, removal efficiencies reduced to 90.01, 89.15, and 85.02 % respectively for benzene, tolueneand xylene.

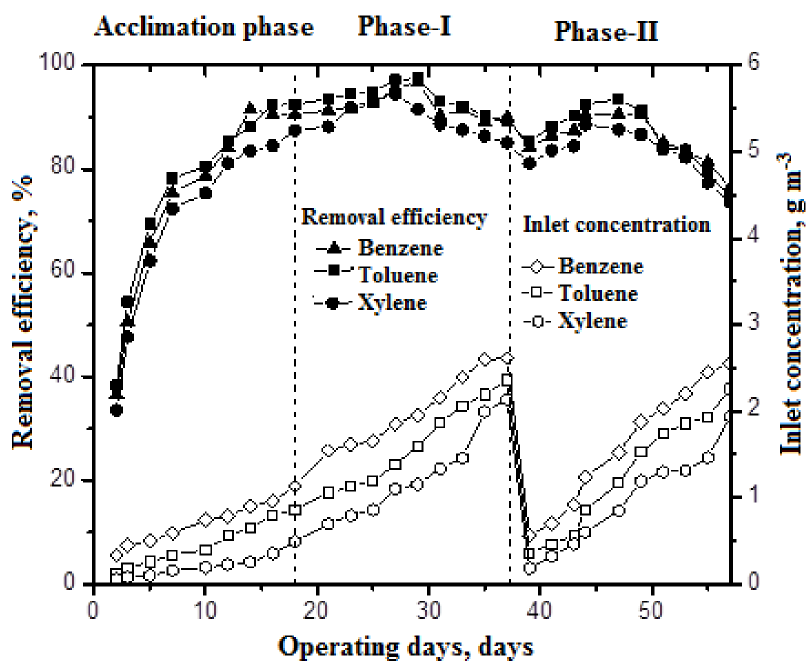

Fig.4.1: Variation of removal efficiency with change in inlet concentration of BTX and gas flow rates

During phase II, thegas flow rate was again increased to 0.19 $m^3 h^{-1}$ corresponding to EBRT of 18.5 sec and inlet concentrations were decreased to 0.55, 0.35, 0.18 g m^{-3} benzene, toluene and xylene respectively. When inlet concentration increased continuously from 0.55, 0.35, 0.18 to 2.55, 2.25, 1.93 g m^{-3} for benzene, toluene and xylene, RE first increased and reached 90.6 %, 93.5 % and 87.6 % on 47th day and then decreased to 70.4 %, 74.6 % and 73.5 % respectively at the end of this phase. Results show that biofilterachieved high level of removal efficiency and responded very quickly to the change in flow rate and inlet concentration of all components of BTX.

Table 4.2: Experimental scheme for continuous benzene, toluene and xylene biodegradation.

Nature of biofilter operation	**Inletconc. range of benzene (g m^{-3})**	**Inletconc. range of toluène (g m^{-3})**	**Inletconc. range of xylene (g m^{-3})**	**Operating Time (Days)**
Acclimation phase	0.3317- 1.1275	0.1221- 0.8565	0.055- 0.4912	18
Phase I	1.5411- 2.61124	1.0555- 2.3611	0.6931- 2.1323	19
Phase II	0.5552- 2.5515	0.3563- 2.2561	0.1811- 1.9356	20

