Effects of Operational Conditions on the Performance of Triethylamine Biofiltration

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ABSTRACT

Nitrogen compounds such as triethylamine are odorants generally found in chemical plants and foundries in which cold-box cores are made. In this study, the efficiency of biofiltration of triethylamine (TEA) vapor was evaluated. Experiments were conducted in two 6-L biofilters arranged in three stages and packed with inoculated compost - wood chips (40:60v/v) as the filter medium. The seed inoculum was obtained from municipal activated sludge. Tests were made to compare effects of initial temperature ($30\pm1°C$, biofilter A) and (23 ± 2 °C, biofilter B) on the performance of the biofilter. TEA elimination rate pattern was evaluated by changing loading rates ($6\text{-}138$ $gm^{-3}h^{-1}$ and hydraulic retention times ($40\text{-}60$ s) while operating at constant temperature and humidity at 50-55%. Results showed that organic loading rates (OLR) of up to 114.4 $gm^{-3}h^{-1}$ (biofilter A) and 90.56 $gm^{-3}h^{-1}$ (biofilter B) could be handled without any apparent indication of maximum elimination capacity and substrate inhibition. The elimination capacity of biofilters could reach up to 72 $gm^{-3}h^{-1}$ (biofilter A) and 61.5 $gm^{-3}h^{-1}$ (biofilter B). When the loading of TEA exceeded the critical values, substrate inhibition occurred and the elimination capacity decreased. However, the requirement of keeping the pressure drop below 4 cm water gauge per meter of bed height to avoid operational problems warranted lower than maximum capacity operation. The optimal OLR values of 90 ± 14 $gm^{-3}h^{-1}$ are suggested for hydraulic retention time value of 48 s and temperature of $30\pm1°C$. Under these conditions, elimination capacity of 71 ± 3 $gm^{-3}h^{-1}$ and removal efficiency of $81\pm14\%$ was achieved.

Keywords*: Biofiltration, Triethylamine, Biodegradation, Air pollution*

INTRODUCTION

A biofiltration system consists mainly of a reactor packed with solid materials (e.g. peat, perlite, compost, wood chips) on which a biofilm is formed, given the proper microbial population. When a contaminated air stream passes through the reactor, the pollutants are transferred to the biofilm where they are biodegraded to simple end products such as water and carbon dioxide (Adler, 2001). A consortium of microbial populations are known to play an important role in this process, but current understanding of the mechanisms and specific microbial enzymes involved is limited (Burgess et al., 2001). In general, natural biomass support materials provide sufficient inorganic nutrients for microorganisms. As such, adding nutrients is not needed. The required moisture is provided by saturating influent

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stream before its inflowing the reactor and /or by supplying liquid water intermittently.

Studies on biofiltration over the last several decades have primarily been focused on odorous compounds such as hydrogen sulfide, ammonia, mercaptanes, etc. (Strikauska et al., 1999; Wani et al., 1999; Busca and Pistarino, 2003). However, adoption of stricter emission policies in recent years has greatly increased the inventory of compounds subject to regulation. Furthermore, increasing costs of chemicals and disposal of hazardous wastes have provided further incentive for development and optimization of biological treatment methods. Biofiltration has emerged as one of the cost effective biological air pollution control technologies for treatment of volatile organic compounds (VOCs) emitted from chemical and process industries (Yoon and Park, 2002).

Amines are widely used as catalysts in casting operations. They are also the major pollutants in the gaseous emissions of chemical manufacturing factories. During the production of casting cores with the so called "cold-box-process", polyurethane is used as a binder in the sand core. Considerable amount of amine vapor is used in this process and is partly liberated to the ambient air. Tertiary amines, such as triethylamine, are the main gaseous catalysts comprising the majority of nitrogenous emissions (Borger et al., 1997). Previous studies have suggested suitable biodegradation potential of amines (Tang and Hawang, 1996; Chou and Shiu, 1997). As such, biofiltration seems to be an appropriate method to treat waste gases containing these pollutants.

The objective of this study was to examine the response of biofilter systems to the variations of inlet concentration, temperature, and loading (organic and hydraulic) conditions. Specifically, the effect of inlet concentration and organic loading rate on the performance of biofilter in treating TEA in a pilot plant system was studied.

