3. Method and Material

Biofiltration of Methyl ethyl ketone, Toluene, Xylene (Collectively known as MTX), Benzene, Toluene and Xylene (Collectively known as BTX) and Styrene have been investigated in a laboratory scale biofilter packed with physicochemicallymodified biofilter packing media.

3.1 Selection of Packing Media

Three novel modifiedbiofilterpacking media using compost, wood charcoal and a mixture of compost and wood charcoal as abase material have been prepared in our present study with theaim to carry out the biofiltration operation without external supply of nutrients.

Selection of compost and wood charcoal is based on the fact that these materialspossess many of qualities such as large specific area, larger water retention capacity, lower bulk density, ease of availability and lower cost. Compost also contain most of the nutrients required for growth of the microorganism and known for superior performance with only limitation of durability and some times higher pressure drop whereas wood charcoal has good adsorption properties which is very helpful in successful biofiltration operation.

3.2 Selection of Target VOCs

Paint solvent mixture methyl ethyl ketone, toluene and xylene (MTX),petrochemical solvent mixture i.e. benzene, toluene and xylene (BTX) and styrene were used as target VOCs.All chemicals used were analytical grade and laboratory grade reagent from Merck Specialities Pvt. Ltd., Mumbai, India. The chemical and physical properties of these chemicals are given in thefollowingtable.

Methyl ethyl ketone (MEK) is a volatile and potentially explosive colorless organic solvent.It is mainly used in the paint industries.MEK is known to have chronic toxicity if inhaled. Eye and lung irritation, drowsiness and dizziness and central nervous system

depression in human beingscaused by MEK present in theair in high concentration.MEK is generally not regarded as a carcinogenic agent.

Clean Air Act Amendment (CAAA 90) proposed by US EPA regarded toluene as a hazardous air pollutant.It is highly volatile organic compound. It is colorless liquid. Water solubility of toluene is poor. It has asweetodour.It is used to produce benzene and also used as a solvent. Toluene is added to gasoline to improve its octane ratings. It is used in the manufacturing of many polymer products like nylon, plastic soda bottles and polyurethanes. It is also used in the synthesis of pharmaceuticals. The central nervous system (CNS) may be affected by the exposure of toluene. It has been reported that central nervous system depression may occur in thehuman body if exposed to high concentrations of toluene. However, limited or no evidence of the carcinogenic potential of toluene is reported yet.

An aromatic hydrocarbon consisting of a benzene ring with two methyl substituents is known as xylene with a molecular formula of C_8H_{10}.There are three isomers of xylenes ortho, para and metaxylene. It is used in pesticide and leather industries as asolvent.Xylene can cause Irritation of the eyes, gastrointestinal effects and neurological effects to the human body. Headache, dizziness, fatigue, tremors, incoordination, cardiovascular, and kidney effects have also been reported. However, carcinogenic effects of mixed xylenes in humans being are not known.

Organic compounds such as benzene, toluene, and xylene (collectively known as BTX) are the most common contaminants from petrochemical industries because of their increasing use as gasoline and solvent. Due to their toxic and carcinogenic properties, these compounds are athreat to human health. BTX are classified as main pollutants by the US Environmental Protection Agency because they are acommon organic contaminant in oxygen-limited soils. A

Mixture of Benzene, Toluene and Xylene (BTX) were selected as target pollutants in our second biofiltration study.

Benzene is a natural constituent of crude oil.Abbreviated form of benzene is Ph–H. It is colorless, highlyflammable liquid with a sweet smell. It is an important component of gasoline because it has high octane number.The central nervous system in both humans and animals may be affected badly due to toluene toxicity.Fatigue, sleepiness, headaches, and nauseaare other bad results after inhalation.

As per Title III of US 1990 Clean Air Act Amendments styrene has been declared as a toxic chemical.A Large quantity of styrene is emitted in the atmosphere during the manufacturing of styrene–butadiene rubber, acrylonitrile–butadiene–styrene and copolymers resins.It is widely used thechemical in any polymer industry. Styrene was selected as target pollutant in our third and fourth biofiltration study.Styrene belongs to anaromatic hydrocarbon group and its molecular formula is $C_6H_5CH=CH_2$. Styrene is also known as ethenylbenzene, vinylbenzene, and phenylephrine.It is acolorless oily liquid that is known to have high volatility and a sweet smell.It is widely usedchemical in thepolymer industry. Styrene is produced by the catalyticdehydrogenation of ethylbenzene. Styrene is regarded as a chemical. The U.S. Environmental Protection Agency (EPA) has described styrene to be a suspected toxin to the gastrointestinal tract, kidney, and respiratory system.

