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Fate of intermediate biodegradation products of triethyl amine in a compost-based biofiltration system

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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 (40:60 v/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 $g/m^3/h$), 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 $g/m^3/h$ for Hydraulic Retention Time (HRT) value of 48 s were suggested. Under these conditions, elimination capacity of 71±3 $g/m^3/h$ 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

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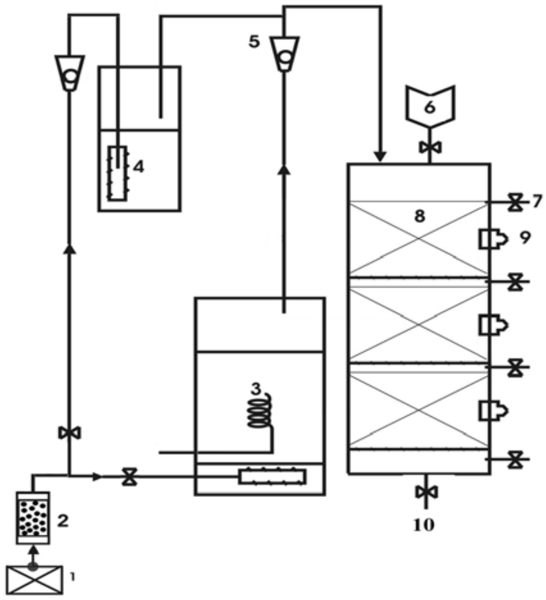
INTRODUCTION

Gas-phase biotreatment has emerged as an effective and inexpensive alternative to conventional physicochemical treatment systems for treating large air streams with low concentrations (Kim, *et al.*, 2000). Adoption of stricter emission policies in recent years and increasing costs of chemicals and disposal 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, contaminated air to be treated is passed through a packed bed where biodegradable gases or volatile compounds are absorbed into the biofilm in which diffusion and aerobic biodegradation occur simultaneously in a complex set of physical, chemical and biological interactions (Baquerizo, *et al.*, 2005).

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 and 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 and Hwang (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 and Hwang, 1996; Chou and 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.



(1-compressor, 2-carbon filter, 3-humidifier, 4- pollutant vessel, 5-rotameter, 6-nutrient, 7-gas sampling port, 8-biofilter bed, 9-bed sampling port, 10-leachate)

Fig. 1. Schematic of biofilter system

MATERIALS & METHODS

Experiments were conducted in a laboratory scale reactor shown in Fig. 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 absorber 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 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).

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 an 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. 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 & DISCUSSIONS

At the startup of biofilter, influent TEA concentration was adjusted to 20 ppm at an organic loading rate of 6 $g/m^3/h$ and relative humidity of 50-55%. Also, water temperature in humidifier was adjusted to 28±2 °C. Superficial gas velocity was 57.3 m/h, corresponding to a residence time of 48 s. 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. Excess biomass development was initially observed leading to high pressure drops. Input loading was adjusted to prevent accumulation of biomass in the filter bed, even though different biomass concentrations were present along the bed height. Further details are provided elsewhere (Keshavarzi, *et al.*, 2005). 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 Fig. 2, 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%).