MATERIALS AND METHODS

Experimental setup   Experiments were conducted in a laboratory scale reactor shown in Fig.1. The column had an inner diameter of 5 cm and an effective height of 100 cm; perforated plexiglas plates (pore diameter =3 mm) were placed between sections acted as a support for the packing material as well as for flow redistribution. A 5 cm space between the sections allowed for representative gas sampling. Provision of two sampling ports at midpoint within each section allowed temperature measurements as well as bed media access.

The main air stream was provided by sending compressed air through an activated carbon adsorber for residual oil capture. A side stream of purified air was sent through a 1-L bottle containing pure liquid TEA. The rest was humidified and mixed with the exiting side stream containing pollutant vapor. Air flow rates were appropriately controlled using pressure regulators and flow meters to generate feed air with the needed concentration. Variation of humidity in the influent gas stream and biofilter material was controlled by changing water temperature in the humidifier.

Temperature control of the bed material was achieved by circulating water around the exterior of reactor wall. Heated element was used for temperature control in the water tank. During the steady state operational period of the study, bed temperature and humidity were maintained at $30 \pm 1^\circ$ C and 50-55%, respectively.

In order to understand the process of the biofilter and the physical adsorption capacity of the filter material, at the startup, experiment was performed in active and poisoned (sterilized by $HgCl_2$ solution) biofilter.

Filter media and microbial culture   Filter media was prepared by blending of sieved compost and wood chips. Municipal compost (equivalent diameter of 2-5 mm) with a C: N: P ratio of 100:7:2, 37.8% organic matter, and a

pH value of 6.8 was obtained from a local composting facility. Wood chips (2-5mm) were added as bulking material to produce a 60:40 v/v ratio of compost-wood chip. The inoculum consisted of municipal activated sludge from the local regional wastewater treatment plant. The following nutrient and buffering solutions were also added to the activated sludge (gdm^{-3}): KH_2PO_4= 5; K_2HPO_4= 2.5; potassium= 0.2; sodium=0.64; calcium=5; magnesium=2; chloride=3.7; phosphorus=1.15 (Auria et al., 2000).

Operational and performance parameters
Operational and performance parameters include empty-bed residence time, loading rates, removal efficiency and elimination capacity. Empty-Bed Residence Time (EBRT) is the time a parcel of air will remain in an empty biofilter and overestimates the actual treatment time. Mass loading rate defines the amount of contaminant entering the biofilter per unit area or volume of filter material per unit time. Both terms are normalized, allowing for comparison between reactors of different sizes. Removal efficiency (RE) and Elimination Capacity (EC) are used to describe the performance of a biofilter. Elimination capacity (EC) is a good performance indicator of biofiltration systems in that it shows what portion of the incoming organic loading is being biodegraded. As the loading rate is increased, a point of saturation or maximum EC corresponding to maximum microbial substrate utilization rate is observed. This limitation is due to the effect of high concentrations on the Monod kinetics of biodegradation (Nevin and Arford, 2000). In some cases, it is known that very high concentration of substrate can become inhibitory (Devinny et al., 1999). RE is the fraction of contaminant removed by biofilter and EC is the mass of the contaminant degraded per unit volume of filter material per unit time. Removal efficiency is an incomplete descriptor of biofilter performance because it varies with contaminant concentration, air flow, and biofilter size and reflects only the specific conditions under which is

measured. The elimination capacity is normalized with respect to volume by definition and allows for direct comparison of the results of two different biofilter systems.

Analytical methods   Gas samples were collected at the inlet, outlet, and in the 5 cm plenum between the sections by passing the gas through the impinger containing 20 ml methanol as TEA solvent. The flow rate of gas was 340 ml/min for 15 min of sampling time. The amount of TEA in methanol was measured by UV spectrophotometer (UV/VIS-911, GBC CO. Australia) at a wavelength of 215 nm. Standards were prepared by introducing known volumes of TEA into the 5 L Tedlar bag. Appropriate volumes were selected based on vapor pressure calculations at room temperature and pressure. The equilibrium vapor pressures were calculated as 7.7 kPa (759 ppm) at 25ºC and 101.325 kPa for TEA. Considering the volume of Tedlar bag and maximum concentrations possible at equilibrium, known liquid volumes were injected. For example, for a 5 L Tedlar bag, 5.67 µl TEA should be injected to achieve 200 ppm concentration. Concentrations of the actual experiments were determined from the calibration curve prepared using absorption observed for known concentration of TEA.

For measuring pH, one gram of biofilter bed material and 20 ml distilled water were blended and agitated for 10 min and measured by a pH meter (691-Metrohm, Switzerland).

