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Biofiltration and kinetic aspects of a biotrickling filter for the removal of paint solvent mixture laden air stream

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Abstract

In the present study, removal of methyl ethyl ketone (MEK), toluene, *n*-butyl acetate and *o*-xylene (MTBX) emitted from the paint industry was carried out in a coal based biotrickling filter. When the influent MTBX loadings were less than 120 g m^{-3} h^{-1}, nearly 100% removal could be achieved. A maximum elimination capacity of 184.86 g m^{-3} h^{-1} was obtained at a MTBX load of 278.27 g m^{-3} h^{-1} with an empty bed residence time of 42.4 s in phase V. Results showed that the condition was the most favorable for *n*-butyl acetate degradation followed by MEK, toluene and then *o*-xylene. The corresponding maximum removal rate, r_{max} values of MTBX were calculated as 0.085, 0.033, 0.16 and 0.024 g m^{-3} h^{-1}, respectively. Standard deviation of error in prediction of MEK, toluene and *o*-xylene removal were within limit of 10%, while in the case of *n*-butyl acetate this was approximately 60%. The MTBX concentration profiles along the depth were also determined by using convection-diffusion reaction (CDR) model. It was observed that at low concentration and low flow rate, the model is in good agreement with the experimental values for MEK, toluene and *n*-butyl acetate, but for *o*-xylene the model results deviated from the experimental.

Keywords: Activated sludge; Biofiltration; CDR model; Kinetics; MTBX vapour

1. Introduction

Volatile organic compounds (VOCs) in ambient air are associated with emissions from a range of sources such as motor vehicle exhaust, motor vehicle fuel evapourative losses, industrial activities, petroleum refining, petroleum storage and dispensing facilities, surface coating and solvent use, domestic wood heaters, biomass burning, environmental tobacco smoke, use of solvents and glues and cleaners in arts and crafts [1]. VOC emissions from surface coating and solvent use sources may build up in residences, office buildings, indoor recreational areas, vehicles occupied for transport and locations for catching or servicing transport as well as partially enclosed public places and private residences in the ambient urban atmosphere where people spend their time.

According to National Emission Trends (NET) database from the U.S. EPA, total estimates of annual emissions of VOCs into the air from stationary and mobile sources in the U.S. were approximately two million tons nationally in 1999. Annual emissions of VOCs from coating and allied facilities were estimated to be 26,500 tonnes. Commonly used organic solvents include aromatics, acetates, ethers and ketones [2]. The contaminated constituents from automobile industries and paint spray booth off gases vary depending on the type of paint utilized. However, a typical composition includes a mixture of solvents including ketones (e.g., methyl ethyl ketone, methyl isobutyl ketone, methyl propyl ketone), aromatic hydrocarbons (e.g., toluene and xylenes), and esters (e.g., *n*-butyl acetate). Although the use of reformulated paints containing reduced quantities of VOCs can markedly decrease emissions from many facilities, there is also an increasing need for cost-effective and reliable air pollution control technologies that can remove VOCs from these emissions [3].

There are number of removal technologies available including biological methods to treat VOC polluted air stream. Among the biological waste gas treatment methods, biofiltration has attracted considerable interest in the last few years. It is cost-effective and very efficient removal process without generating any secondary air pollutants. It is used to eliminate contami-

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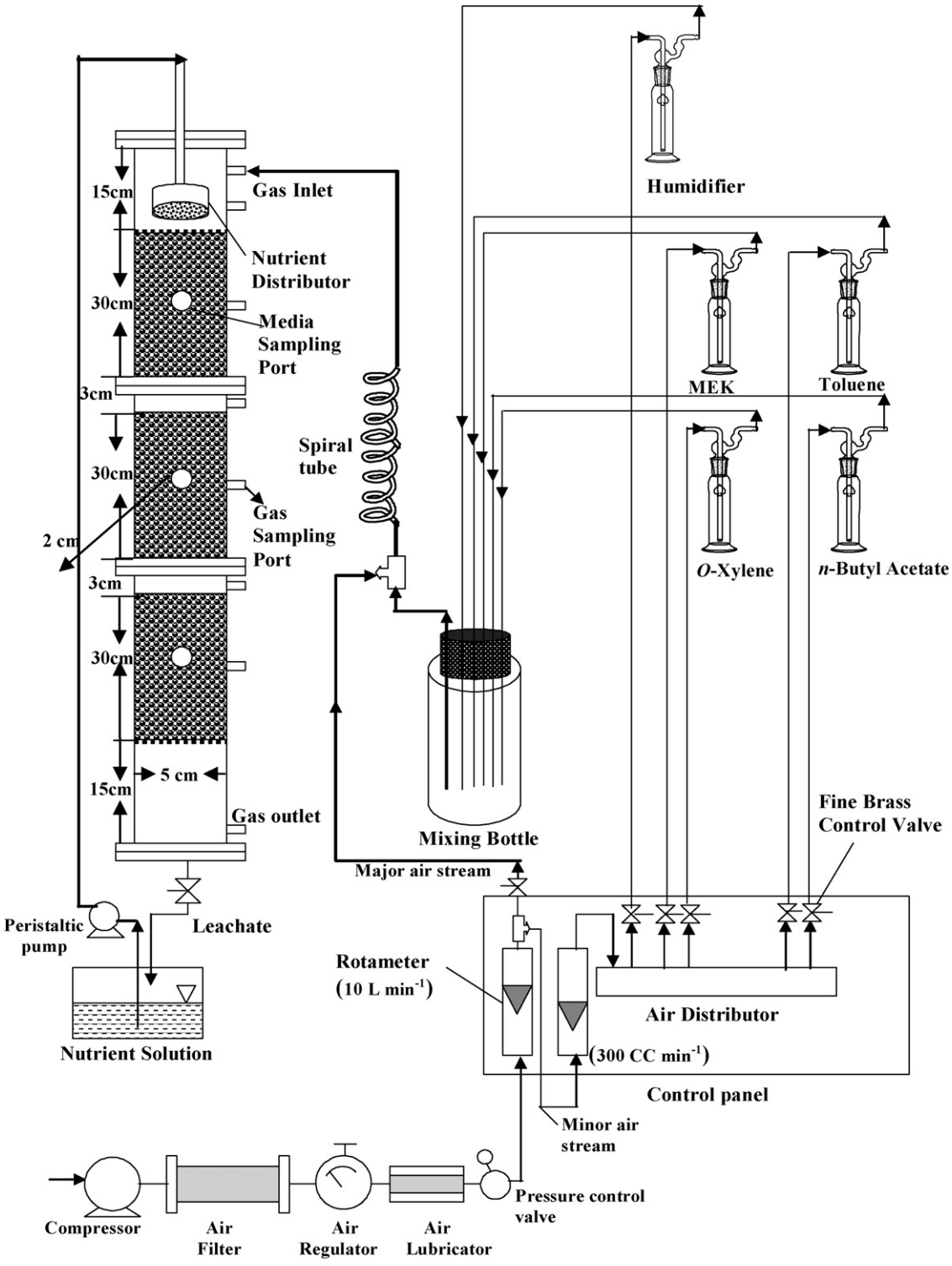

