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Performance evaluation of hybrid reactor for bio filtration of n-hexane–styrene mixture

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ABSTRACT

Bio filtration of n-hexane and styrene mixture is always a difficult and challenging process due to the hydrophobicity and recalcitrant nature of the components. In this research study, a novel nano composite based adsorber was employed as the pre-treatment stage before biofilter to treat the VOC mixture. The hybrid reactor yielded better results compared to the stand alone biofilter. The concentration range employed in this study was 0.5–2.0 g m^{-3} for n-hexane and 0.25–1.0 g m^{-3} for styrene. Higher removal efficiencies were achieved at lower inlet concentrations at maximum EBRT of 90 s. Styrene removal efficiencies were found to be better than n-hexane removal efficiencies. The comparison between hybrid model and conventional biofilter proved the superior performance of the hybrid model. The carbon dioxide production was found to be proportional to the degradation rate represented in terms of elimination capacity. The correlation was proposed and actual yield coefficient was found to be lesser than the theoretical value. Biomass growth was studied across the height of the biofilter and found to be appreciable in the lower sections.

Keywords: Hybrid biofilter; n-hexane; Biofilm; Gas production

1. Introduction

The industrial gas emissions consisting of wide variety of pollutants has gained significant attention due to public awareness and environmental legislations. Human exposure to these hazardous industrial emissions has led to temporary and permanent disorders. Air pollution control methods employed across the broad spectrum of industries involve physical or chemical or biological principles as their operating methodology. Implementation of physico-chemical methods have been attributed to their quick start-up phase, reduced residence time, established know-how and design of the process [1]. Even though methods like activated carbon adsorption, thermal and catalytic oxidation are popular, higher operating costs and temperature maintenance discourage their uses. Moreover, production of secondary pollutants is a serious concern associated with these methods [2]. Biological methods are chosen as a suitable alternative to the conventional physico-chemical methods because their ability to handle low pollutant concentration, easy design and simple operational procedure [3,4]. Biological methods are superior from other methods in terms of removal effiency and operational costs [5–7]. The two most common biological techniques employed for treatment of polluted air are biofilters and bio trickling filters. These methods involve transfer of contaminant from gas phase into an immobilized microbial film formed on the solid packing media in the bioreactor. The contaminant is biodegraded through microbial action and converted to less harmful end products. Hexane is a hydrophobic volatile organic compound which is released by rubber and plastic products industries and categorized as priority pollutant in US clean air act due to its carcinogenicity [8,9]. Styrene is an aromatic compound used in the manufacturing of polystyrene, butadiene-styrene latex and copolymer resins and reported to have pneumo toxic and hepatotoxic effects [10]. Both these compounds are susceptible to be present together in the above said industrial emissions and pose a serious threat to human health. Experimental studies on photo-biological removal of n-hexane as a single pollutant [4], biological removal of n-hexane – benzene mixture

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[8] and biological removal of n-hexane – methanol [9] have been conducted. Biofiltration of styrene as a single component was successfully carried out in a trickle bed bioreactor [10] and biofilter [11]. However, no detailed study is available on treating n-hexane–styrene mixture using biofilters. In this research study, the biofiltration of n-hexane–styrene mixture was investigated in a hybrid biofilter. Hybrid biofilter was designed to incorporate a conventional biofilter with nano composite adsorber as the primary stage. The performance of the hybrid biofilter model will be assessed under varying inlet loading rates and compared with the conventional biofilter. The carbon di oxide production profile was recorded and interpreted in relation to elimination capacities. Biomass profile was observed at different sections of the biofilter and scanning electron microscope imaging was performed.