Physicochemical properties of targeted pollutants used in the present study is given in Table 3.1.

Table3.1: The chemical and physical properties of target VOCs of thepresent study.

Property	**Methyl ethyl ketone**	**Toluene**	**Xylene**	**Benzene**	**Styrene**
Formula	CH_3C (O) CH2CH3.	$C_6H_5CH_3$	C8H10	C_6H_6	$C_6H_5CH=CH_2$.
Molecular weight	72.104	92.14 g/mol	106.16 g/mol	78.11 g/mol	104.15
Form and color	Colorless liquid	Colorless liquid	Colorless liquid	Clear, colorless liquid	Colorless to yellowish Liquid
Specific gravity(20^0C)	0.80	0.866	0.866	0.87	0.90
Melting point	-86.35 ^{0}C	-95^{0}C	−47.4 °C	5.5 °C	-30.6 °C
Boiling point	79.6^{0}C	110.8^{0}C	137-140^{0}C	80.1 °C	145.2 °C
Solubility in water	24.0% w/w (20°C)	0.05 ppm (16^{0}C)	106 mg/l (25^{0}C)	0.188% w/w (25^{0}C)	300 mg/l (20^{0}C)

3.3 Chemicals and Reagents

Polyvinyl alcohol (PVA), Boric Acid (H_3BO_3), Potassium Nitrate (KNO_3), Sodium monobasic phosphate ($NaH_2PO_4.2H_2O$) and Sodium dibasic phosphate ($Na_2HPO_4.12H_2O$) have been used in this study. All chemicals used were analytical grade and laboratory grade reagent purchased from Merck Specialities Pvt. Ltd., Mumbai, India.

3.4 Filter Media

Wood charcoal was purchased from the local market.Compost was procured from the dairy form of the Banaras Hindu University, Varanasi,India.These were physicochemically modified to adhere nutrients on their respective surface to make modified biofilter media.

3.5 Inocolumn

The microbial inoculum culture was obtained by acclimating the activated sludge taken from the local wastewater treatment plant. Glucose supply (5 g/day) was added to the suspension during the initial phase of acclimation but was gradually replaced by target VOCs as the only carbon source. This whole long process increased the colony of desirable VOCs degrading microorganism in the mixture.

3.6 Characterization of Filter Media

Physical and chemical characterization were done using standard method. These results are given in subsequent sections..

3.6.1 Dry Weight/Mass Measurement

After preparing composite beads were dried in an oven at 100^0C for one day then cooled in a desiccator. Weights of beads were measured using electronic balance.

3.6.2 Moisture Retention Capacity

Composite beads samples were placed in a beaker, filled with water. The samples were submerged for to fill pores with water. Samples were removed from the beaker and placed over a net of stainless steel.When excess water was removed from the woodcharcoal it was weighed using an electronic balance.The difference in the weights of moist and dry samples gives the water retention capacity.

3.6.3 Bed Porosity

Bed porosity of the modified media sample was determined by the void space of sample to volume ratio. The void space in the modified media was measured using water absorption method. Dry pieces of known volume were placed in a graduated cylinder (500 ml) and water was added toit.The modified media was submerged and then allowed to fill with water. A glass rod was used to dislodge the air bubbles from the wood charcoal pieces. After completely filling the void spaces, the volume of water used to fill the void spaces was noted. Extra precaution was taken to ensure moisture content should not go with samples charcoal. This procedure was repeated three times using different pieces. The porosity of samples was calculated as.,

% Porosity=Volume of water used to fill the void space x100/Volume of Sample

3.6.4 CHN Content

Micro-analysis of carbon, hydrogen and nitrogen were done with the help of CHN analyzer (Perkin Elmer).

