Fate of Intermediate Biodegradation Products of Triethyl Amine in a Compost-based Biofiltration System

Ayoob Torkian*[1], Homa Keshavarzi Shirazi[2], Majid Hakimjavadi[1]

Abstract

Biofiltration of Triethylamine (TEA) vapor used as a catalyst in casting operations was evaluated in this study. The unit consisted of a 6-L three-stage biofilter containing a mixture of compost and wood chips (40:60v/v) as the filter medium. Seed microbial population from municipal activated sludge was acclimated for a period of three weeks prior to the actual experimental runs. In the startup period, high pH values up to 10 was observed due to alkaline nature of TEA and inadequate formation of biofilm and low overall biodegradation. Steady increase of organic-N concentration along with gradual upward trend of pressure drop indicated sound establishment of microbial population. Operational parameters studied included loading rate (6-116 g $m^{-3}h^{-1}$), hydraulic detention times (40-60 s), temperature (30±1°C), and humidity (50-55%).

Results indicated effluent ammonia concentrations meeting standards of 25 ppm can be obtained after 2.5 months of operation. Optimal organic loading rates (OLRs) of 90±14 g $m^{-3}h^{-1}$ for Hydraulic Retention Time (HRT) value of 48 s was suggested. Under these conditions, elimination capacity of 71±3 g $m^{-3}h^{-1}$ and removal efficiency 81±14% were achieved. Mass balance was performed on different forms of nitrogen products for a constant inlet concentration of 180 ppm TEA with a relatively stable removal efficiency of about 90% maintained for over a month. Both liquid (leachate) and gas (different sections, inlet, and outlet) phase measurements were made for the purpose of performing calculations. Ammonium-N and Nitrate-N were dominant in the first and third sections of the reactor, respectively. Cumulative TEA-N mass balance over a 2-month period indicated an equal proportion breakdown into ammonia-N, nitrate-N, and ammonium & organic-N. The fact that up to 30% of TEA-N could not be accounted for in the leachate and gas measurements can be attributed to incorporation into the cellular constituents.

Key words: Biofiltration, triethyl amine, biodegradation, air pollution, casting

Introduction

Biodegradation of organic pollutants is becoming increasingly popular for process industries generating large flows of flue gas with low pollutants' concentration. Adoption of stricter emission policies in recent years and increasing costs of chemicals and disposal

1 Institute of Water and Energy, Sharif University of Technology, Azadi Avenue, P.O. Box 11365- 688 Tehran, Iran, *Corresponding author (torkian@sharif.edu)

2 Department of Environmental Engineering, Faculty of Environment, University of Tehran, P.O Box 14155-6135, Tehran, Iran,

of hazardous wastes generated from chemical treatment technologies have been the main driving force behind the development and optimization of biological treatment systems. The technology is still under development in terms of economics, equipment, process kinetics, and operational skills and different layouts and flow trains are being proposed including biofiltration, biotrickling filter, and bioscrubber (Burgess et. al., 2001). In biofiltration, microorganisms immobilized on an organic porous support bed metabolize pollutants in contaminated gaseous stream passing through into less harmful products (van Groenestijn & Hesselink, 1993; Ergas et. al., 1994). Apart from nutritional and environmental requirements of the biomass, porosity and bulk density of the bed media are important for the effect they have on the gas phase pressure drop across the bed.

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 triethyl amine (TEA) are the main gaseous catalysts for polymerization reactions comprising the majority of nitrogenous emissions (Borger et. al., 1997; Strikauska et. al., 1999; Busca & Pistarino, 2003). TEA has a very low odor threshold and exposure to it may cause adverse health effects such as asthma and visual disturbances (Belin et al., 1983; A kesson et al., 1985).

Metabolic pathways of TEA in humans have been studied (A kesson et al., 1988) but information on microbial degradation of TEA is limited. In contrast to poor results obtained under anaerobic conditions (Kawahara et al., 1999), Tang et al. (1996) reported that 100% removal efficiency of TEA at loads up to 140 $gm^{-3}h^{-1}$ in a laboratory-scale reactor. Other studies have suggested suitable biodegradation potential of amines (Tang et. al., 1996; Chou & Shiu, 1997). As such, biofiltration seems to be an appropriate method to treat waste gases containing these pollutants.

This study was conducted to investigate the performance of biofiltration system in treating triethyl amine-laden flue gas from casting operations under various conditions of inlet concentration, moisture content, and loading (organic and hydraulic). Specifically, the fate of intermediate products of TEA in a pilot plant system is evaluated.

Materials and Methods

Experimental Setup

Experiments were conducted in a laboratory scale reactor shown in Figure 1. The column had an inner diameter of 5 and an effective height of 100 cm. Perforated Plexiglas plates (pore diameter = 3 mm) placed between sections acted as a support for the packing material as well as for flow redistribution. A 5 cm space in 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 prepared 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±1 °C and 50-55%, respectively.