2. Materials and methods

2.1. Experimental set-up of hybrid reactor

A four stage upflow biofilter was constructed using acrylic with a column height of 100 cm, diameter of 5 cm, 10 cm bottom space for leachate collection and 10 cm headspace for collection of the effluent gas and nutrient feed addition. The sketch of the biofilter along with its components is shown in Fig.1. Provisions of sampling ports at the tail end of each section from the direction of flow of air were made to collect samples. Perforated acrylic plates were provided between the two sections to allow the passage of treated air and nutrient solution. The biofilter set up consisted of two units; the primary adsorber followed by the biofilter. An adsorber with an internal diameter of 2.5 cm and height of 50 cm was employed as a pre-treatment stage in the hybrid set-up. Nano hydroxy apatite synthesized with a stoichiometric Ca: P ratio of 1.67:1 using wet chemical precipitation method [12] was used in the form of pellets in the adsorber. The pollutant laden air was sent in upflow mode through the nano composite adsorber at a constant EBRT of 90 s in all the experiments. Biofilter employs the natural biomass *Phoenix dactylifera* tree barks, as a filter media in the column and the mixed microbial culture collected from the activated sludge system of the municipal sewage treatment plant located nearby was immobilized on the filter media. Preliminary culturing of the inoculum in an aerated batch reactor was explained elsewhere [13]. A nutrient distribution system involving the use of a peristaltic pump was utilized to pump the nutrient solution in a periodic interval. The composition of the nutrient media was given as follows (per litre volume): 0.694 g KH_2PO_4, 0.854 g K_2HPO_4, 1.234 g $(NH_4)_2SO_4$, 0.46 g $MgSO_4{\cdot}H_2O$, 0.176 g $CaCl_2{\cdot}2H_2O$ and 0.001 $FeSO_4{\cdot}7H_2O$. A 5 ml volume of trace nutrient solution with the following composition (per litre volume) was added to the above said solution: 60 mg H_3BO_3, 40 mg $CoCl_2{\cdot}6H_2O$, 20 mg $ZnSO_4{\cdot}7H_2O$, 6 mg $MnCl_2{\cdot}4H_2O$, 6 mg $NaMoO_4{\cdot}2H_2O$, 4 mg $NiCl_2{\cdot}6H_2O$ and 2 mg $CuCl_2{\cdot}2H_2O$. The VOC laden air is produced using the following procedure. Air stream from a compressor was divided into two streams; the main one sent to the VOC storage tanks and the auxiliary one to the mixing tank for dilution of concentration. The main air stream was passed into the storage tanks containing n-Hexane (99% purity, Fischer scientific) and toluene (99% purity, Sigma Aldrich) and then through the humidifier. The main air stream loaded with VOC mixture was mixed with the secondary air stream in the mixing chamber in order to attain the desired VOC concentration. The flow rates of these flow streams were regulated and fed into the adsorber and the exit stream from the adsorber was fed to the biofilter reactor in an upflow mode. The air samples were collected at periodic intervals for analysis for residual n-hexane and styrene by gas chromatograph (Per-