3.7 Design and Operating Parameters

The various design and operating parametersforbiofiltration process are defined as;

$$\text{Removal Efficiency (R.E.)} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\,(\%)$$

$$\text{Elimination capacity (E.C.)} = \frac{C_{in} - C_{out}}{V} \times Q \quad (g/m^3.h)$$

$$\text{Pollutant loading (L)} = \frac{C_{in}}{V} \times Q \quad (g/m^3.h)$$

$$\text{Empty Bed Retention Time (EBRT)} = \frac{V}{Q} \quad \text{(s or min)}$$

3.8 Biofilter Setup and Operation

A schematic diagram of the biofiltration column used in the present study is shown in Fig. 3.2.It consisted of four sampling ports, leachate collection section, inlet and outlet ports. The biofilter was made of cylindrical glass column with an inner diameter of 5 cm and overall height of 80 cm. A 15 cm headspace at the bottom was used for the gas inlet and leachate collection while a 15 cm at the top was used for gas outlet. Bed was filled with previously humidified prepared biofilter media up to aheight of 50 cm. The filter material in the column was supported on a stainless steel sieve plate for avoiding excess compression of media at thebottom.Sampling ports are provided at a distance of 12.5 cm each. The gas samples were collected in 15 ml gas samplers from sampling port. The leachate was collected at the bottom of the column. The oil free air compressor (ElgiEquipments Ltd, Coimbatore, India) was used to supply air in up-flowmode.In order to generate pollutant saturated air stream of desirable concentration, the main air stream was divided into two parts. One part of thestream was allowed to bubble through the bubbler containing pure VOC_S. Outlet stream from the bubbler was mixed with humidified main-stream. Controllers were provided in each stream to generate the pollutant saturated air of desirable concentration for the inlet to the biofilter bed. Flow rates of the main air stream and stream to bubbler were measured by rotameters of 0.48-4.8 LPM and 0.08-0.8 LPM capacities,respectively.VOCs loaded air stream were passed through the packing material on which a biofilm was formed. The volumetric composition of Methyl ethyl ketone, toluene and xylene in the bubbler was taken in the ration of 40:45:15.Same volumetric composition was employed forthe benzene, toluene and xylene in the other experimental scheme second last

experimental scheme. In the biofilm, VOC was utilized as carbon or energy source by themicrobes. For the growth ofmicroorganism in thebiofilter, available nitrogen and phosphorous were already supplied during the preparation of beads so, anexternal supply of these nutrients is not required for the growth. The pressure drop across the bed height was measured at aregular interval of time, with the help of U-tube manometer filled with water.Samples of inlet and outlet gas were collected from the sampling ports of the biofiltercolumn and analyzed using the Thermo -7610 (Previously CHEMITO) gas chromatograph equipped with the flame-ionization detector (FID) and Chromatopak column (1/8" dia., 2 m length and 80/100 mesh). Nitrogen was used as carrier gas with a flow rate of 30 ml/min. Temperature of injector, detector and oven were maintained at 150, 200, and 80ºC respectively. Hamilton gas (1 ml capacity) and liquid

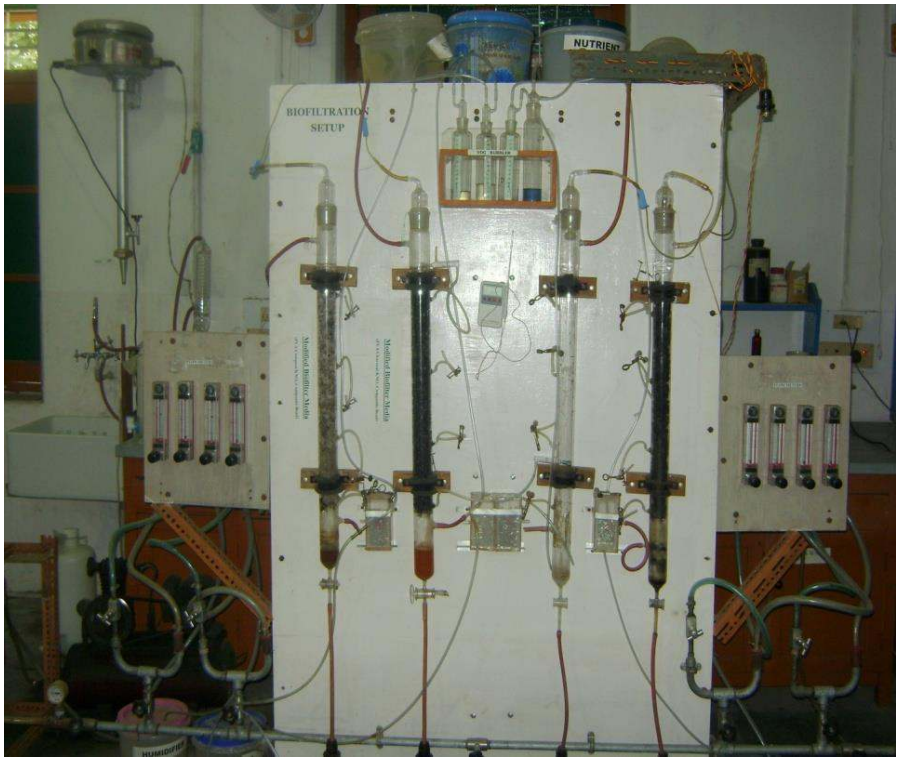

Fig. 3.1: Biofiltration set-up with accessories in our laboratory.