4.2.3 Effect of Inlet Loading Rate on Removal Efficiency and Elimination Capacity

Loading rate is actual amount of pollutants added per unit time for unit volume of the biofilter column. This parameter combines the effect of flow rate as well as inlet concentration and so more reliable operating parameter rather than flow and concentration. Similarly EliminationCapacity (EC) is elimination of pollutants per unit time for unit volume of biofilter column and so it provide better picture of performance of biofilter unit. The biofilter should be operated with high EC and at required level of RE. Figures 4.2, 4.3and 4.4 shows the effect of inlet loading rates on removal efficiencies and elimination capacities for benzene, toluene, and xylene. In the acclimation period EC and RE both increased quickly but after that RE attained almost constant level whereas EC increases linearly with increase in loading rate.A nearly linear relation between the inlet loading rates and elimination capacities were observed till loading rates of 331.00, 299.29 and 252.39 g m^{-3} h^{-1} for benzene, toluene and xylene respectively. Further increase in loading rate, elimination capacities of all three components of BTX mixture were increased gradually and reached their maximum values of 388.33, 327.73 and 276.84 g m^{-3} h^{-1} at inlet loading rates of 477.36, 439.02, and 376.65 g m^{-3} h^{-1} respectively. Beyond loading rates of 331.00, 299.29 and 252.39 g m^{-3} h^{-1} for benzene, toluene and xylene, respectively,RE started decreasing and EC increased with aslow rate. At higher loading rate corresponding to either high flow rate or inlet concentration, the decrease in RE and slow rise in EC may be due to short residence time of the pollutant or the residence time which may not be sufficient to degrade the pollutants, substrate inhibition or production of some intermediates or metabolite which are inhibitory in nature and change in controlling mechanism from mass-transfer to bio-reaction.

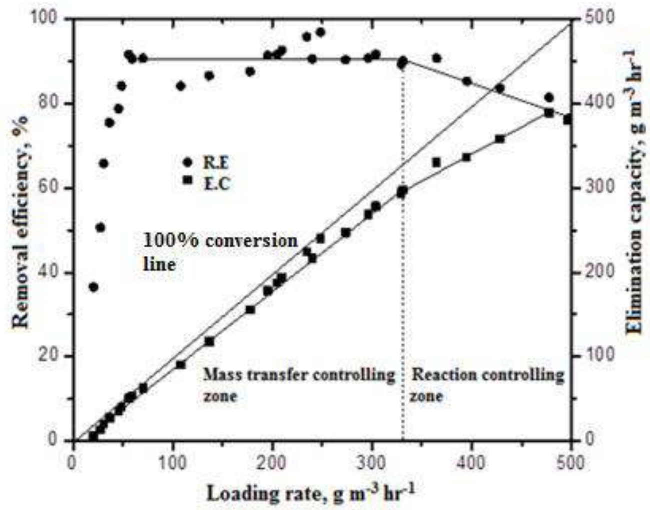

Fig. 4.2: Influence of Benzene loading rate on elimination capacity and removal efficiency of thebiofilter.

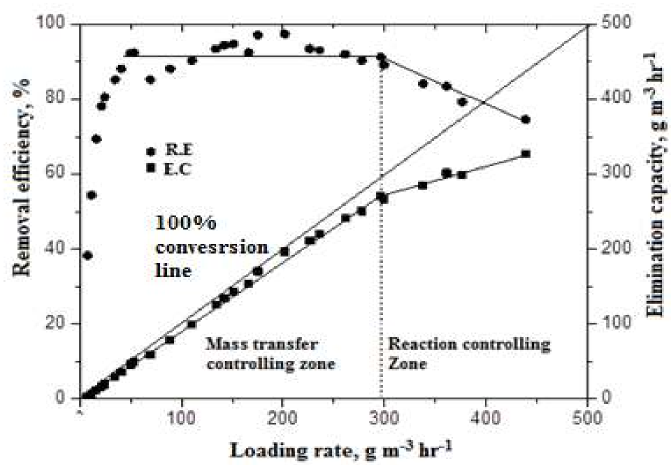

Fig. 4.3: Influence of Toluene loading rate on elimination capacity and removal efficiency of thebiofilter.

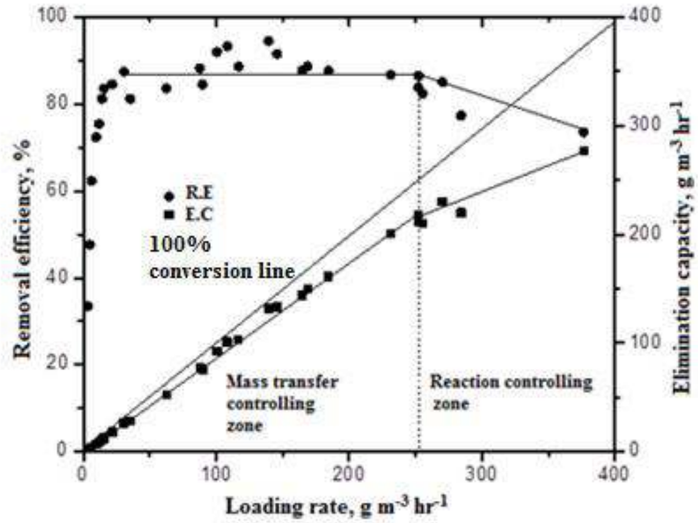

Fig.4.4: Influence of Xylene loading rate on elimination capacity and removal efficiency of thebiofilter.