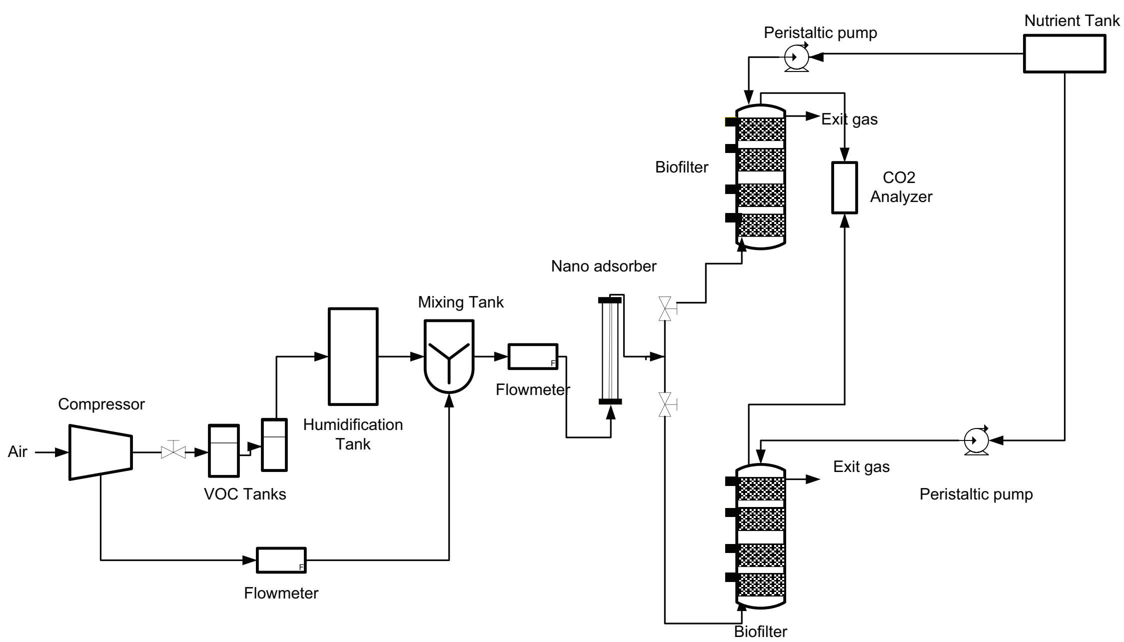

Fig.1. Experimental set up of hybrid biofilter.

kin Elmer, USA). The exit gas was analyzed to determine the carbon dioxide gas concentration. The biomass estimations inside the biofilter column were performed using the procedure given [14]. Biofilm imaging was done using scanning electron microscope (JEOL, JSM-7600F, Japan). The performance of the biofilter was assessed using the following parameters: percentage removal efficiency (% RE), elimination capacity (EC), g m^{-3} h^{-1}, and carbon dioxide gas production rate (GPR), g m^{-3} h^{-1}. These parameters are defined as given below:

$$\%RE = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$EC = \frac{Q(C_0 - C_t)}{V} \tag{2}$$

$$GPR = \frac{Q\left(C_{g,out} - C_{g,in}\right)}{V} \tag{3}$$

where C_0 and C_t represent the exit and inlet concentrations of the individual VOC, (g m^{-3}), Q is the flow rate of the individual VOC (m^3 h^{-1}), V is the volume of the biofilter (m^3), $C_{g,out}$ and $C_{g,in}$ represent exit and inlet concentrations of carbon dioxide (g m^{-3}).

The biofilter empty bed retention time (EBRT), h, is estimated as given below

$$EBRT = \frac{V}{Q} \tag{4}$$

3. Results and discussion

3.1. Effect of operating conditions on the continuous performance of the hybrid biofilter

The experimental studies involved four phases of experimentation with varying inlet VOC concentrations and flow rates conducted over a period of 96 days. The inlet concentration of n-hexane was varied in the range of 0.5–2.0 g m^{-3} at different EBRT of 45, 60, 75 and 90 s. The corresponding ILR values were in the range of 20–160 g m^{-3} h$^{-1.}$ The styrene concentration was varied in the range of 0.25–1.0 g m^{-3} at similar EBRT. The experiments involved treatment of the VOC laden air in the nano hydroxy apatite adsorber followed by biofilter. In order to validate the effectiveness of the hybrid model, parallel experiments were carried out by treating the polluted air in only biofilter. During the start-up phase, all the experiments were conducted at highest EBRT and the lowest flow rate. The biofilter performance was presented in Fig. 2 for n-hexane and Fig. 3 for styrene in terms of removal efficiency at different inlet loading rates. At the maximum EBRT of 90 s, the equilibrium removal efficiency attained was 88% at 0.5 g m^{-3} of n-hexane concentration and the removal efficiency attained was 100% at 0.25 g m^{-3} of styrene concentration in the hybrid reactor. With increase in concentration and decrease in EBRT, the removal efficiencies decreased. Similar observations were reported in biofiltration studies on n-hexane [4], benzene [13] and styrene [11]. The reduction in efficiency was attributed to reduced contact time available for the bio-

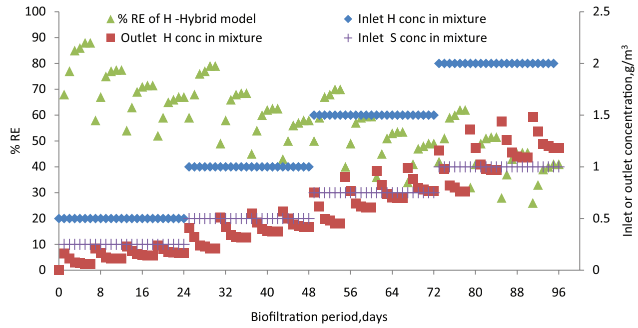

Fig. 2. Effect of concentration and flow rate on the performance of hybrid biofilter for hexane removal.

