

Evaluation of biofilter performance in the co-treatment of styrene and acrylonitrile vapors mixture

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ABSTRACT. Styrene and acrylonitrile are produced in large quantities in the petrochemical industries and have been listed among the 189 hazardous and toxic atmospheric contaminants under United States Clean Air Act Amendments 1990 due to their adverse effects on human health. The experimental work was conducted to evaluate the inhibition effect of biofilter in the presence of co-substrate. Yard waste compost mixed with shredded hard plastics in a 25:75 v/v ratio of plastics:compost as the bed media was inoculated with thickened municipal activated sludge. Acclimation to styrene was achieved at 45 days, but there was a very short acclimation period for acrylonitrile. The results show that performance of biofilter with mixed cultures is better than single strains. Finally application of activated sludge for start up of biofilters in full scale would be practical and economical. Under steady-state conditions, maximum elimination capacity of pure styrene was obtained $44 \text{ g m}^{-3} \text{ h}^{-1}$ but introducing acrylonitrile into the air stream adversely impacted the performance of biofilter in the reduction of styrene. Maximum elimination capacity of $103 \text{ g m}^{-3} \text{ h}^{-1}$ obtained for acrylonitrile at the presence of styrene whereas the maximum removal rate of $120 \text{ g m}^{-3} \text{ h}^{-1}$ acquired for pure acrylonitrile. Removal of acrylonitrile was not affected by the presence of styrene in the air stream. The biofilter removed up to about $85 \text{ g carbon m}^{-3} \text{ h}^{-1}$ at empty bed retention times between 30 and 120 s.

1 INTRODUCTION

Common traditional technologies used to apply in reduction of volatile organic compounds (VOCs). However, significant quantities of hazardous compounds are emitted into the atmosphere by treated off gases. Further treatment of these secondary compounds from the gas stream makes the treatment system even more expensive. Recently biofiltration are becoming the suitable alternative for traditional systems (Ottengraf, 1986). In the biofiltration the contaminated stream passes through porous. Microorganisms are naturally immobilized on porous support particles and form biolayers on the surface of them. As the contaminated stream passes through the filter bed, pollutants are transferred from the gas phase to the biolayer and are metabolized (Ergas *et al.*, 1994). Many researchers have investigated the biofiltration of VOC mixtures including oxygenated, aromatic, and halogenated compounds (Kinney *et al.*, 1996; Quinlan *et al.*, 1999; Veiga and Kennes, 2001), although only a few have studied

interaction effects between the compounds (Mohseni and Allen, 2000; Aizupuru *et al.*, 2001). Aizupuru *et al.* (2001) found that oxygenated VOCs were preferentially degraded in the presence of aromatic and halogenated VOCs. Mohseni and Allen (2000) found that methanol strongly inhibited the removal rate of α -pinene in wood-chip biofilters.

Styrene and acrylonitrile are among the other hazardous and toxic chemicals has been mentioned under Title III of 1990 Clean Air Act Amendments and they are realized into the environment in the manufacture of polystyrene, styrene-butadiene rubber, acrylonitrile-butadiene-styrene and acrylic fibers (USEPA, 1993 and 1999). Biofiltration process is a favorable technology for treatment of gas stream contaminated with dilute concentrations of styrene (Arnold, *et al.*, 1997; Chou and Hsiao, 1998; Pol *et al.*, 1998; Jorio *et al.*, 2000; Juneson *et al.*, 2001; Paca *et al.*, 2001; Zilli, *et al.* 2001, 2003). However the treatability of pure acrylonitrile is relatively limited in the literature. The only research has been conducted by Lu *et al.* (2000), which more than 95% removals were achieved at acrylonitrile loads from 3 to 490 $g\ m^{-3}\ h^{-1}$. Only Lu *et al.* (2002) was evaluated removal of styrene and acrylonitrile mixtures in a biotrickling filter and the removal efficiency of acrylonitrile was higher than those of styrene.