Fig. 1. Schematics of biotrickling filter for treating MTBX waste gases.

nants from air using microorganisms, which are immobilized on a surface of solid support media. This technique has been applied successfully to control a number of air pollutants such as odours, VOCs and hazardous substances [4,5].

Biological removal of paint VOCs in biofilter and biotrickling is very limited in the literature [2,3,6–10]. Particularly, studies on the biofiltration of methyl ethyl ketone (MEK), toluene, *n*-butyl acetate and *o*-xylene (MTBX) in a coal based biotrickling biofilter are scarce in the literature. Only Lu et al. [11] had attempted to evaluate the performance of biotrickling filter by treating mixture of ethyl acetate (EA), toluene (T) and xylene (X) in a coal packed bed. More than 80% removal efficiencies were achieved with influent loadings below 77 g EA m^{-3} h^{-1}, 8 g T m^{-3} h^{-1} and 10 g X m^{-3} h^{-1}, respectively. Boswell [8]

described a full-scale biofilter by treating the off-gas stream from a paint production unit at a paint manufacturing facility. The VOC mixture was dominated by toluene, xylene, MEK, acetone and ethylbenzene. They achieved approximately 60% overall VOC removal in the biofilter. Hsu et al. [2] demonstrated that a pilot-scale biofilter could achieve up to 95% overall VOC removal when the major organic compounds were xylene, toluene, MEK, iso-propanol, and isobutanol. Kazenski and Kinney [9] demonstrated that surrogate paint VOC mixtures could be successfully degraded in a lab-scale biotrickling filter packed with polypropylene pall rings. Even though the overall removal efficiency of 94% was achieved, toluene and *p*-xylene removal was relatively poor (80% toluene and 60% xylene removal).

The aim of present study is to evaluate the performance of a biotrickling filter packed with coal as packing material and inoculated with a mixed culture in treating a mixture of methyl ethyl ketone (MEK), toluene, *n*-butyl acetate and *o*-xylene (MTBX) vapour stream under variable loading conditions. Performance was assessed by determining MTBX removal efficiencies, elimination capacities, pressure drop along the bed and microbial concentration by varying the process parameters and operating conditions. A mixture containing these compounds is complex with respect to biodegradability. Therefore in order to understand transport phenomena and kinetic behaviors of biotrickling filter, the kinetic constants and the MTBX concentrations profile along the depth are determined by using Wani's method [5] of macrokinetic determination based on simple Monod kinetics and CDR model [15].

2. Material and methods

2.1. Biotrickling filter system

Fig. 1 shows the experimental setup for treating the MTBX. The biotrickling filter consisted of Perspex pipe with an internal diameter of 5 cm and effective packing bed depth of 90 cm. The height of the biotrickling filter was 126 cm and volume of the packing bed was 1.767 L. The biotrickling filter column consisted of three individual sections that were bolted together. Each section was packed with packing material to a depth of 30 cm. A 3 cm plenum was located between two sections to allow the sampling of gas and for the redistribution of the contaminant stream between sections. The packing material was supported on the acrylic sieve plate that ensured homogeneous distribution.

Compressed air was passed through the filtration device to remove moisture, oil and particulate matter. After purification, microbial culture was immobilized first on the packing material. After the immobilization, the biotrickling filter was fed with nutrient solution continuously at a rate of 4–5 mL min^{-1} by Peristaltic pump (Model RH-P100-S100, Ravel Hiteks Pvt. Ltd., Chennai, India). The nutrient solution was recirculated over the biotrickling filter to avoid more dissolve of MTBX in the liquid medium. The recycled liquid medium was refreshed in a semi-continuous mode, by replacing 10% of the medium every 2 days, in order to keep the nutrients concentrations sufficiently high. At the start of the experiment MTBX vapour laden air was supplied from the top of the reactor. All experiments were conducted in a temperature controlled chamber at $30 \pm 2\,^{\circ}C$. The filtered air stream was split into two sections: minor and major air stream. For producing MTBX loaded air stream of desired concentration, the minor air stream was passed separately through the glass bottles containing MTBX solution (99% pure) and through the humidifier. The MTBX loaded air streams and humid air were mixed in a glass bottle. Finally, this mixed humidified MTBX loaded air stream were mixed with major stream and then fed to the top of the biotrickling filter in down flow mode of operation. Rate of addition of MTBX in the main stream was controlled by regulating the rate of inflow to the MTBX bottles. The airflow rates were controlled and measured by a rotameter (JTM, Japsin Industrial Instrumentation, India) for high flow rate (1–10 L min^{-1}) and for low flow rate (1–300 cm^3 min^{-1}). Finally, MTBX concentrations were maintained at the desired value by adjusting the fine brass control valves. Pressure control valve was used for constant air flow to the reactor. The biotrickling filter was operated at various inlet MTBX concentrations and gas flow rates. Air samples were drawn from the various sampling ports by using a gas tight syringe and analyzed.

2.2. Packing material

In the present work coal was used as the packing material of the biotrickling filter. Some of the main physico-chemical characteristics of the coal used in the biotrickling filter for treating waste gas containing MTBX are presented in Table 1. The raw coal was obtained from local market. It was sieved through 1–1.5 cm screens, washed three times with Millipore water, dried in an oven at 105 °C for 1 day. After drying, this was sterilized at 15 psi for 20 min. Capability of adsorption–desorption of biotrickling filter was evaluated with the inflow of toluene of 0.2896 g m^{-3} at the flow rate of 1 L min^{-1} and with the pure air at 2 L min^{-1}, respectively. In adsorption studies, the outlet concentration of toluene was started to increase slowly initially, but increased rapidly after 2 h and reached steady state (near to inlet concentration) after 10 h of operation. In desorption experiment, toluene was slowly released from coal particles and after 19 h of operation, 94% of toluene was released from the biotrickling filter. On this basis, startup of the reactor was done.