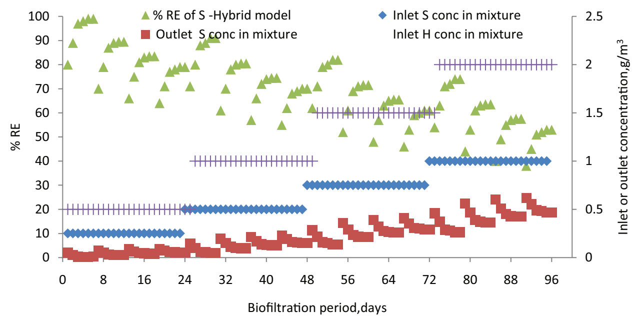

Fig. 3. Effect of concentration and flow rate on the performance of hybrid biofilter for styrene removal.

film and existence of a threshold concentration to withstand for the microbial community inside the bioreactor. The removal efficiencies decreased with increase in inlet VOC concentrations and was clearly shown in Figs. 2 and 3. The experimental values of performance parameters observed in the high concentration phases were comparatively lower exhibiting the limitations of the hybrid model. The difference in removal patterns of n-hexane and styrene could be related to the difference on hydrophobicity and Henry's law constants [8]. The VOC removal patterns in the absence of nano composite adsorber were evaluated by treating the mixture in the biofilter directly and the treatment performance was inferior to the hybrid reactor as shown in Figs. 4 and 5. From these figures, it was inferred that the removal efficiencies of the stand-alone biofilter reactor were less by a rough estimate of 20% in comparison to hybrid biofilter. Thus, the combined effectiveness of the adsorber-biofilter was proved as an effective research attempt. Studies on ethylene removal on hybrid photo catalytic based biofiltration system have demonstrated better performance [15].

3.2. Correlation between elimination capacity and gas production rate

Elimination capacity is a significant performance evaluation parameter as it reflects the rate of removal. The quantity of pollutant degraded per unit volume of the reactor per unit time was represented by elimination capacity [13]. The biodegradation of organic compounds results in the formation of carbon dioxide and water vapor as end products [8,16]. The follow up of

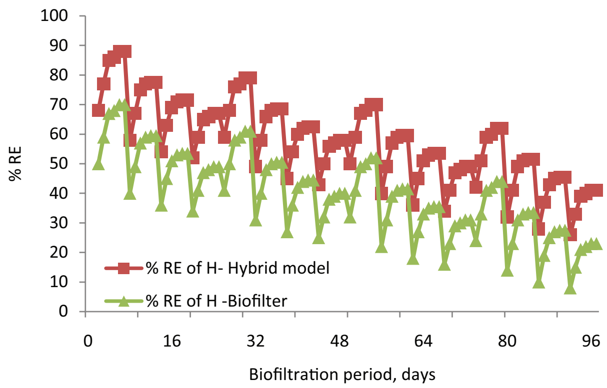

Fig. 4. Comparative evaluation of biofilter and hybrid model for hexane removal.

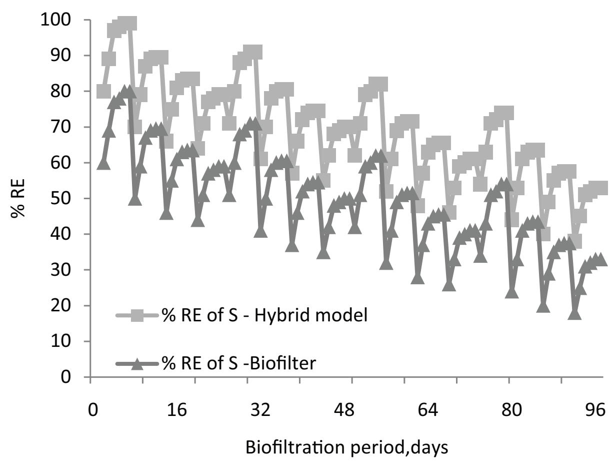

Fig. 5. Comparative evaluation of biofilter and hybrid model for styrene removal.