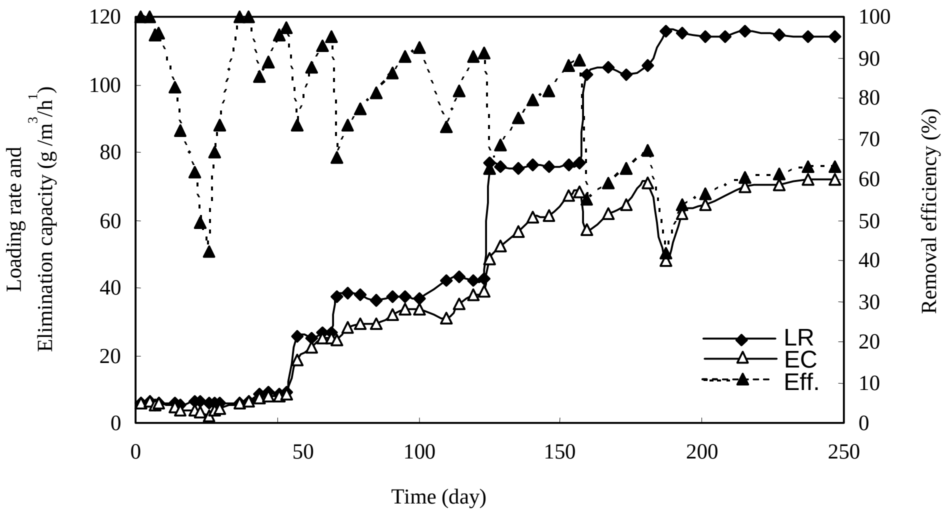


Fig. 2. Removal efficiency and elimination capacity of biofilter at different inlet TEA concentrations

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 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 Fig. 3, there is a linear relationship between EC and OLR up to an OLR value of 72.3 $g/m^3/h$. (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 $g/m^3/h$. This is a bit lower than the results reported before (Tang and Hwan, 1996) on the onset of inhibitory effects at loading rate of 140 $g/m^3/h$. 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. As expected, there was an indication of an increasing trend for the elimination capacity with time and a sharper decrease in the ammonia concentration observed in the last section indicating a higher concentration of nitrifying biomass had in the section closest to the outlet of the biofilter. Organic nitrogen measurements presented in Fig. 4 showed a four fold increase by day 70 indicating a consistent trend for biomass development. While large biomass concentration is essential for optimized performance, operational constraints of pressure drop warrant a balanced growth and decay for microbial population. At inlet TEA concentration of 180 ppm, there was no excessive pressure drop and/or biomass accumulation with subsequent balanced performance.

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 Fig. 6, 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. A summary of mass balance calculations for inlet concentration of 180 ppm are presented in Table 1. All the values are normalized on the basis of mg N/d and the column on TEA-N indicates observed removals. As shown in the table, a third of the total nitrogen is associated with ammonia gas, a third with ammonium ion, and the rest for organic and nitrate nitrogen. Cumulative results shown in Fig. 7 indicates increasing trend for TEA removal but incomplete ammonia conversion to nitrate. This could be the result of various factors including insufficient microbial population, interface diffusion resistance, and temperature effects on ammonia-ammonium equilibrium conditions.