The main objective of this research was to evaluate the feasibility of biofiltration technology and to extend the application of this process to the control of VOCs emitted from petrochemical industries. The first goal was performance evaluation of biofilter in the elimination of acrylonitrile as a hydrophilic hydrocarbon in comparison with the biofiltration of a nearly hydrophobic hydrocarbon like styrene and the second goal was reveal the inhibition effects of acrylonitrile in the biofiltration of mixture of styrene and acrylonitrile.

2 MATERIALS AND METHODS

A three-stage downward flow bench-scale biofilter was used to removal of styrene and acrylonitrile from synthetic gas stream. The biofilter was constructed from galvanized iron (Figure 1). The column had an inner diameter of 8 cm with an effective bed height of 120 cm. Perforated steel plate plenums (pore diameter = 2 mm) placed between sections acted as a support for the packing material as well as for gas flow redistribution. A 7-cm height space in between the sections allowed for representative gas sampling. Provision of sampling ports at the top, midpoint and the end of each section allowed bed media access. The waste gas stream was prepared by passing compressed air through a granular activated carbon canister to capture residual oil and particles then has been sparged through a 15 l water container equipped with heated element for adjusting gas stream temperature and humidification. Pollutant vapor was prepared by introducing low flow air stream into a container receiving drop-wise styrene feed from a burette. The main air stream was mixed with the stream containing pollutant vapor to generate feed air with the needed concentration. Temperature control of the bed material to $30\pm 1^\circ\text{C}$ was achieved by using a heated tape wrapped around the exterior of the reactor wall. Water content of the bed material was maintained at 60-65% during the study period.

Bed Media was prepared by mixing yard waste compost and shredded high-density plastics (PVC) with the size between 1.5 \times 1.0 cm as bulking agent to produce a volumetric ratio of about 25:75 v/v ratio of plastics:compost with the overall porosity of 54%. Thickened activated sludge obtained from municipal wastewater treatment plant was added to this mixture to increase microbial density and improve homogeneity of compost particles and bulking agents. Nutrient and buffering solution was added to the

bed medium according to the quantity of inlet carbon to keep the C: N: P ratio around 100:5:1. The nutrient solution had the following composition (per liter of tap water): 0.694 g KH_2PO_4 , 0.854 g K_2HPO_4 , 1.234 g $(\text{NH}_4)_2\text{SO}_4$, 0.46 g $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, 0.176 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.001 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 5 ml trace element solution consisting of 60 mg l^{-1} H_3BO_3 , 40 mg l^{-1} $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 20 mg l^{-1} $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 6 mg l^{-1} $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 6 mg l^{-1} $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, 4 mg l^{-1} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 2 mg l^{-1} $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with an overall pH around 6.9 ± 2 (Ergas *et al.*, 1994).

Gas phase concentrations of styrene and acrylonitrile was determined via gas chromatographic (model SRI 110 Inc. USA) analysis. The gas chromatograph equipped with a flame ionization detector and a 30 m stainless steel capillary column. Operating conditions were as follows: temperature schedule (injector 200 °C, oven with initial temperature of 100 °C and ramp of 40 °C per min to reach the final temperature of 220 °C with holding time of 0.1 min and detector 230 °C) and N_2 carrier gas at 8 ml min^{-1} , H_2 as makeup gas with flow rate of 25 ml min^{-1} and O_2 in 6 ml min^{-1} flow rate. The average standard deviation for the GC was about 5% and 8% at very low concentrations of styrene and acrylonitrile, respectively.

3 RESULTS AND DISCUSSION

Figure 2 shows the performance of the biofilter treating mixtures of styrene and acrylonitrile during the start-up period. The experiment was started with a biofilter that was under operation with styrene vapor for more than 1 year, then acrylonitrile injected with concentration of about 200 ppmv and EBRT of 120 s. The removal of acrylonitrile was reached to more than 80% in 10 days and closed to 95% after about 20 days. There was a very short acclimation period for acrylonitrile degrading community in the biofilter. The removal of styrene after introducing acrylonitrile into the gas stream was decreased from 100% to about 80%.