Table 1
Shows physico-chemical characteristics of the coal

Parameters	
Particle diameter (cm)	1–1.5
Moisture content (%)	42
Specific gravity	2.514
BET surface area (m^2 g^{-1})	4.898
Total pore volume of pores (cm^3 g^{-1})	0.007
Average pore diameter (A)	63.497
Maximum pore volume (cm^3 g^{-1})	0.0077
Median pore diameter (A)	180.035
Porosity (%)	66.1

2.3. Culturing and immobilization

Activated sludge was collected from the secondary clarifier of the Kankhal Municipal Treatment Plant at Hardwar, India and was used in the biotrickling filter. The activated sludge was allowed to settle for 5 h to obtain the concentrated sludge. The concentrated sludge had suspended solids (SS) concentration of 3000 mg L^{-1} and volatile suspended solids (VSS) concentration of 2100 mg L^{-1}. 100 mL of concentrated activated sludge was used for the preparation of seed culture in a 250 mL flask. Four separate flasks containing 95 mL of nutrient solution were inoculated with 5 mL of activated sludge from the above 250 mL flask. Each of these four flasks contains 50 μL of each of four VOCs (MTBX). All flasks were shaken at 120 rpm and 30 °C in a temperature controlled orbital incubator cum shaker (Matrex Scientific Instruments Pvt. Ltd., New Delhi, India). The composition of the nutrient solution is presented elsewhere [4]. After 48 h of incubation, 5 mL of these cultures were added separately to four 95 mL fresh nutrient solutions containing 50 μL of each of MTBX. The MTBX adopted cultures were transferred into fresh nutrient solutions every 48 h for a period of 6 days. 100 mL of these adopted four cultures were then transferred into a 4 L nutrient solution, stirred and introduced from the top of the biotrickling filter and recirculated for 24 h for the immobilization on the packing materials.

2.4. Analytical methods

MTBX were analyzed by using a Netel India Limited (model-MICHRO 9100) gas chromatograph equipped with a capillary column type HP5 (30 m × 0.249 mm × 0.25 μm film thickness) and a flame ionization detector. The injector, oven and detector temperature were maintained at 210 °C, 60 °C, and 230 °C, respectively. The hydrogen gas was used as the fuel and nitrogen was used as the carrier gas at a flow rate of 20 mL min^{-1}. CO_2 concentration was determined by using the same GC equipped with a Porapack Q column (2 m length, 1/8 in. i.d., 80/100 mesh) and thermal conductivity detector (TCD). The calibration curve was prepared by injecting known amounts of the MTBX into a sealed bottle equipped with a Teflon septum according to the standard procedure [12]. The injected amount of MTBX was allowed to evapourate in the air space within the bottle at the experimental temperature (30 °C). Air samples are then drawn from the bottle by a 1 mL gas tight syringe (Hamilton-Bonaduz-Schweiz) and analyzed by gas chromatograph. The air samples were drawn from the various sampling ports by using a gas tight syringe and analyzed. The following parameters were determined according to the Standard Method [13]: suspended solid SS (2540-D) and volatile suspended solid (VSS) (2540-G). The pH values of nutrients solution and leachate were measured by a digital pH meter. Scanning electron micrograph of the coal, at the beginning and after 5 months of operation was carried out by using a scanning electron microscope (SEM) (Model LEO435VP, LEO Electron Microscopy Ltd., England). Sizes of the particles were done using the standard sieves. The specific surface area and the pore diameter of the coal were measured by nitrogen adsorption isotherm using an ASAP 2010 V2.00 C Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method by using the software of Micromeritics. Nitrogen was used as cold bath (77.12 K).

2.5. Measurement of concentration of microorganism

The plate count technique was used for the measurement of microbial concentration. When the steady state removal of MTBX was established, one gram of solid sample was taken with sterile steel tweezers from the sampling port provided at the top, middle and bottom of the biotrickling filter. The sample was replaced with fresh sterilized coal (1 g) each time. The withdrawn samples were mixed with 10 mL of sterilized Millipore water and then shaken in a vortex shaker for 10 min and then converted to desired concentration through serial dilution technique. Diluted sample was then allowed to stand for 30 min. One milliliter of this sample was serially diluted up to 10^{-10} in sterile buffer (phosphate buffer, pH 7.0). Serially diluted sample was then spread aseptically on the solid nutrient agar plate and the plates were incubated at 30 °C for 2 days and the colony forming units (CFUs) were counted. The results for microorganism concentration were expressed as CFU g^{-1} of packing material on wet basis.

2.6. Kinetic analysis

In the gas-phase biotrickling filters, the degradation rate of VOCs within the biofilm was investigated. For this reason, the mathematical model expressed by Eq. (1) was used. Details of method for determination of kinetic constants are presented elsewhere [5].

$$\frac{V/Q}{C_{gi} - C_{go}} = \frac{K_s}{r_{max}} \frac{1}{C_{ln}} + \frac{1}{r_{max}} \tag{1}$$

where C_{gi} and C_{go} is the inlet and outlet MTBX concentration. C_{ln} the log mean concentration $[(C_{gi} - C_{go})/\ln(C_{gi}/C_{go})]$, V the biofilter volume (m^3), and Q is the volumetric flow rate ($m^3\ s^{-1}$). r_{max} is the maximum degradation rate per unit filter volume ($g\ m^{-3}\ h^{-1}$) and K_s is the saturation (Michaelis–Menten) constant ($g\ m^{-3}$) in the gas phase.