Moisture of biofilter bed material was measured by weight loss of 2 g solid sample after being dried at 106°C for 24 h.

Heated water was circulated around the bed exterior and connected to a precision thermostat (Atbin Co.) to control temperature within 1°C. Temperature was maintained at 30°C and measured using alcohol in a glass thermometer of -10°C to 110°C and a scale division of 1°C.

A water-filled manometer with a minimum division length reading of 1-mm water column was used to measure pressure drop across the column.

RESULTS

Startup   At the startup of biofilter, influent TEA concentration was adjusted at 20 ppm at an organic loading rate of 6 $gm^{-3}h^{-1}$ and relative humidity of 50-55%. Besides, water temperature in humidifier was adjusted to 28± 2° C. Superficial gas velocity was 57.3 mhr^{-1}, corresponding to a residence time of 48 s.

The results of biofiltration of TEA in poisoned and normal reactors, at the startup, are shown in Fig. 2. Adsorption on solid media in biofilter was studied by Freundlich model in which it was assumed that sites for adsorption were not limited. As shown in Fig. 3, k_f (Freundlich coefficient) and 1/n (a constant) were 10.5 and 0.4522, respectively, according to the following equation:

$$x/m = 10.5 * C_e^{0.4522}$$

Where C_e = equilibrium concentration of adsorbate in fluid and x/m= mass of adsorbate per mass unit of adsorbent.

Removal efficiency   Time variation of removal efficiency as a function of TEA concentration is shown in Fig. 4. Inlet TEA concentration was increased up to 385 ppm (1.5 gm^{-3}) stepwise at the hydraulic residence time of 48 s, so mass loading changed proportionally.

Elimination capacity   By increasing inlet TEA concentrations while maintaining constant flow rate (HRT=48 s), OLR was increased. The results are shown in Fig.5.

Concentration gradient   The results of TEA concentration along the bed are presented in Fig. 6

Hydraulic retention time   Effect of hydraulic retention time (HRT) at constant TEA concentration of 220 ppm, on the elimination capacity along the biofilter is shown in Fig.7. The total mass of TEA entering the biofilter increased with an increase in flow rate. While at the same time, there was a reduced contact time due to lower HRT values ensuing reduced EC values.
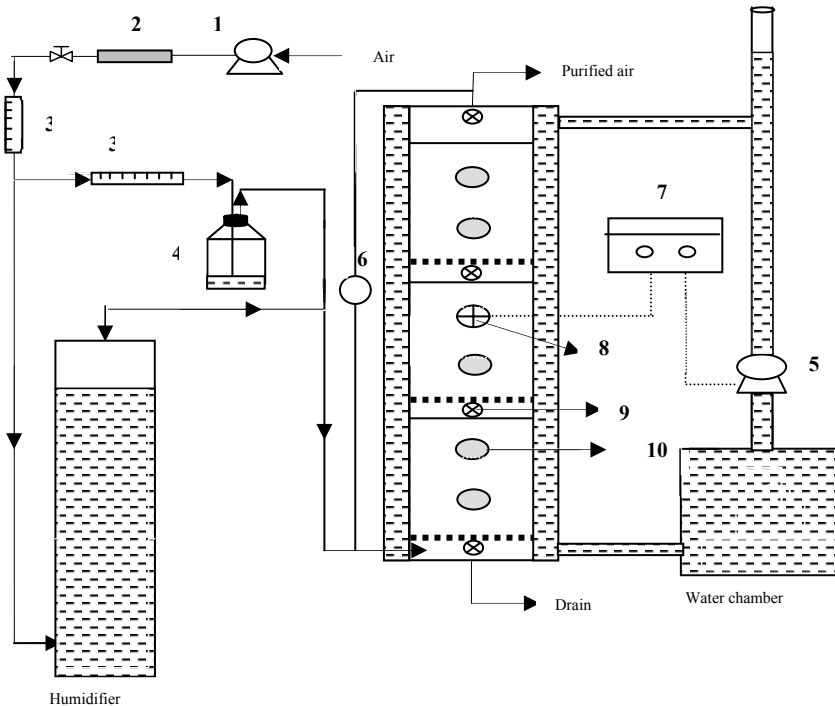