carbon dioxide gas production profile is an effective way to quantify the extent of mineralization of VOCs. The complete oxidation reaction of n-hexane (C_6H_{14}) and styrene (C_8H_8) occurring in the biofilter can be represented through Eqs. 5 and 6 [8,11].

$$C_6H_{14} + 9.5O_2 \xrightarrow{\textit{aerobic microbes}} 6CO_2 + 3H_2O \tag{5}$$

$$C_8H_8 + 10O_2 \xrightarrow{\textit{Microorganisms}} 8CO_2 + 4H_2O \tag{6}$$

The carbon dioxide concentration was analyzed at the top exit of the biofilter and the gas production rate was calculated using Eq. (3). Fig. 6 presents the relationship between carbon di oxide production rate and the elimination capacity. A high degree of linearity was observed with R^2 value of 0.9924. Under conditions of complete mineralization, the theoretical carbon dioxide yield coefficient defined as mass of CO_2 produced per unit g of C (calculated from stoichiometry) is 3.06 for n-hexane and 3.38 for n-styrene. The slope of the linear plot represented the cumulative actual carbon dioxide yield coefficient (5.57) which was less than the theoretical value of 6.44. The difference between the theoretical and actual yield coefficients was

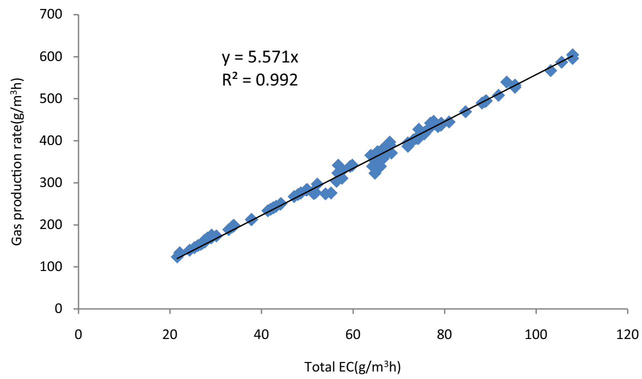

Fig. 6. Correlation between Cumulative Carbon dioxide production rate and elimination capacity

attributed to partial adsorption of VOCs in the nano composite adsorber and accumulation of carbon dioxide in the liquid phase. Research studies on biofiltration of n-hexane, styrene and benzene reported similar observations on gas production – elimination capacity correlation [8,11,13].

3.3. Biomass profile in the biofilter

Biomass growth inside the biofilter always helps to identify the microbial mechanism and substrate consumption pattern associated with the transformation of pollutants. The dry cell mass was estimated across the height of the biofilter in order to identify the differential growth and substrate consumption pattern axially. A plot of dry cell mass versus biofiltration period was presented in Fig. 7 at different biofilter heights. The biomass growth patterns show better values in the lower and middle sections compared to the third and fourth section towards the top of the column. This fact was related to the increased availability of substrate near the point of entry in the biofilter column and decreasing humidity in the upper sections biofilter. Biofiltration studies on xylene [17] presented similar biomass profiles in their results.

3.4. Biofilter stability test

In this set of experiments, the stability of the hybrid biofilter to withstand fluctuations in inlet VOC loading has been studied by varying the inlet concentrations within short time. During this study, the concentrations were varied randomly in the range of 0.5–2.0 g m^{-3} for n-hexane and 0.25–1.0 g m^{-3} for styrene within 8 h at fixed EBRT and the response of the hybrid biofilter was recorded. Fig. 8 proved that hybrid biofilter was found to withstand the short time shock loads and the removal efficiencies attained were consistently high. Biofilter stability test confirmed the acclimation of the microbial community to handle sudden fluctuations in inlet VOC loading and proved the adaptability of the hybrid model.