The pattern of VOCs removal capacity along the depth of the trickling filter was also studied. For this reason, a first order kinetic mathematical model based on convection- diffusion reaction (CDR) was used. This method has also been successfully applied by Morgan-Sagastume and Noyola [15] for hydrogen sulfide degradation in biotrickling filter. The CDR model is represented as follows:

$$\frac{C_{go}}{C_{gi}} = \exp\left[-\frac{Da_s ZRT}{H_c U_0 \delta} \phi \tanh(\phi)\right] \tag{2}$$

and

$$\phi = \delta \sqrt{\frac{k}{D}} \tag{3}$$

where D is the diffusion coefficient in liquid phase ($m^2\ s^{-1}$), H_c the Henry's law constant ($Pa\ m^3\ mol^{-1}$), Z the depth of packed

Table 2
Operating conditions of each phase in the biotrickling filter experiments for MTBX

Phase	Operating period (days)	Flow rate (L min^{-1})	Range of average pollution concentration (g m^{-3}) in ± 1 standard deviation				Average loading (g MTBX m^{-3} h^{-1})	EBRT (s)
			M	T	B	X		
I	0–40	1	0.0736 ± 0.0026	0.0953 ± 0.0016	0.121 ± 0.0044	0.111 ± 0.0023	13.62	106
II	41–64	1	0.148 ± 0.0029	0.155 ± 0.0061	0.472 ± 0.0114	0.1105 ± 0.0025	30.125	106
III	65–101	2	0.299 ± 0.0034	0.318 ± 0.0188	0.949 ± 0.0086	0.216 ± 0.0085	121.27	53
IV	102–116	2	0.414 ± 0.3424	0.584 ± 0.3804	0.654 ± 0.4571	0.215 ± 0.0095	126.88	53
V	117–149	2.5	0.292 ± 0.0074	0.5704 ± 0.0103	1.90 ± 0.0156	0.440 ± 0.0168	272.16	42.4

bed (m), δ the biofilm thickness (m), U_0 the superficial velocity (m s^{-1}), and k is the reaction rate constant (s^{-1}).

3. Results and discussions

3.1. Over all system performance under variable loading condition

To evaluate the biotrickling filter performance under fluctuating loading conditions, change in influent MTBX concentration or empty bed residence time (EBRT) were conducted for a period of 150 days (phases I–IV). The relative proportions of the VOC components in the mixture for each loading condition are shown in Table 2. To ensure accuracy and repeatability of the results, various conditions were tested for several times and for various time intervals. Overall performance of the bed in the form of inlet concentration and removal efficiency for a period of 5 months has been presented in Fig. 2. This shows the profiles of MTBX removal efficiency and corresponding MTBX removal in the trickling filter during phase I to phase V. The starting nominal concentrations of MTBX in inlet air were 0.0746, 0.0965, 0.1201, and 0.1109 g m^{-3}, respectively. Gradual increase in removal efficiency was observed by more than 99.5% after 40 days of operation for all compounds. Time required for achieving more than 99.5% removal for MTBX are 26, 32, 20 and 38 days, respectively. The results showed that the time required for achieving more than 99.5% removal of *n*-butyl acetate was the lowest followed by MEK, toluene and *o*-xylene. Qi et al. [3] reported similar results for the degradation of mixture MEK, methyl propyl ketone, toluene and *n*-butyl acetate in biotrickling filter. At the end of first phase, more than 99% removal of all four compounds was achieved at the steady state condition. The result is consistent with the reported acclimation periods from few days to several weeks [16]. Inoculation of the biofilter media with adapted microbial aggregates greatly reduces the acclimation time of biofilter [17–19] to as low as 2 days [20,21].

As shown in Fig. 2, in the starting of phase II (on day 41) loading rate was increased more than twice of the average loading from 13.62 to 30.12 g m^{-3} h^{-1}. This increases the concentration accordingly. In this phase, the target MEK, toluene and *n*-butyl

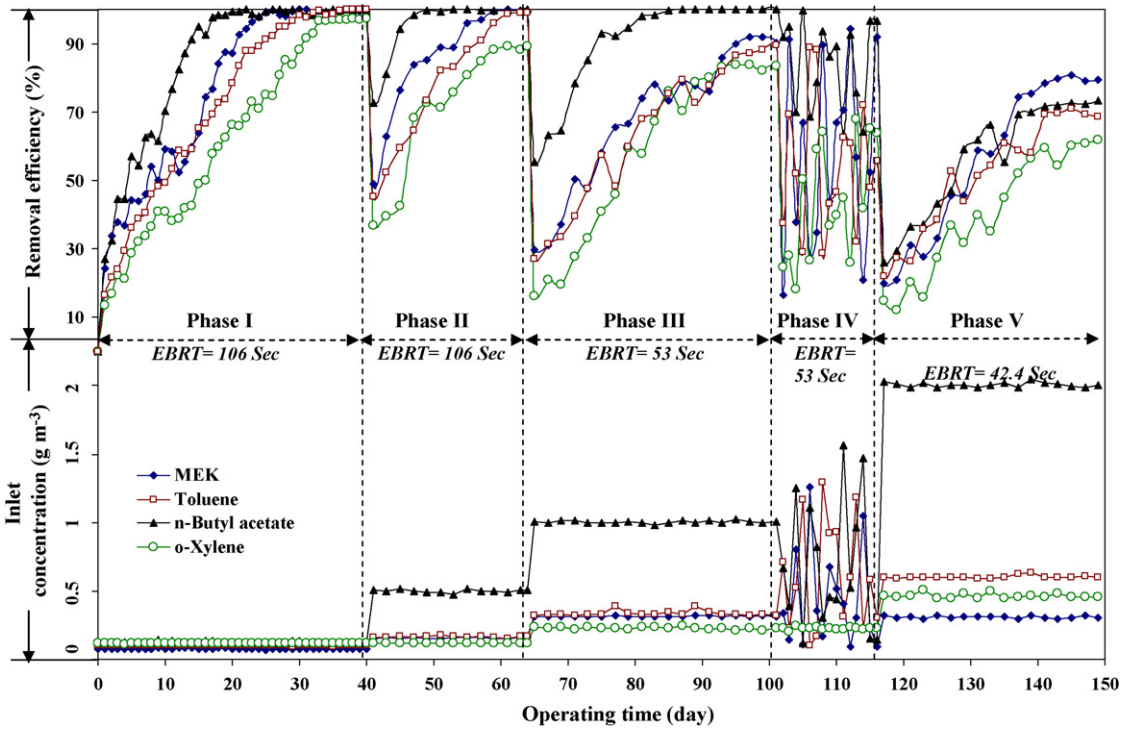

Fig. 2. Over all performance of coal based biotrickling filter in the removal of MEK, toluene, *n*-acetate and *o*-xylene with time.

acetate average inlet concentrations were varied from 0.0736 to 0.148, 0.0953 to 0.155, 0.121 to 0.4724 g m^{-3}, respectively, while an average inlet concentration 0.111 g m^{-3} of *o*-xylene was remain unchanged. In this phase, the flow rate of mainstream was kept constant at 1 L min^{-1} as phase I. Due to sudden change in loading rate to the reactor, the removal efficiency of MTBX was decreased from 99.9% to 49, 45, 72.5, and 38%, respectively. The removal efficiencies have been increased subsequently over a time period. Removal efficiency of *n*-butyl acetate increases to more than 99.5% after 8 days of the operation and that of MEK and toluene are more than 98% after 18 days of operation. *o*-Xylene removal was more slow than the other three compounds, but eventually increased to more than 88%. In this phase the inlet conditions of *o*-xylene (inlet concentration and flow rate) remained unchange to observe the effect of other compounds on the removal of *o*-xylene. When all the other conditions are kept constant and varying the inlet concentrations of MEK, toluene and *n*-butyl acetate are varied removal efficiency of *o*-xylene is decreased from 98 to 89%.