Fig. 1: Schematic diagram of the experimental system: 1-air pump. 2-air filter. 3-rotameter. 4-aqueous solution of TEA. 5-water pump. 6-manometer. 7-temperature controller. 8- temperature sensor 9-gas sampling port. 10-solid sampling port
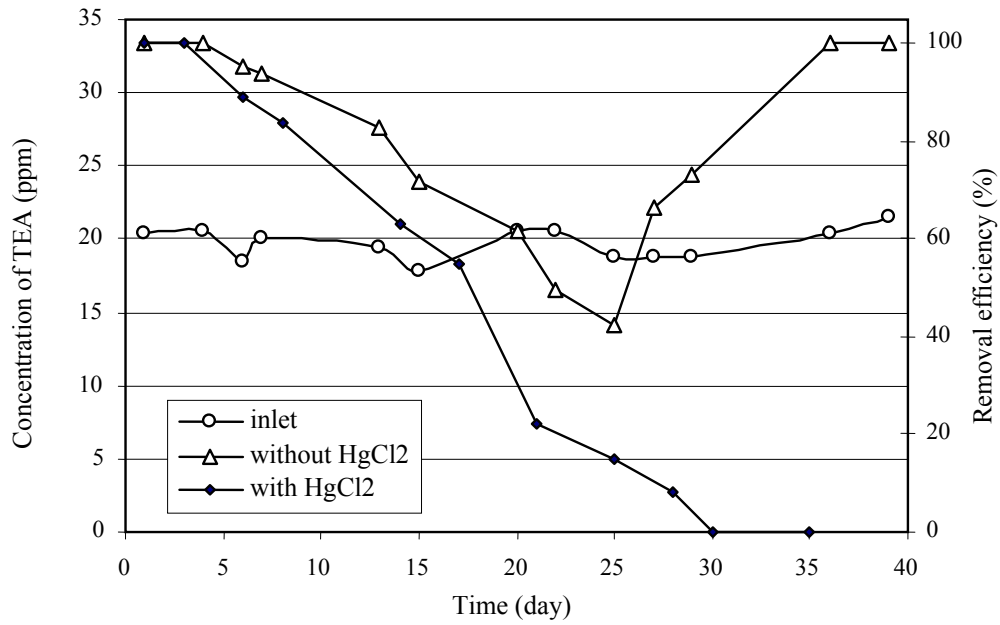
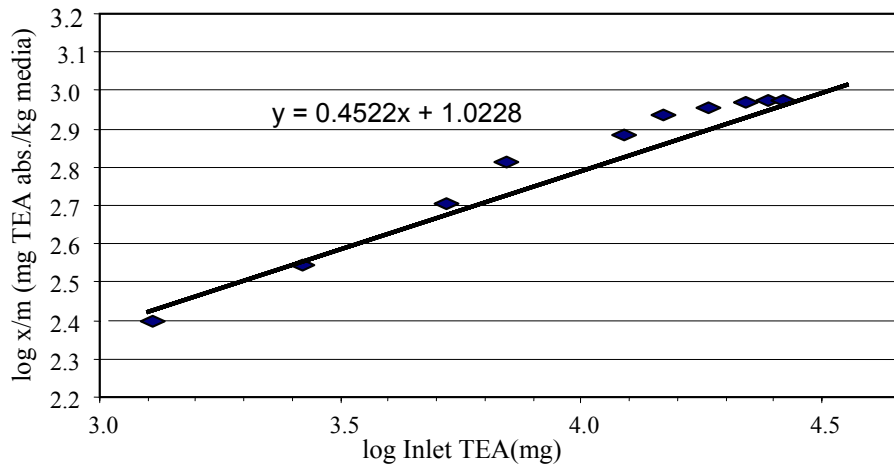**Fig. 2:** Time variation of removal efficiency during the biofilter start up