The performance of the biofilter during the start-up period was further studied by monitoring the concentration profiles of styrene and acrylonitrile (Figure 3). Acrylonitrile was removed in the top sections of the biofilter. There was complete biodegradation of styrene before introducing of acrylonitrile throughout the biofilter, but the concentration profile of styrene along the biofilter came up in the following days, thereby indicating that the styrene degrading microorganisms suppressed by presence of acrylonitrile. Acrylonitrile is a hydrophilic and easily biodegradable compound; hence, it may suppress the growth of styrene degrading community during the biodegradation of mixtures of acrylonitrile and styrene in the top section where both compounds are largely present.

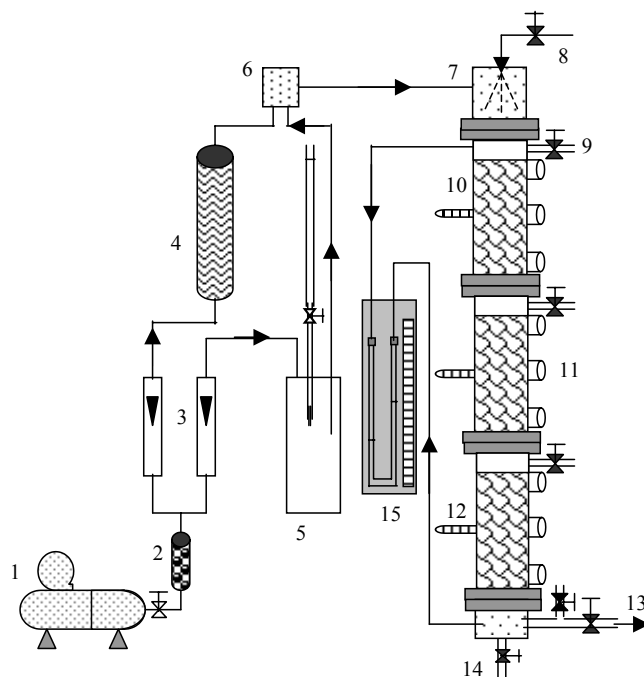


Figure 1. Schematics of biofilter system (1-compressor, 2-carbon filter, 3- rotameter, 4- humidifier, 5-pollutant vessel with styrene and/or acrylonitrile injector, 6-mixing chamber, 7-gas inlet, 8-nutrient inlet, 9-gas sampling port, 10- biofilter bed, 11-bed sampling port, 12- thermometer, 13-gas outlet, 14-leachate discharge, 15-manometer).

Figure 4 shows the overall performance of the biofilter in removing of styrene and acrylonitrile, in terms of total carbon loadings. The biofilter removed up to about $85 \text{ g carbon m}^{-3} \text{ h}^{-1}$ at EBRTs between 30 and 120 s. Mohseni *et al.* (2001) reported maximum $80 \text{ g carbon m}^{-3} \text{ h}^{-1}$ at EBRT of 30 s on the removal of mixed of α -pinene and methanol. The overall VOC removal rate in this study is comparable to (or higher than) the results obtained by other researchers (e.g. Baltzis *et al.*, 1997; Deshusses and Johnson, 2000; Govind *et al.*, 1993; Shareefdeen *et al.*, 1993) working on single and/or mixed VOCs.

The continuously monitored concentrations of styrene and acrylonitrile along the biofilter are illustrated in Figure 5. The first section of the biofilter had the highest microbial activity and removed up to about 70% of the total inlet concentration. Also, acrylonitrile biodegradation was not affected by the presence of styrene in the air stream. The biofilter provided similar acrylonitrile removals in the absence and the presence of styrene in the air stream. The biodegradation rate of styrene increased in the lower sections of the biofilter where acrylonitrile was depleted or where there was little acrylonitrile in the air stream. This implies a kind of inhibitory kinetics for the biodegradation of styrene in that its removal rate is affected by the concentration of acrylonitrile.