Phase III lasted from day 65 to 101. Flow rate of the gas mixture and average concentration of MTBX were maintained at 2 L min^{-1} (EBRT of 53 s) and at 0.299, 0.318, 0.949, and 0.216 g m^{-3}, respectively, so that the average organic loading rate to the biotrickling filter was increased to 121.27 g m^{-3} h^{-1}. As shown in Fig. 2, removal of *n*-butyl acetate was consistently greater than 99% after day 85, although the average inlet concentration of *n*-butyl acetate was approximately three times than the other three compounds. In this phase also same response similar to phase II had been observed once again, the maximum removal efficiencies of MEK, toluene, *n*-butyl acetate and *o*-xylene were 92, 89, 99 and 84%, respectively.

After achieving steady conditions for the different loading rates at the inlet point during phase I, II and III, inlet loading rates were quickly changed during phase IV to study the adaptability of the microbial cultures and the required times. These had been done also for repeatability of the bioreactor and to encounter the fluctuating conditions in the practical application. Accordingly, changes were observed at the outlet against those shock loads. Results, obtained were quite predictable. In the phase IV on the day 102, the gas flow rate entering the biotrickling filter remained unchanged at 2 L min^{-1} similar to the previous phase, but the concentrations of MTBX were changed on daily basis and moisture content in the bed was also not properly maintained. 60–80% moisture concentration was maintained in biotrickling filter throughout its operation, but moisture concentration in phase IV was not maintained and was lower than 60% in this phase. Due to daily change in inlet concentration, the loading rate was varied from 50 to 190 g m^{-3} h^{-1}. This was done to observe the changes in the performance of the trickling filter, when the concentrations of MTBX are quickly changed. During this phase it was observed that the removal efficiency was also changed of all four compounds. But the effect on removal due to the sudden change in inlet concentration of *n*-butyl acetate was minimal. The maximum removal of *n*-butyl acetate was mostly greater than 80%. The removal efficiency in the initial stage of this phase was less. This could be due to the insufficient moisture content and substrate inhibition at the sudden change in MTBX.

Phase V lasted from day 117 to 149, for 33 days. The MTBX average concentrations were maintained at 0.292, 0.5704, 1.90 and 0.440 g m^{-3}, respectively. The gas flow rate entering the biotrickling filter was increased from 2 to 2.5 L min^{-1}, thereby reducing the EBRT to 42.4 s. Increase in the inlet concentration of MTBX and gas flow rate increases the average organic loading rate to the biotrickling filter. This was increased approximately by a factor of 2.5 (272.16 g m^{-3} h^{-1}) from phase III (121.27 g m^{-3} h^{-1}). Initially, steep sudden decrease in removal efficiency was observed. In this phase the removal efficiency was gradually increased but not reached greater than 79, 69, 73, and 62% for MTBX, respectively. Decrease in the performance of the reactor was observed in this phase. This could be due to the decrease in biomass concentration in biotrickling filter after sudden change in the flow rate and concentrations of MTBX in phase IV. Lack in maintaining the proper concentrations could be the other factor. Biomass concentration is also an important factor for biotrickling filter performance.

The biotrickling filter performance was also evaluated in terms of the elimination capacity (EC) of MTBX for the various loading rates, which is defined as the amount of MTBX degraded per unit of the reactor volume and time for the various loading rates. The EC, which reflects the capacity of the biotrickling filter to remove the pollutants has been plotted in Fig. 3 as a function of inlet average MTBX load. Square symbol represents the experimental data of MTBX while the dotted line indicates the 100% removal. Significant variation of the EC in various phases was observed in the change of influent concentration and removal rate. The elimination capacities of MTBX were increased with the increase in the influent MTBX loading, but an opposite trend was observed for the removal efficiency. From Fig. 3, it is clear that when the influent MTBX loadings were less than 120 g m^{-3} h^{-1}, nearly 100% removal could be achieved. The maximum elimination capacity of the biofilter was 184.86 g m^{-3} h^{-1} at the average MTBX load of 278.27 g m^{-3} h^{-1} in phase V. During phase III, when the biotrickling filter was operated at an average MTBX load of 121.27 g m^{-3} h^{-1}, the maximum EC was achieved as 113.67 g m^{-3} h^{-1}. But the EC was achieved only 96 g m^{-3} h^{-1},

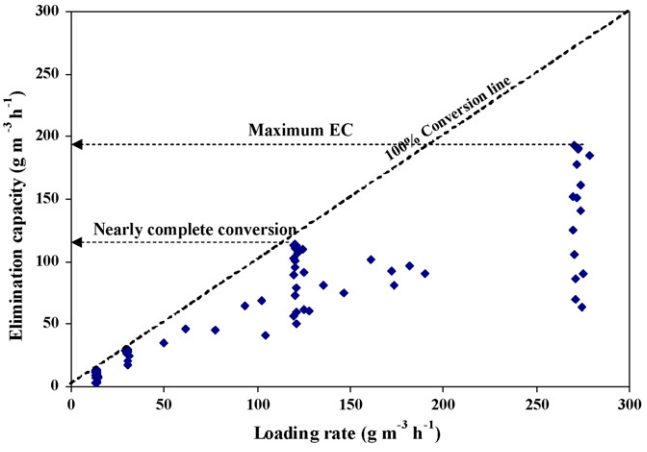

Fig. 3. Influence of MTBX loading rate on the elimination capacity of the biotrickling filter.

when the biotrickling filter was operated nearly at the same average MTBX load of 126.88 g m^{-3} h^{-1} in phase IV at fluctuating conditions. This could be due to the poor removal in the phase IV, because the EC is maximum at the maximum removal efficiency. The literature reveals that the most of the biofilters for treatment of paint VOCs are operated at EBRTs in the range from 40 s to 2 min with loading rates in the range from 6 to 40 g m^{-3} h^{-1} [9,10]. In the comparison with other reported values on the biofiltration of paint mixture [3,7,22] the elimination capacity and removal efficiency are quite high in this study. Qi et al. [3] observed that the average total elimination capacity of methyl propyl ketone, MEK, toluene, and *n*-butyl acetate mixture in biofilters inoculated with fungus *Cladosporium sphaerospermum* and packed with polyurethane foam was 92 g m^{-3} h^{-1} at an EBRT of 15 s. Moe and Qi [22] also studied the removal of five component mixture acetone, MEK, toluene, ethyl benzene and *p*-xylene in two biofilters inoculated with enrichment culture derived from compost and achieved maximum removal efficiency greater than 99% at a loading rate of 80.3 g m^{-3} h^{-1} and an EBRT of 59 s.