Filter Media and Microbial Culture

Filter media was prepared by blending of sieved compost and wood chips. Municipal compost (equivalent diameter 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 solution was also added to the activated sludge (g dm^{-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

The critical parameters include Empty-Bed Residence Time (EBRT), Mass Loading Rates (MLR), Removal Efficiency (RE) and Elimination Capacity (EC). EBRT is the time a parcel of air will remain in a empty biofilter and overestimates the actual treatment time. MLR define 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.

RE and EC are used to describe the performance of a biofilter. 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 it is measured. The EC is normalized with respect to volume by definition and allows for direct comparison of the results of two different biofilter systems.

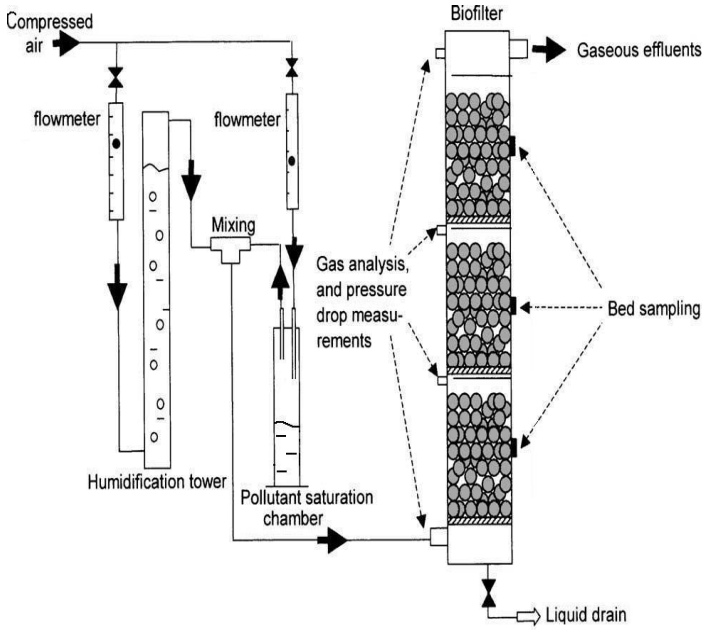

Figure 1- Schematic diagram of the experimental biofiltration system

Analytical methods

Gas samples were collected at the inlet, outlet, and in the 5cm plenum between the sections. The amount of TEA was measured by UV spectrophotometer (UV/VIS-911, GBC CO, Australia) at a wavelength of 215 nm. For measuring pH, 1 g 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 with a range from –10 to 110 and a scale division of 1°C. Gas flow rate was measured using flow meter (Omega Fl-2016) with units of l/min. 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 and Discussion

Startup

At the startup of biofilter, influent TEA concentration was adjusted to 20 ppm at an organic loading rate of 6 g $m^{-3}h^{-1}$ and relative humidity of 50-55%. Also, water temperature in humidifier was adjusted to 28±2°C. Superficial gas velocity was 57.3 m hr^{-1}, corresponding to a residence time of 48 seconds. The observed acclimation period was 3 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. Further details are provided elsewhere (Keshavarzi et. al., 2005)

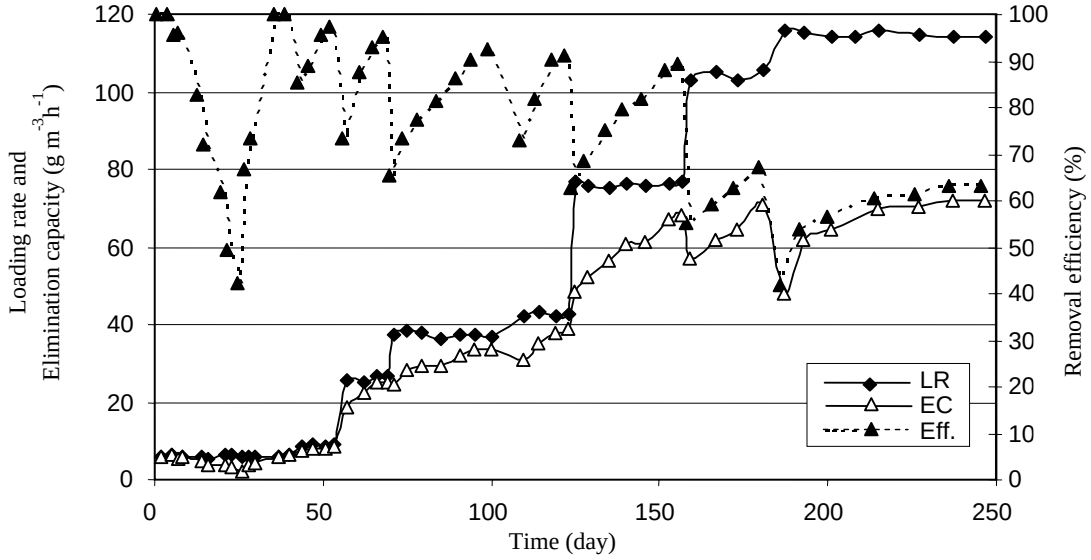

Figure 2 – Removal efficiency and Elimination capacity of biofilter at different inlet TEA concentrations