4.2.4 Performance of biofilter under combined loading rates of BTX

The results and discussion presented in above section is for individual loading rate of BTX. The performance of the biofilter for combined inlet loading rate of pollutant is presented in the subsequent section. Operating conditions of each phase in the biofilter experiments for combined loading rate of BTX biodegradation are shown in Table 4.3.

Table 4.3: Experimental scheme for continuous BTX biodegradation

Nature of biofilter operation	Flow Rate (m^3 h^{-1})	EBR T (sec)	Inlet Concentration range (g m^{-3})	Removal Efficiency (%)	Operating Time (Days)
Acclimation phase	0.06	57.9	0.50 – 2.47	36.6-90.62	0-18
Phase I	0.12	28.4	3.28 – 7.10	91.35-88.22	19-37
Phase II	0.19	18.5	1.09 – 6.74	83.99-74.98	38-57

During the starting period, the biofilter was operated with an initial flow rate of 0.061 m^3 h^{-1} corresponding to an EBRT of 57.9 s for 18 days. Removal efficiency gradually increased during this phase with achange in inlet concentration and removal efficiency of 90.62 % was achieved on the 18th day. It is observed that initial removal efficiency of BTX was as low as 36.6 % which further increases with time up to 90.62 % at steady state. Microbes take some time to get acclimated and microbial population on the biofilter media increases with increase in time. Removal efficiency increased from very low value (36.6 %) to 90.62 % with the increase in microbial population. During Phase I, theflow rate was increased to 0.124 m^3 h^{-1} with corresponding EBRT of 28.4 s. The inlet concentration of benzene, toluene and xylene (BTX) vapour was varied in the range of 1.54 - 2.61, 1.05-2.36, 0.69-2.13 gm^{-3} and the overall removal efficiency was observed in the range of 88 to95%. The maximum overall removal efficiency of 95.83% was achieved at an average inlet concentration of 1.443 g m^{-3} and under high total loading rates of 549.02 g/m^3h. Further increase in inlet concentration and loading rates, reduced the removal efficiency to 88.22 % due to high concentration.

During last phase (II) gas flow rate was increased to 0.191 m^3h^{-1} with corresponding EBRT of 18.5 s. The inlet concentration of benzene, toluene and xylene vapour was varied between 0.55 to 2.55 g m^{-3}, 0.35 to 2.25 g m^{-3}, and 0.18 to 1.93 g m^{-3}.The removal efficiency increased and reached to 90.83 % with adecrease in concentration. With further increase in concentration along with loading rates the removal efficiency decreased and reached a value of 74.98 % at a high total loading rate of 1312.19 g $m^{-1}h^{-1}$.

In the present study, the RE of 95.83 % is achieved during Phase I (on 27th day) by the use of Composite Beads bed made of compost for a total inlet BTX load of 549 g m^{-3} h^{-1}.