3.2. Bed pressure-drop

Another essential parameter for the biological air pollution control technology is the pressure drop across the bed because it is related to the development of biomass accumulation in the trickling filter. The pressure drop across the bed plays an important role in determining the amount of energy needed by the compressor or blower to force the VOC contaminated gas stream through the bed. The pressure drop across the bed should not be too high since this will result in high energy requirements [23–25]. The pressure drop across the bed slightly increased with the increase in the influent VOC concentration (see Fig. 4). This can be attributed to the fact that more microorganisms were produced for high VOC feed, which might be minimize the external porosity of the coal particles and thus led to high pressure drop across the bed [26].

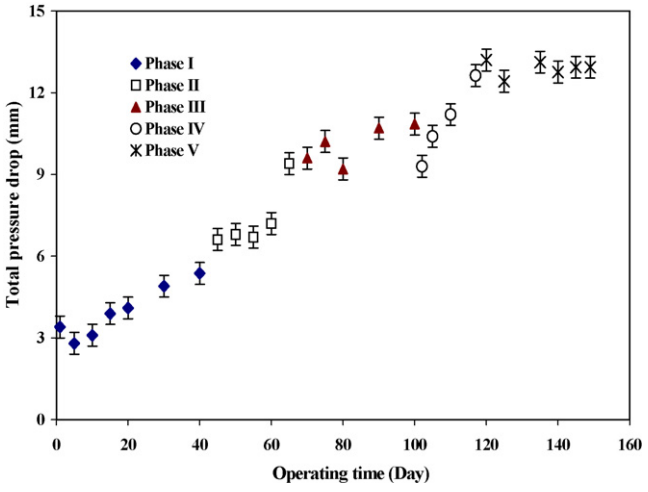

Fig. 4. Total pressure drop along coal based biotrickling filter at various phase of the operation.

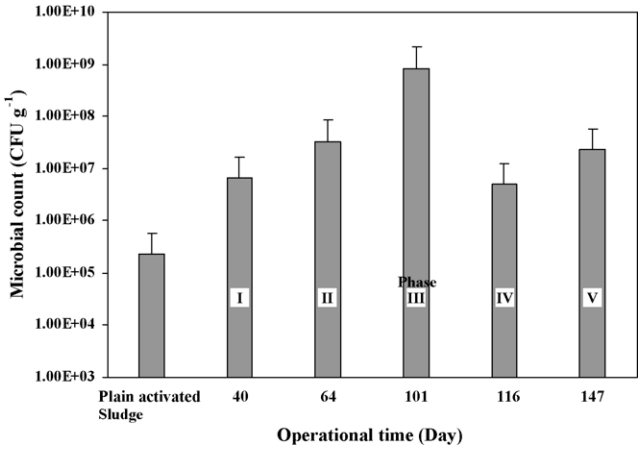

Fig. 5. Total microbial count during various phase of biotrickling filter.

As mentioned earlier, biomass accumulation is directly related to the pressure drop in the biotrickling filter. Therefore, the observation of biomass concentration with time also played a very important role to check the biotrickling filter performance. Performance of the biotrickling filter with respect to the biomass concentration in terms of colony forming units per gram (CFU g^{-1}) was determined when the system achieving steady state removal efficiencies for various experimental phases of operation in Fig. 5. The microbial concentration in the initial activated sludge was 2.36×10^5 CFU g^{-1} and increased by 28-fold (6.68×10^6 CFU g^{-1}) after 40 days operation. The microbial concentration increases significantly with the concentration from phase I to III. The maximum microbial concentration was achieved as 8.46×10^8 CFU g^{-1} in phase III. The microbial concentration decreased from 8.46×10^8 CFU g^{-1} to 4.86×10^6 CFU g^{-1} in the phase IV. As discussed already in Section 3.1, the concentration of MTBX was changed daily basis and moisture content in the bed was also not properly maintained in phase IV. Due to the daily change in the inlet concentration of MTBX and the loading rate, the microbial concentration was decreased significantly. The microbial concentration again recovered gradually when all the other conditions are kept constant in the phase V.

3.3. Column kinetics analysis

The kinetic parameters have to be calculated in order to understand transport phenomena and kinetic behavior of biotrickling filters, since the four compounds in the VOC mixture possess vastly different characteristics with their solubility, volatility and biodegradability. Therefore, it is anticipated that various mechanisms may be responsible for their removal capacities. The kinetics of the system can be expressed by a Michaelis–Menten relationship by assuming that oxygen limitation was not present in the system and the conversion takes place in the reaction-controlled regime (i.e. the biofilm was fully active). At the steady state, the growth rate of microorganisms was balanced by its own decay rate, resulting in the biological equilibrium of the system. Hence, kinetic constants remained constant over the period of time considered. The kinetic constants were determined by

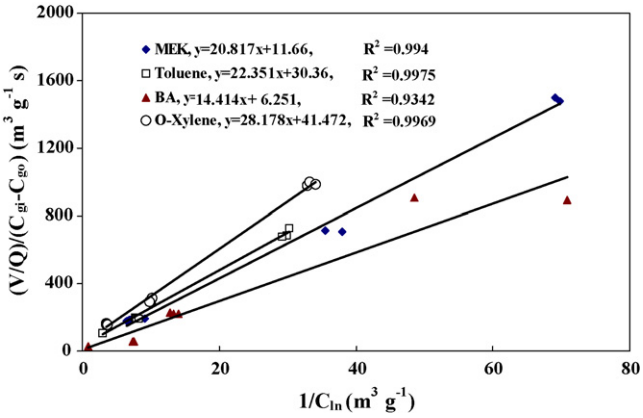

Fig. 6. Macrokinetic determination of Michaelis–Menten kinetic constants of MEK, toluene, *n*-acetate and *o*-xylene.