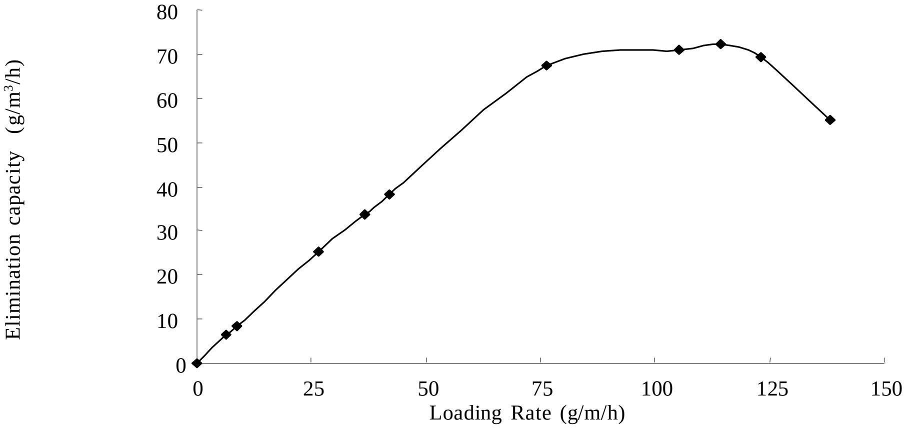


Fig. 3. Elimination capacity of biofilter at different TEA loading rates

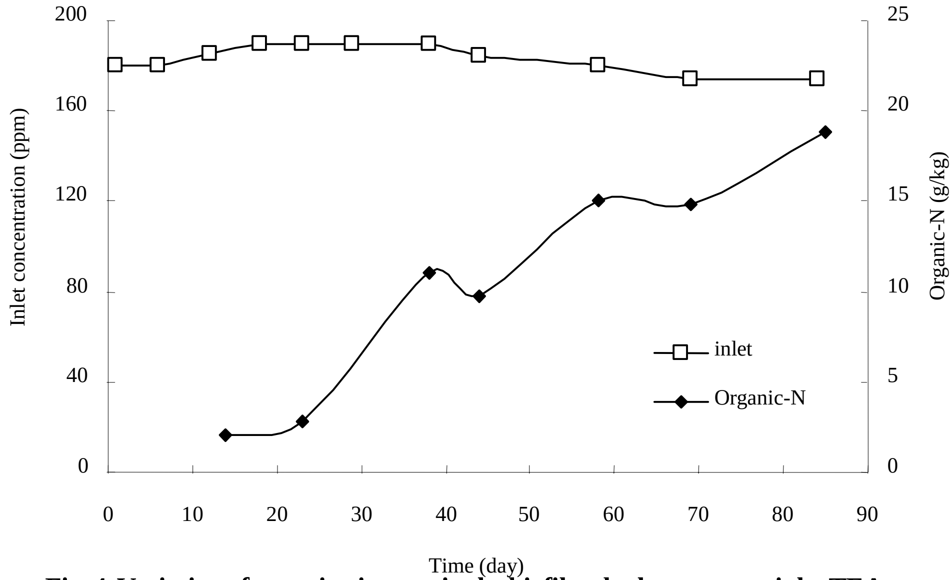


Fig. 4. Variation of organic nitrogen in the biofilter bed at constant inlet TEA concentration of 180 ppm

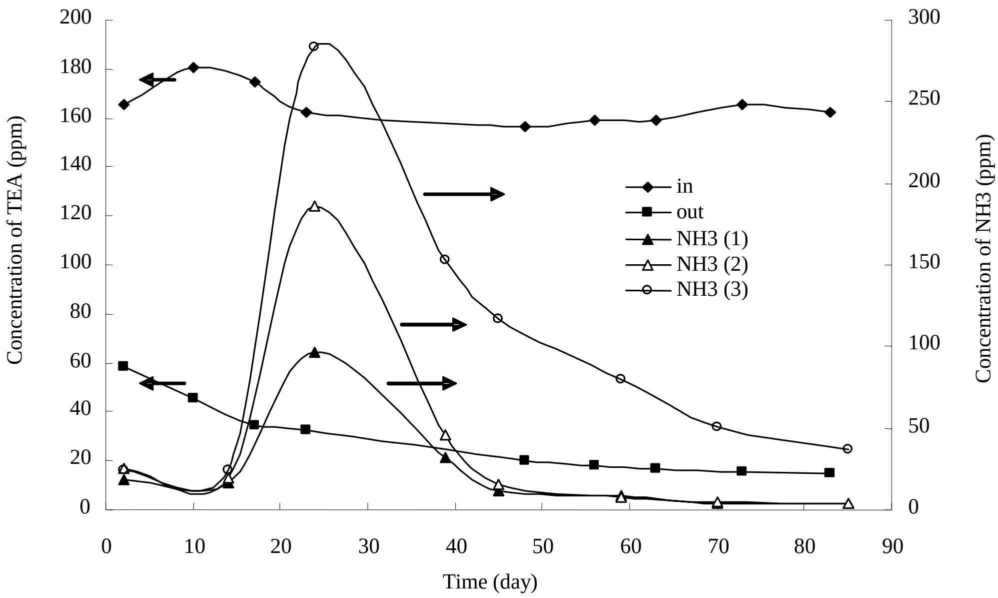


Fig. 5. Variation of ammonia nitrogen concentration throughout different sections

Table 1. Summary of mass balance calculations for different nitrogen forms for inlet TEA concentration of 180 ppm (all values in mg/d)

Day	TEA-N	NH3-N	Org-N (mg/day)	leachate		Reactor bed	
				NO3-N	NH4-N	NO3-N	NH4-N
13	1145	709.7	?	0.03	0.15	110.3	114.6
23	1173	573	284.6	0.07	0.22	62.2	134.6
38	1173	419.6	546.4	0.03	0.20	-5.4	183.9
44	1136	373.3	-220.3	0.45	10	224.3	678.3
58	1111	342.5	376.4	0.23	14.7	72.9	234.9
69	1074	284.2	-15.5	0.29	16.2	306	306
84	1074	200.9	253.1	0.20	11.2	95	275.1