(10 µl capacity) sampling syringes were used for collection and injection of samples.Samples were directly injected into the injection port of the gas chromatograph using these pressure-lock gas syringes with a push-button valve. The gas chromatograph was standardized regularly using known reagent grade mixture. During the experimental period ambient and filter bed temperature, p^H of the leachate and moisture content of the bed were measured periodically. Temperature and humidity were measured using Humidity meter-Thermometer (Model No.DT-615). P^H was measured with adigital p^H meter. CO2 was measured by bubbling outlet gas into N/10 KOH solution for a fixed interval of time and titrating it by N/10 HCL solution using phenolphthalein as indicator.

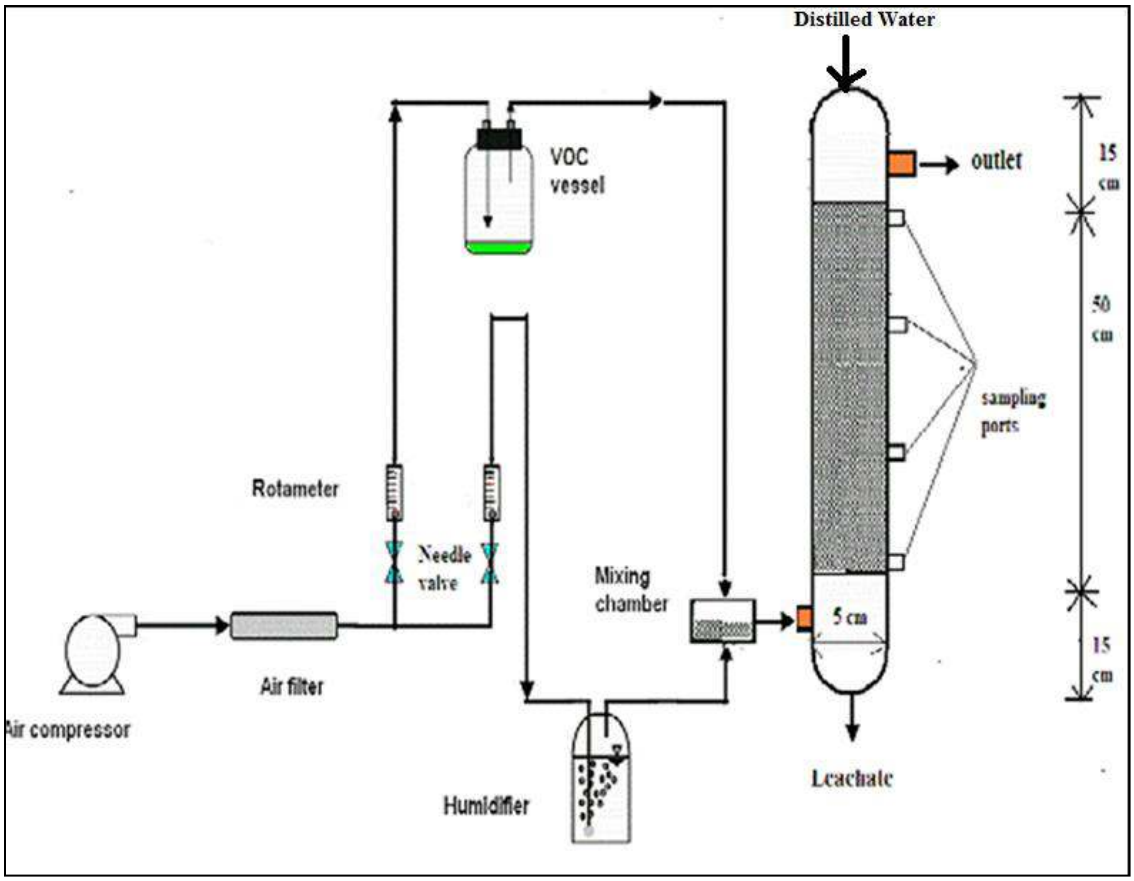

Fig. 3.2: Schematic set-up for the biofilter column.