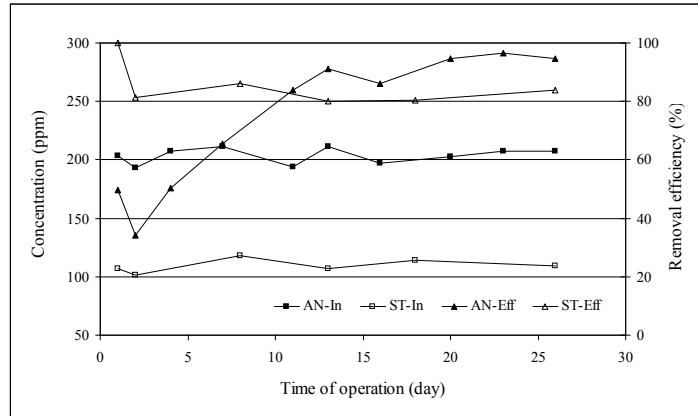


Figure 2. Acclimation period of biofilter for removal of acrylonitrile in the presence of styrene.

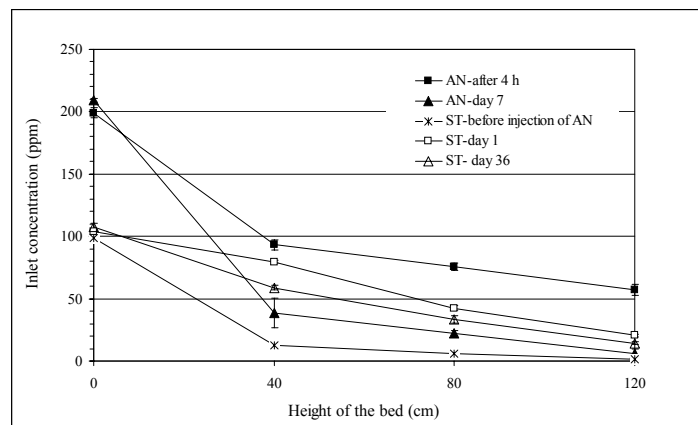


Figure 3. Concentration profile along biofilter column for co-treatment of styrene and acrylonitrile at the start up time.

Figure 6 shows the elimination capacity of styrene without acrylonitrile and mixed with acrylonitrile. It seems that the elimination capacity of pure styrene as a magnitude of second is higher than for mixed of styrene and acrylonitrile. This can be contributed to the competition for the biocatalytic activity among multiple substrates in biodegradation reactions. The difference in the elimination capacity of pure and mixed VOC feeds increased with increasing organic loading rates of both hydrocarbons, indicating that the competition effects were enhanced under high carbon loading rates. Maximum elimination capacity of $103 \text{ g m}^{-3} \text{ h}^{-1}$ for acrylonitrile was occurred at $EBRT$ of 60 s that was corresponding to removal efficiency of about 70%. At loading rates up to $80 \text{ g m}^{-3} \text{ h}^{-1}$ the biofilter performed complete degradation of acrylonitrile and removal efficiency of biofilter increased gradually, whereas at loading rates of higher than $80 \text{ g m}^{-3} \text{ h}^{-1}$ the removal rate of biofilter started to decline and reached to constant level of about $100 \text{ g m}^{-3} \text{ h}^{-1}$.

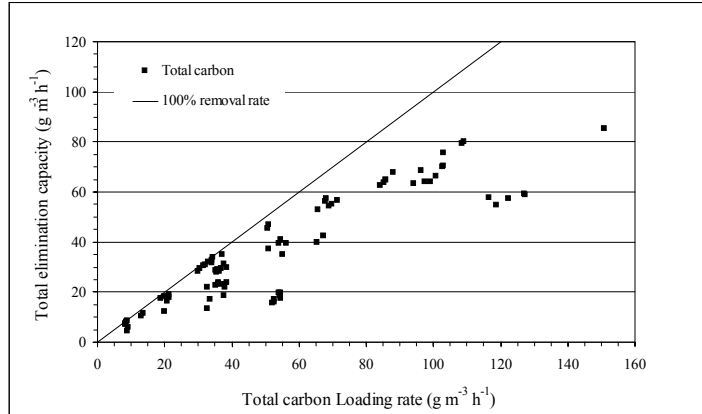


Figure 4. Overall performance of biofilter in treating total inlet organic carbon.