Removal efficiency

Inlet TEA concentration was increased up to 385 ppm (1.5 g m^{-3}) stepwise at the HRT of 48 s, so mass loading changed proportionally. As shown in Figure 3, at the beginning of each step change in feed concentration, there was a decreasing in RE with gradual recovery with time. For low concentrations RE was higher than 90% (below 90 ppm, 95-100%, below 180 ppm, 90-95%).

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.

Elimination Capacity

EC 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 & Barford, 2000). In some cases, it is known that very high concentration of substrate can become inhibitory (Devinney et. al., 1999).

In order to evaluate EC, OLR can be increased through increased influent concentration or flow rate (reduced HRT). By increasing inlet TEA concentrations while maintaining constant flow rate (HRT=48 s), OLR was increased. As shown in Figure 3,

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

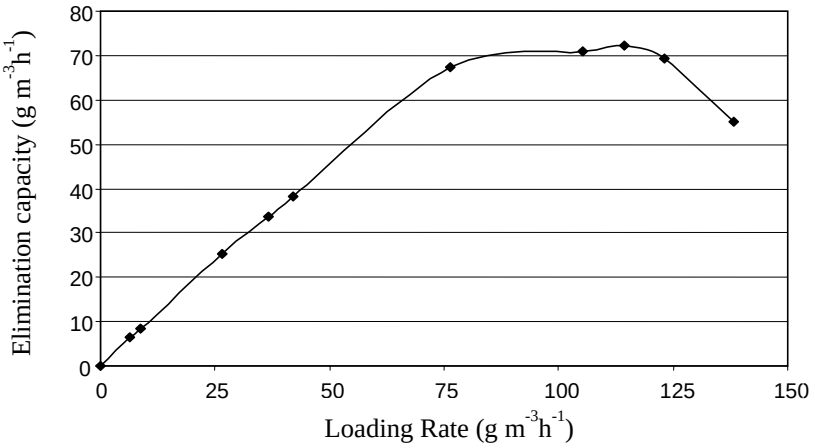

Figure 3 - Elimination capacity of biofilter at different TEA loading rates.

Ammonia/Ammonium

Due to the alkaline nature of TEA, initially an increase in pH was observed. Because of equilibrium relationships, fraction of ammonium ion at high pH is low and observed effluent ammonia concentration was high. With time, further adaptation of microbial population resulted in degradation of TEA and consequent reduction of pH in the system. It took more than a month after the startup period for the effluent ammonia concentration to fall below the 25 ppm level. Ammonium concentration inside bed increased with time with the first section having the highest levels measured. As has been suggested previously (Sheridan, Curran, and Dodd, 2002), ammonia in the first step is absorbed on to the biofilter packing material, giving rise to the formation of ammonium ion. The bacterial consortium then degrades this ammonium to nitrite producing H^+, which reduces the pH of the system, thus increasing the ability of the biofilter to absorb more and more.