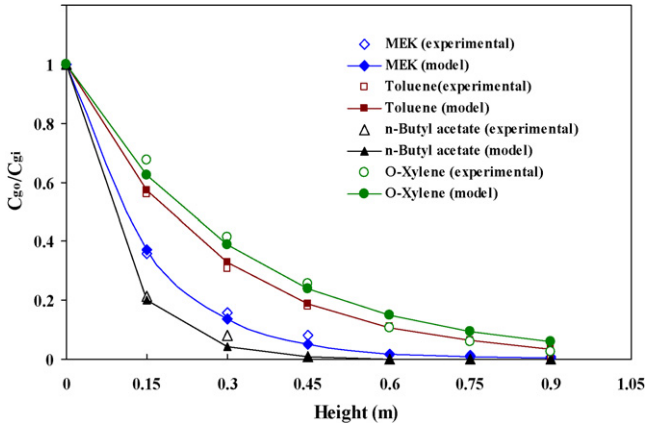

Fig. 7. Experimental and model predicted concentration profiles of MEK, toluene, *n*-acetate and *o*-xylene along the bed depth for low concentration (phase I).

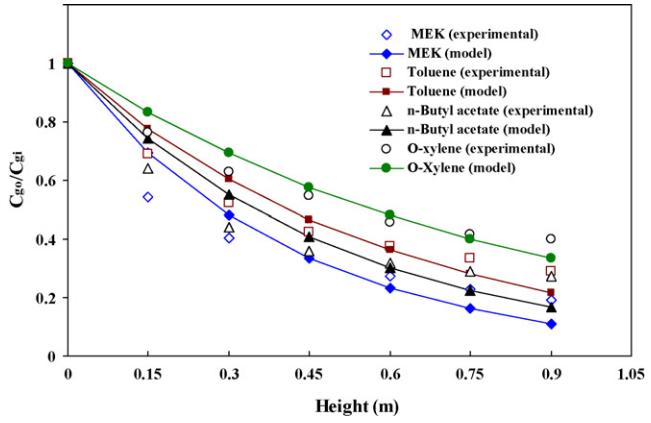

Fig. 8. Experimental and model predicted concentration profiles of MEK, toluene, *n*-acetate and *o*-xylene along the bed depth for high concentration (phase V).

using Eq. (1) with correlation coefficient (R^2) of 0.994, 0.9975, 0.9342 and 0.9969 and standard deviation of error in prediction were 10.053, 7.02, 59.488 and 8.85 of MTBX, respectively. From Fig. 6, the r_{max} values for MTBX were 0.085, 0.033, 0.16 and 0.024 g m^{-3} h^{-1}, and K_m values were calculated as 1.785, 0.736, 2.305 and 0.679 g m^{-3}, respectively. In our previous study for the biofiltration of mono-chlorobenzene, the r_{max} and K_m were evaluated 0.121 g m^{-3} s^{-1} and 7.45 g m^{-3}, respectively [5]. Krailas et al. [34] also reported r_{max} and K_m values for isopropanol as 0.12 g m^{-3} s^{-1} and 2.72 g m^{-3}, respectively.

3.4. Kinetic behavior of MTBX inlet concentration along the bed depth

This experiment was conducted to determine the local MTBX concentration along the depth of the biotrickling filter. Samples were taken from the various sampling ports at the distances 15, 30, 45, 60 and 90 cm from the top of the bed. At the time of measuring these distances from the top, plenum height of 3 cm and distance of outlet from the bottom of the bed have not been considered since it is assumed that there are not any conversion takes place in these sections. In order to predict the microbial kinetics behavior at MTBX inlet concentration along the bed depth, an attempt was made to fit a first order kinetic mathematical model based on convection-diffusion reaction (CDR). Contaminated profiles within the biofilter bed during phase I on day 40 and during phase V on day 145, have been shown in Figs. 7 and 8. Here, it is observed that the removal of *o*-xylene is slow and slightly different from the other compounds. Qi et al. [3] observed similar trend for methyl propyl ketone, MEK, toluene and *n*-butyl acetate mixture removal in biofilters inoculated with fungus *Cladosporium sphaerospermum* and packed with polyurethane, and concluded that *n*-butyl acetate was the most quickly degraded followed by MEK, methyl propyl ketone and then toluene.

Moreover, the variations of experimental concentration along the bed depth and the fitted curve (CDR model) have been presented in Figs. 7 and 8. Parameters used in this work for solving

Table 3
The parameters used for solving model equations

Parameters	Values				Source
	MEK	Toluene	*n*-Butyl acetate	*o*-Xylene	
H_c (Pa m^3 mol^{-1})	11.01	808	28.5–32.5	626	[31]
D (m^2 s^{-1})	9.8×10^{-10}	8.9063×10^{-10}	8.07×10^{-10}	1×10^{-9}	[32,33]
a_s (m^2 m^{-3})	303				[27]
δ (cm)	0.008–0.025				[27]
U_0 (for gas flow rate 1 L min^{-1}) (m s^{-1})	8.5×10^{-3}				Present work
U_0 (for gas flow rate 2.5 L min^{-1}) (m s^{-1})	0.0212				Present work