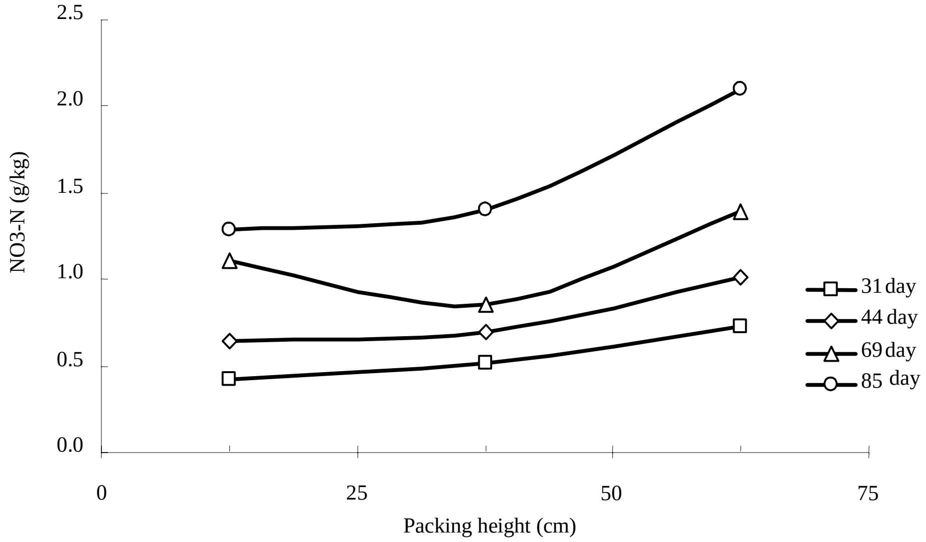


Fig. 6. Variation of nitrate concentration in different sections of the biofilter

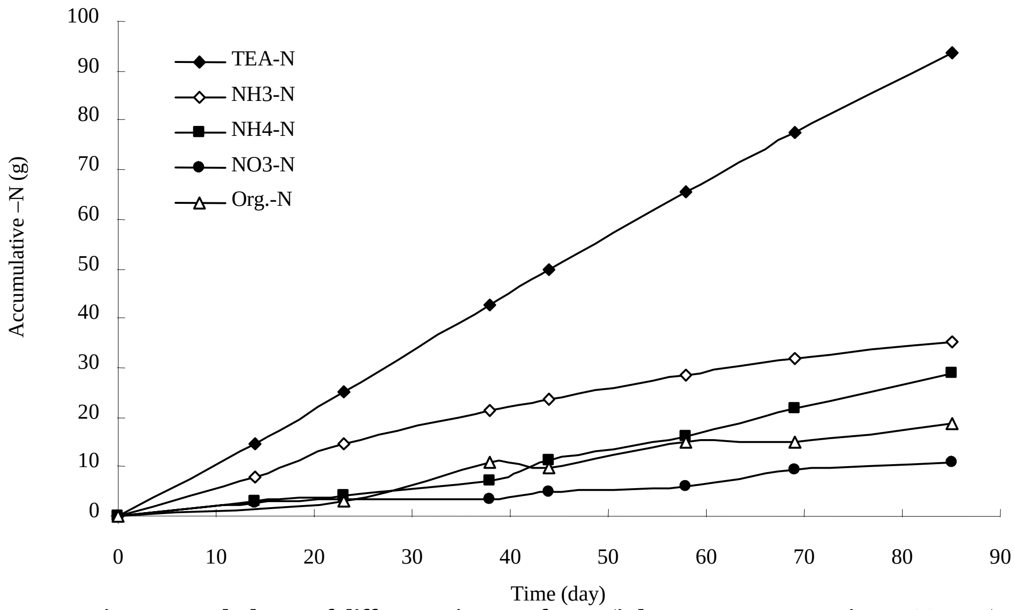


Fig. 7. Mass balance of different nitrogen forms (inlet TEA concentration=180 ppm)

CONCLUSION

Biofiltration of triethylamine (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 $g/m^3/h$ at an OLR of 114 $g/m^3/h$.
- 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 s, and a maximum loading rate for 100% and 81±14% RE, are 53±1 and 71±3 $g/m^3/h$, 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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