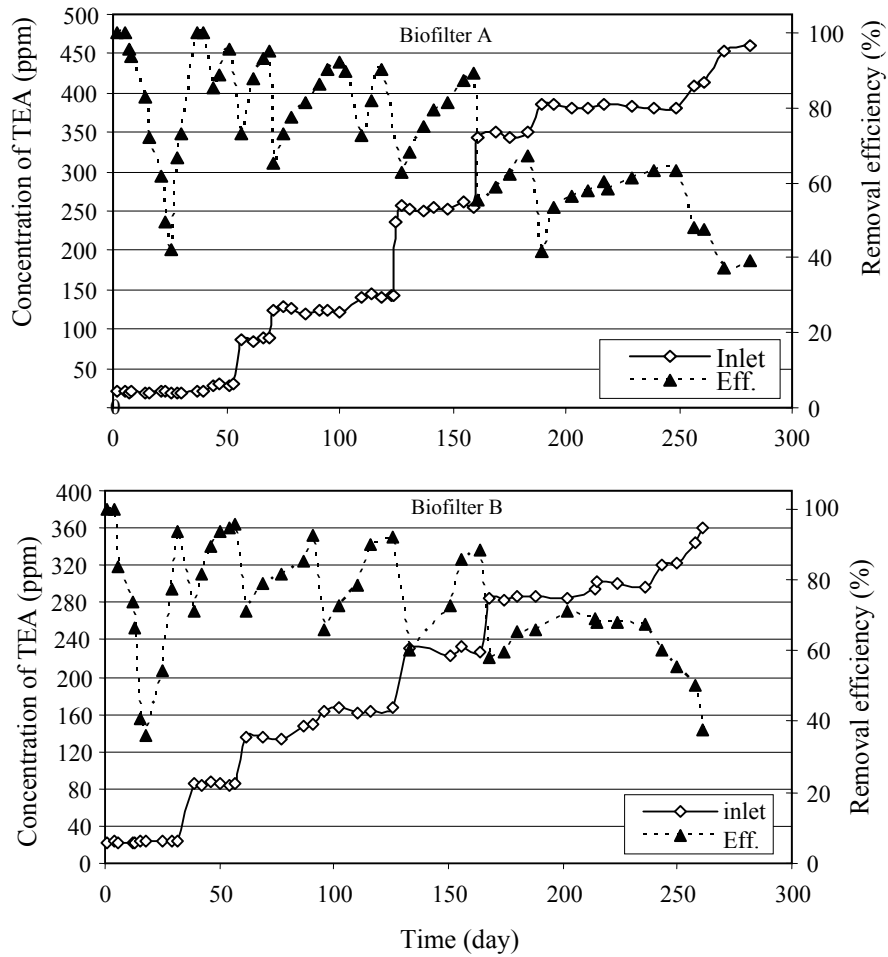**Fig. 3:** Adsorption capacity of biofilter medium based on Freundlich model in the poisoned biofilter

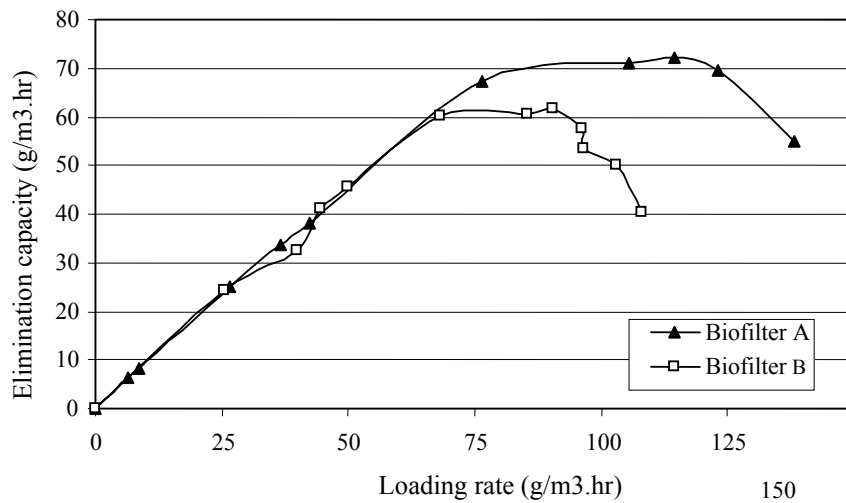**Fig. 4:** Removal efficiency and elimination capacity of biofilters (A) and (B) at different inlet TEA Concentrations