3.5. Biofilm imaging using SEM

Biofilm formation inside the biofilter column was characterized using SEM imaging as shown in Fig.9. The figure confirmed the presence of biofilm on the surface of the

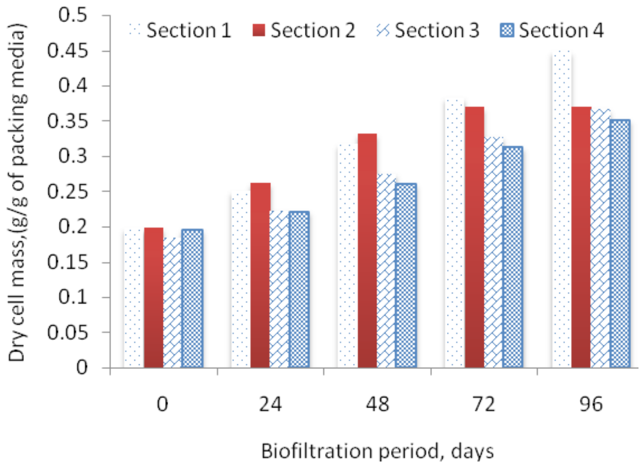

Fig. 7. Section-wise biomass growth inside the biofilter.

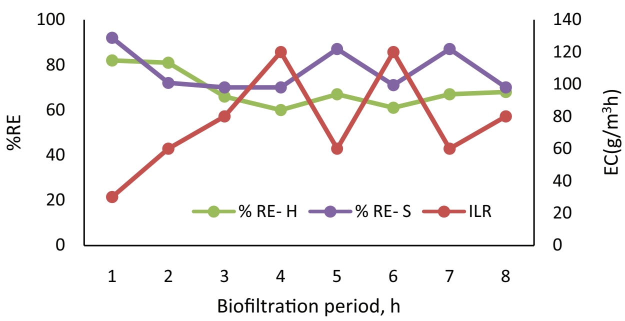

Fig. 8. Effect of shock loading on biofilter performance.

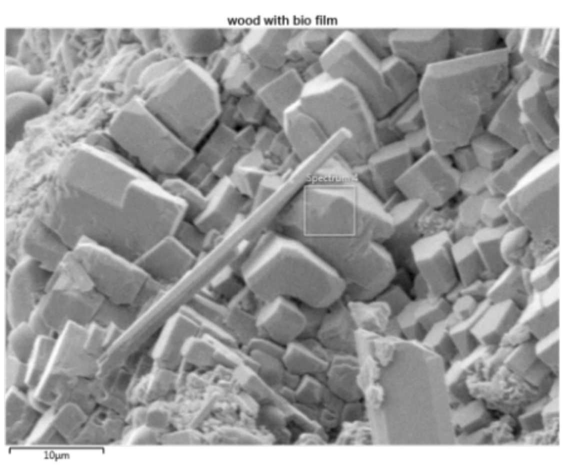

Fig. 9. SEM imaging of biofilm.

biofilter media, tree barks. The biofilter performance was always related to successful formation of biofilm and acclimation of the microbes to the pollutant laden air.

4. Conclusions

Hybrid biofilter was successfully demonstrated as an effective reactor to treat n-hexane–styrene mixture and proved to be superior to the conventional biofilter due to the addition of nano composite adsorber. Higher removal efficiencies were attained in this reactor set up and the maximum total elimination capacity was determined as 108.0 g m^{-3} h^{-1} .The individual VOC removal efficiencies decreased with increase inlet concentration. At higher inlet VOC concentrations, increased EBRT produced better results which confirmed the requirement of prolonged degradation time by the microbes inside the biofilter. Carbon dioxide gas production was monitored and found to have a god linear correlation with the total elimination capacity. The total actual yield coefficient was estimated as 5.57. Axial biomass profile was studied through dry cell mass estimations and better biomass growth was found to exist in the lower and middle sections of the biofilter. Biofilm formation was studied through scanning electron microscope imaging.

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