The effect of inlet concentration on the removal rate of styrene and acrylonitrile has been indicated in the Figure 7. Acrylonitrile elimination capacity was dependent to inlet concentration and progressively increased up to 1.85 g m^{-3} . When acrylonitrile inlet concentration is higher than 0.75 g m^{-3} , styrene removal rate decreases respect to pure styrene treatment while at low acrylonitrile concentration the degradation of styrene was not influenced. McGrath *et al.* (1999) fund that at butylacetate inlet concentrations of greater than 0.2 g m^{-3} the removal efficiency of styrene dropped about 50%.

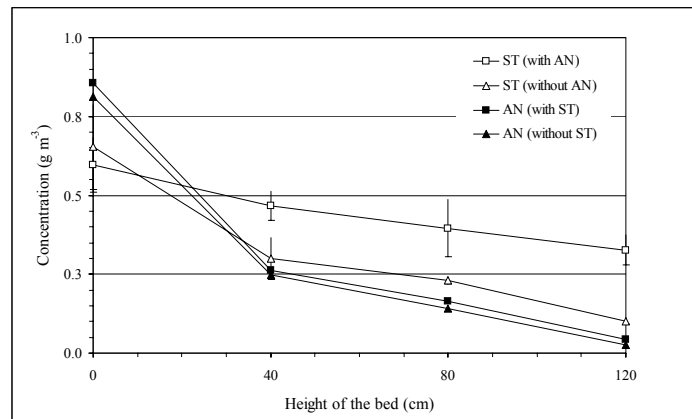


Figure 5. Concentration profile along the bed height of the biofilter in co-treatment of acrylonitrile and styrene.

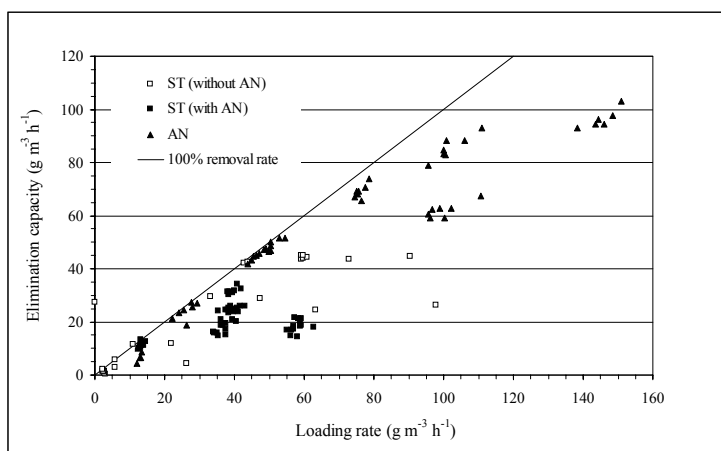


Figure 6. Evaluation of the biofilter performance in the elimination of styrene and acrylonitrile mixture at different loading rates

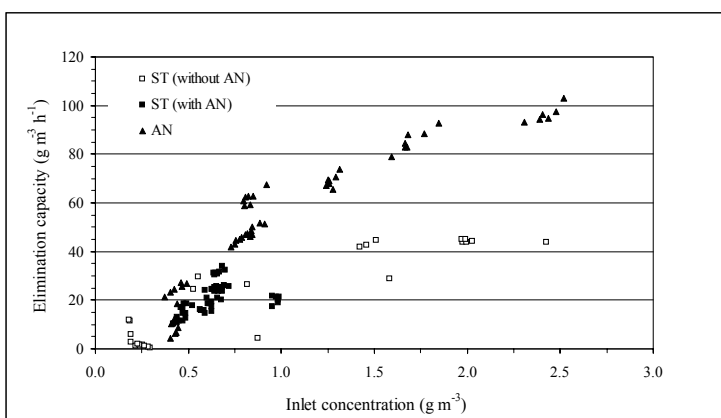


Figure 7. Effect of inlet concentration at the removal of styrene and acrylonitrile mixture in the biofilter

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