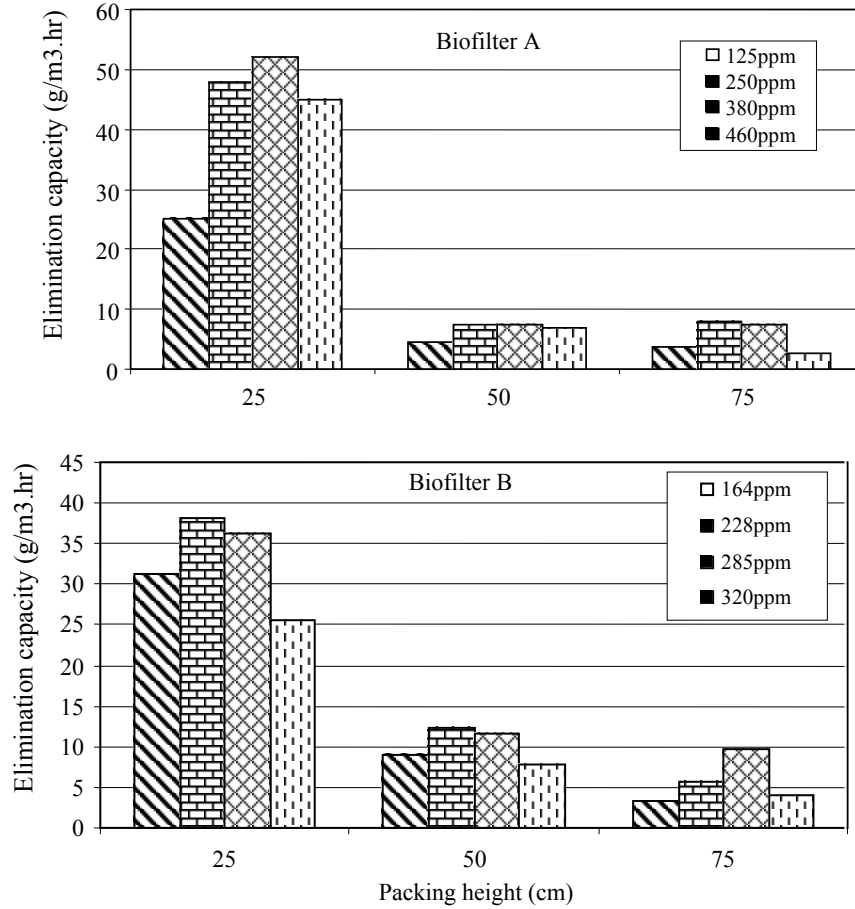**Fig. 5:** Elimination capacity of biofilters at different TEA loading rates

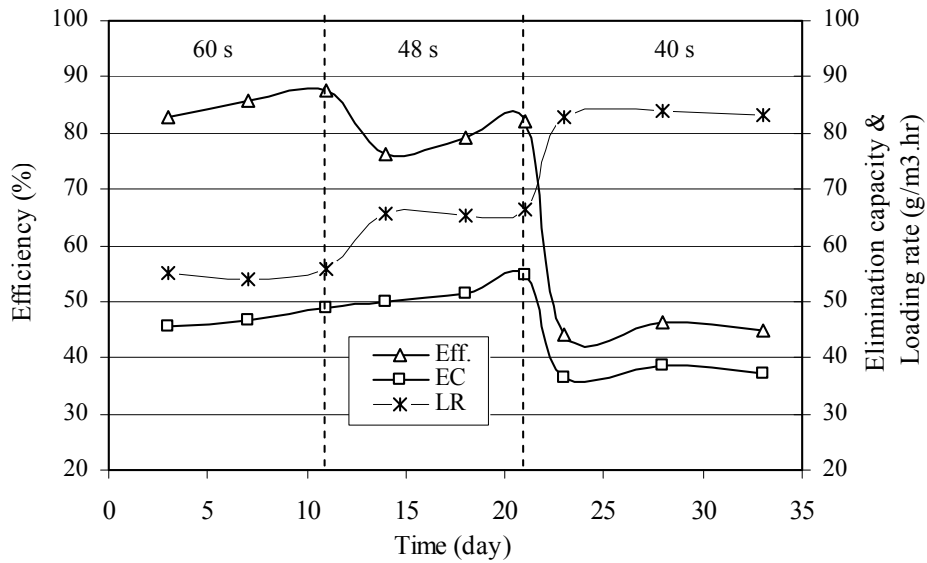**Fig. 6:** Effect of inlet TEA concentration on the biodegradation potential along the bed for biofilters A and B

Fig. 7: Effect of the Hydraulic Retention Time on the elimination capacity along the biofilter at constant inlet concentration of TEA

DISCUSSION

In this study, biofiltration of triethylamine vapor from waste gas was evaluated under different operational conditions. Generally, contaminant molecules may be simply dissolved in the water, but they may also be adsorbed on the surface of the medium, taken up by living cells, absorbed within organic matter in the biofilm or medium, or collected at the surface of water. For highly soluble contaminants, the dissolved form may be dominant, but for more hydrophobic contaminants, the major reservoir may be materials adsorbed on the surface of the medium and absorbed within the organic matter (Hodge and Devinny, 1997). Results showed that, at the beginning of biofiltration (about 2 weeks), probably adsorption was the main mechanism to remove TEA, but after a lapse of 25 d of the beginning of operation, efficiency decreased from 100 to 42% and again, increased to about 100% during the period of 11 d.