4.2.5 Effect of BTX Loading Rate on Removal Efficiency (RE) and Elimination Capacity (EC)

Fig. 4.5shows the effect of different inlet loading rates on removal efficiency and elimination capacity. The total inlet load of BTX during the experiment was in the range of 31.63 to 1312.19 g m^{-3} h^{-1}.During the acclimation phase, the removal efficiency of BTX increased from 36.6 % to 90.62 % as total inlet load varied from 31.63 to 153.89 g m^{-3} h^{-1}. In Phase I, total inlet load was increased from 417 to 900.58 g m^{-3} h^{-1} and removal efficiency varied in the range of 91.35 % to 88.22 %. The maximum removal efficiency of 95.83 % was achieved at a total inlet load of 549.02 g m^{-3} h^{-1}. In phase II, the total inlet load increased to 212.61g m^{-3} h^{-1} due to adecrease in inlet concentration and varied up to 1312.19 g m^{-3} h^{-1}. With the increase in inlet loading rate,RE first increased up to inlet loading 892.33 g m^{-3} h^{-1} and then it became almost constant. At total inlet loading 892.33 g m^{-3} h^{-1} (approx.) of BTX, the controlling mechanism changes from mass transfer to bioreaction.A nearly linear relation between the inlet load and the EC was observed till a total loading rate of 892.3 g m^{-3} $h^{-1}$and after this, EC increased slowly and reached its maximum value of 983.9 g m^{-3} h^{-1}. The results clearly indicate that increase in loading rate resulted in better utilization of the biofilm present in the biofilter and that is why RE remained almost constant and EC increased rapidly. The results are quite promising because without supply of nutrient the biofilter was continuously operated for 57days at very high combined loading rate and successfully degraded all component of BTX. In the similar experiments, Mathur and Majumder (2007) showed a removal efficiency of around 99.5 % after 30 days for the removal of BTEX using compost and GAC as the packing material for a lower inlet load.

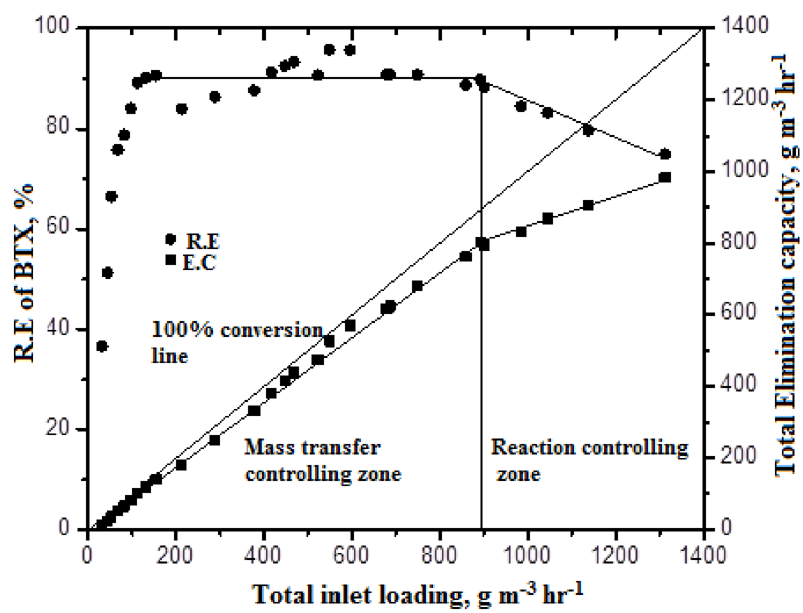

Fig.4.5: Influence of BTX loading rate on elimination capacity and removal efficiency of thebiofilter.

4.3 Kinetic Analysis

In the past, many researchers (Ramirez et al., 2008; Sologar et al., 2003, Hirari et al., 1990) used Michaelis–Menten equation in their respective studies to describe thekinetics of

VOCs biodegradation because of its simplicity.It is widely used to explain the behavior of the system under steady state condition. In the biofilter, if overall biodegradation rate is being controlled only by the bio-reaction, the EC should commonly follow the Michaelis-Menten model (Hirai *et al.,* 1990; Ramirez *et al*., 2008) under the condition of no oxygen limitation. In this model, it is assumed that at the steady state, the microorganism's growth rate is balanced by its own decay rate, resulting in the biological equilibrium of the system. The linear form of the Michaelis-Menten model is commonly known as Line weaver–Burk equation.