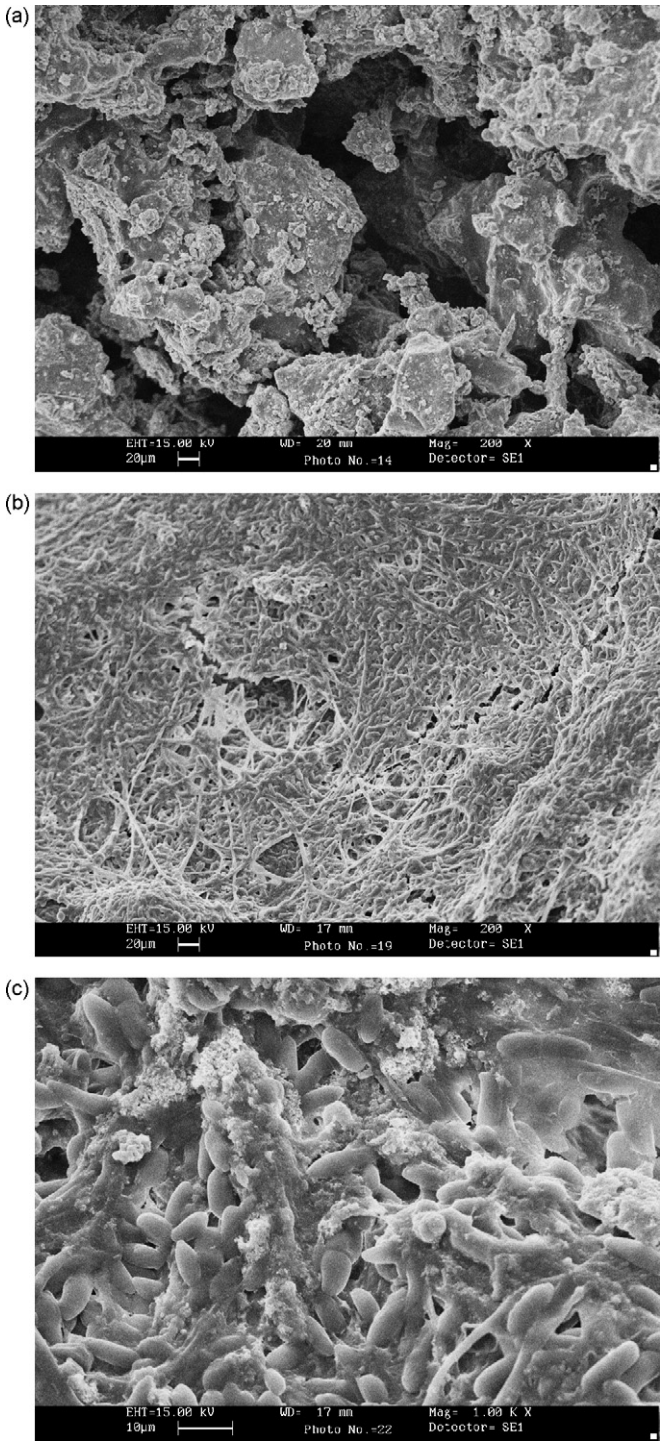

Fig. 9. The biofilm morphology of microorganisms on the surface of coal by SEM: (a) at the beginning and (b) after 149 day operation (c) at high magnification.

model equations are listed in Table 3. Fig. 7 shows that for a low concentration and low flow rate the model is in good agreement with the experimental values for MEK, toluene and *n*-butyl acetate but for *o*-xylene the model results were deviated from experimental. At higher concentration and flow rate (Fig. 8), the model predicts more deviation in comparison with the experimental results for MEK than others. It was observed that the good agreement between the measured data and the predicted results for both concentrations (low and high) is obtained in the middle part of the biotrickling filter. A similar trend was also observed for the mixture of isopropyl alcohol and acetone [27]. This small variation in the model results from the experimental values can be attributed to numerous factors, such as experimental error induced in the estimation of the kinetic model parameters. Overall, the discrepancy between the model and the experimental results is not significant, if one considers complexity of the model and its numerous simplifying assumptions and the experimental error in both the biofiltration performance results and the kinetic model parameters estimated [19].

3.5. Microscopic observations

The Scanning Electron Micrograph (SEM) can provide crucial quantitative and qualitative information about the microbial community on the biofilter media. The biomass of individual particle can be mapped. From such precision, important factor such as filter media coverage, thickness and activity can be determined for modelling. The SEM can also determine the characteristics of the filter material that are important to system's success. If the filter bed is showing increase in pressure drop or poor performance because of channeling, SEM may show whether clogging is arising from the accumulation of biomass [28]. The SEM of microbial growth on various types of media before and after experiment has already been shown by some researchers [14,29]. Fig. 9 presents the microbial growth on the surface of the coal filling material before and after experiment. Compared to the initial coal media, a biofilm on the surface of the coal was observed clearly after 149 days of operation. An even growth of microbial community on the surface of the coal is clearly visible. Initially, the degree of acclimatization depends upon the adaptive capacity of the microorganisms on the coal, substrate concentration, its availability and other necessary environmental condition. Acuna et al. [18] reported that, after 88 days of biofiltration, diverse microbial morphologies, such as bacterial colonies, single cell and budding yeasts, mycelial structures, and also some non-colonized regions on the surface of a peat biofiler were observed under SEM. Even though biofilms seem to consist of a homogeneous layer, there is a considerable non-uniformity within biofilms. Several groups of microorganisms are involved in the degradation of air pollutants in biofilters, including bacteria, actinomycetes, and fungi [30].

4. Conclusions

Data presented in the study demonstrated that when microbial population are acclimated and maintained, they can achieve the complete degradation of mixture of MTBX (more than 99%). This shows that the use of coal as a packing media in the biotrickling filter inoculation with municipal activated sludge reliable, efficient and easy to operate and maintain. The results obtained revealed that when the influent MTBX loadings were less than 120 $g\,m^{-3}\,h^{-1}$, nearly 100% removal could be achieved. The maximum elimination capacity of the biotrickling filter was 184.86 $g\,m^{-3}\,h^{-1}$ at inlet MTBX load of 278.27 $g\,m^{-3}\,h^{-1}$ in

phase V. Analysis of the results showed that the conditions were most favorable for *n*-butyl acetate degradation followed by MEK, toluene and then *o*-xylene. In order to understand the transport phenomena and kinetic behaviors of biotrickling filter, the kinetic constants and the MTBX concentration profiles along the depth by using CDR model were also determined. The r_{max} values for MEK, toluene, *n*-butyl acetate and *o*-xylene were 0.085, 0.033, 0.16 and 0.024 g m^{-3} h^{-1}, and K_s values were calculated as 1.785, 0.736, 2.305 and 0.679 g m^{-3}, respectively. For this system the regression coefficient (R^2) of MEK, toluene and then *o*-xylene were grater than 0.99 and standard deviation of error in prediction of MEK, toluene and *o*-xylene removal were within limit of 10%, while in the case of *n*-butyl acetate this was approximately 60%. The MTBX concentrations profile along the depth at low concentration and low flow rate shows that the model is in good agreement with the experimental values for MEK, toluene and *n*-butyl acetate but for *o*-xylene the model results deviate from experimental. It is our view that the information contained herein shall be useful for designing of coal based biotrickling filter for the degradation of MTBX laden air stream successfully.

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