In general, higher substrate concentrations will improve treatment efficiency up to a point where biological kinetics drives the degradation rate to zero order. In a case of diffusion limitation, higher gas-phase concentration of substrate drives the contaminant into the biofilm more rapidly (Devinny et al., 1999). As such, gradual increase during the initial phases of reactor operation is essential for proper microbial growth and development. The observed acclimation period in this study was 3-4 weeks, because microorganisms in municipal activated sludge had not been acclimated to the target pollutant. Decreasing of removal efficiency was observed with a lag period after increasing the inlet concentration with subsequent increase in the removal efficiency after gradual acclimation of microbes to the pollutant.

At the beginning of each step in feed concentration, as shown in Fig.3, there was a decrease in removal efficiency with gradual recovery with time. For low concentrations, in both reactors, removal efficiency was higher than 90% (below 90 ppm). When the inlet concentration is increased, initially, the biofilm may be affected by a pseudo shock load with consequent increase TEA in effluent air from the column. At lower concentrations, the degree of drop in RE as a result of increased concentration is lower than at higher concentrations, due to lower microbial population demand. The time to recover from the drop is increasing with increased inlet TEA, due to an apparent increased inhibitory effect at higher concentration. This is more pronounced in regions where the concentration is approaching saturation EC.

The obtained data showed that there was a linear relationship between elimination capacity and organic loading rate up to an OLR value of 72.3 $gm^{-3}h^{-1}$ (inlet TEA concentration of 250 ppm for biofilter A) and 68 $gm^{-3}h^{-1}$ (inlet TEA concentration of 227 ppm for biofilter B). Beyond this value, a flattening of the curve is observed with eventual decreasing trend for OLR values greater than 120 $gm^{-3}h^{-1}$ (biofilter A) and 96 $gm^{-3}h^{-1}$ (biofilter B). This is a bit lower than the results reported by Tang et al. (1996) on the onset of inhibitory effects at loading rate of 140 $gm^{-3}h^{-1}$ for the compost/chaff biofilter. The difference may be attributable to the higher column length of 100 cm and HRT value of 60 s vs 48 s for this study.

In both reactors, the first section had the highest removal capacity due to exposure to higher relative concentrations of TEA. At low OLR values, up to 75% of the overall removals occurred in the initial section. As organic loading was increased, more penetration of substrate occurred and latter sections showed increased elimination capacities. Slight reduction in the biodegradation potential of the first section and an increased activity in latter sections can be attributed to overall microbial density limitations and saturation of specific activity for microorganisms in the first section. Dry patches due to higher biological activity and increased water evaporation due to energy released from biooxidation, observed in the initial portion of the column, may also provide additional insight

in the reduction of differences in elimination capacity for different sections at higher influent concentrations.

In order to evaluate elimination capacity, OLR can be increased through increased influent concentration or flow rate (reduced HRT).

Maximum EC was observed at HRT of 60 s which was in agreement with the range of minutes for alcohols to 3 h for 90% removal of trichloroethylene reported in literature (Bohn, 1992). The reduction in EC as a result of decreasing HRT to 48 s was minimal but further reduction of HRT to 40 s adversely affected the performance. While lower HRT value is favored since it implies more removal per unit volume of reactor, constraints of mass transfer from the gas phase to the biofilm limits optimum operating ranges. The results were similar for two biofilters (data for biofilter B not shown here).

Several conclusions could be deduced from the results as follows:

- Maximum EC value for TEA removal was observed as 72 $gm^{-3}h^{-1}$ at an OLR of 114 $gm^{-3}h^{-1}$ (biofilter A), and 61.5 $gm^{-3}h^{-1}$ at 90.5 $gm^{-3}h^{-1}$ (biofilter B).
- In both reactors, up to 75% of TEA removals were observed in the initial section of the biofilter.
- Operation conditions for optimum bioconversion of TEA in biofilter are recommended as follows; HRT: 48 s, temperature: 30±1°C, and a maximum loading rate for 100% and 81±14% removal efficiency, of 53±1 $gm^{-3}h^{-1}$ and 71±3 $gm^{-3}h^{-1}$, respectively.

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