$$\frac{1}{EC} = \frac{Ks}{EC_{max}}\frac{1}{C_{ln}} + \frac{1}{EC_{max}}$$

Here ECmax is the maximum EC in the biofilter without any inhibition or substrate limitation, *K*s is the saturation constant corresponding to Cin at which EC = (ECmax/2), and C_{ln} is the logarithmic average of the inlet and outlet concentrations of VOCs in the gas phase.Fig.4.6 represents the plot between 1/EC versus $1/C_{ln}$ and based on the plot the Michaelis-Menten constants were evaluated. The value of EC_{max} was found to be 0.218, 0.255, 0.123 g $m^{-3}s^{-1}$ for benzene, toluene and xylene respectively. Similarly, the values of *K*s for BTX were found to be 1.72, 2.21, 0.79 g m^{-3} respectively. In all calculations correlation coefficient (R^2) was more than 0.95. The EC_{max} and Ks values reported for benzene, toluene and xylene in a coal based biofilter degrading MTBX in the biofiltration study done by Mathur and Majumder (2008) were 0.16, 0.033, 0.024 g $m^{-3}sec^{-1}$, and, 2.305, 0.736, 0.679 g m^{-3} respectively which is well comparable with the values obtained in this work. The EC_{max} value predicted by the model equation were higher than the experimentally observed maximum elimination capacity for benzene (0.0107 g $m^{-3}s^{-1}$), toluene (0.091 g $m^{-3}s^{-1}$) and xylene (0.077 g $m^{-3}s^{-1}$) respectively. The results indicate that there is still scope to optimize the process parameters for getting higher elimination capacity.

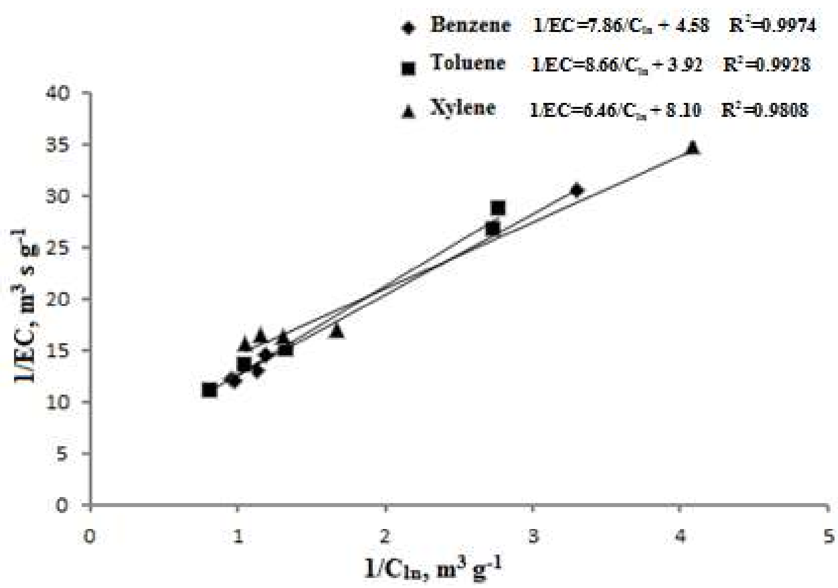

Fig. 4.6: Determination of Michaelis–Menten kinetic constants of benzene, toluene, and xylene.

At last, we can summarize that biodegradation of BTX in the biofilter packed with compost modified composite beads was demonstrated very good results even at higher loading rates without asupply of nutrients for 57 days of operation.Physicochemical characterization results indicated that the composite beads possess most of the favorable properties required for successful biofilteroperation. As compare to compost beads used by Mathur*et al*, 2007 the present modified media has better characteristics.The compost based modified biofilter achieved amaximum removal efficiencyof95.8% at an inlet load of 549 g$m^{-3}h^{-1}$.Maximum elimination capacity of 983.9 g $m^{-3}h^{-1}$ was obtained at a total BTX loading of1312.19 g $m^{-3}h^{-1}$. The maximum removal efficiency for toluene was obtained followed by benzene and xylene. No medium compaction and very little pressure drop were seen in the biofilter media throughout the experiment.Bed temperature was always found more than inlet stream temperature indicating exothermic biochemical reaction in the biofilter.During thewhole operation, variations in inlet stream and bed temperatures were found in the range of 26.8-31.2 and 28.9-36.2^{o}C, respectively, and small fluctuation was observed in the pH (6.95-7.28) of the leachate. Relative humidity of inlet stream was found in the range of 87-95%. And pressure drop across the bed was found to be 4-6 mm water/unit bed length during the whole experiment.

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