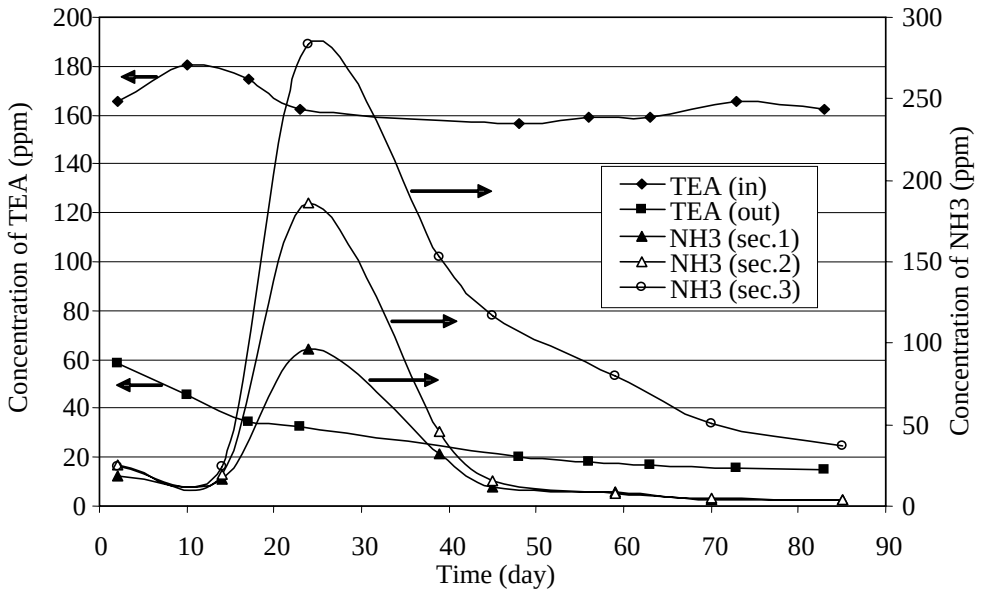

Figure 4 – Variation of ammonia nitrogen concentration throughout different sections

Nitrate

Presence of ammonia in the effluent is a function of the degree of nitrification in different sections of the reactor. An equilibrium relationship between fractions of ammonia gas-ammonium ion determines the availability of ammonium ion for onset of nitrification by nitrifiers. In actual operational conditions, the degree of approach to equilibrium is difficult to ascertain but the ratio of ammonia-ammonium is a function of many factors including temperature and pH. The higher the population of nitrifiers, the higher the rate of disappearance of ammonium ion and subsequent rate of dissolution of ammonia gas into the solution. As seen in figure 5, minimal nitrate levels are observed in the first section and the highest concentrations are in the third section implying low microbial population at the inlet section. The rate of increase in nitrate concentration is not uniform in the reactor indicating a gradual adaptation of nitrifiers with optimal conditions finally

reached in the third section. A potential ramification of the trend of nitrate increase is that sufficient contact time should be allowed in the reactor so as to avoid high outlet ammonia concentrations and better utilization of available reactor length for establishment of nitrifiers. Periodic reversal of flow direction may aid in increasing the overall nitrifier biomass but the dynamics of microbial population under different conditions warrants further research.

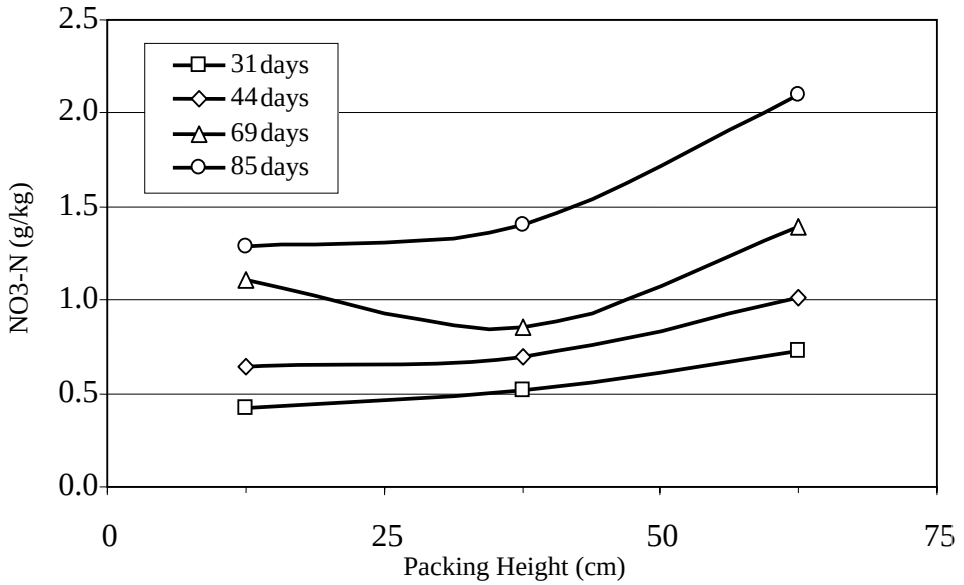

Figure 5- Variation of nitrate concentration in different sections of the biofilter

Conclusions

Biofiltration of triethyl amine (TEA) vapor from waste gas evaluated under different operational conditions in this study. Several conclusions can be surmised from the results as follows:

- Maximum EC value for TEA removal was observed to be 72 g $m^{-3}h^{-1}$ at an OLR of 114 g $m^{-3}h^{-1}$.
- 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: moisture content, 50-55%; HRT, 48 sec, and a maximum loading rate for 100% and 81±14% RE, are 53±1 and 71±3 g $m^{-3}h^{-1}$, respectively.
- During the initial operation period, there was an increased pH due to the alkaline nature of TEA. It took about a month for microbial population to establish to reduce effluent ammonia concentration to fall below the 25 ppm level
- Nitrate levels were lowest in the first section and highest at the last indicating a gradual adaptation of nitrifiers in the reactor. Optimum HRT should be seen in light of the dynamics of microbial population to ensure compliance with effluent ammonia concentration.

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