Using UV pretreatment to enhance biofiltration of mixtures of aromatic VOCs

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Abstract

Mixtures of airborne toluene and o-xylene, two relatively recalcitrant volatile organic compounds (VOCs), were treated effectively using integrated UV-biofiltration. The set-up consisted of a biofilter receiving UV-pretreated stream and a reference biofilter receiving no pretreatment. Experimental conditions included UV fluences of 6 and 12 mJ cm^{-2} as well as air flow rates of 6.3 and 9.4 L min^{-1}, corresponding to biofilter empty bed retention times (EBRTs) of 45 and 30 s, respectively. The inlet concentration of organics (toluene and o-xylene) ranged between 70 and 650 mg$_{carbon}$ m^{-3}. The UV-biofilter consistently provided removal efficiencies of greater than 95% over the range of toluene and o-xylene inlet concentrations. Also, the coupled UV-biofiltration system provided up to 60% additional contaminant removal compared to the sum of that offered by UV and reference biofilter, demonstrating the synergistic effect of UV on biofilter performance. The UV photooxidation partially oxidized a fraction of toluene and o-xylene into water soluble and more biodegradable intermediates, such as acetaldehyde and formaldehyde, which were readily removed in the downstream biofilter. These intermediates along with up to 20 ppmv ozone, formed through the photolysis of oxygen by 185 nm UV, contributed to the enhanced degradation of parent VOCs in the biofilter as well as the absence of any inhibitory effects of the VOCs on one another. Also, the presence of ozone helped control the growth of excess biofilm in the UV-coupled biofilter. While the standalone biofilter showed significant pressure drop increase (of up to 14 mm H$_2$O m^{-1} of the bed) over the course of experiment, the UV-coupled biofilter maintained a relatively low pressure drop of less than 3 mm H$_2$O m^{-1} of the bed.
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1. Introduction

Air emissions from many industrial manufacturing operations as well as hazardous sites and ground water remediation facilities [1–3] contain volatile organic compounds (VOCs) that are potentially harmful to human health and the environment. Of particular concern are aromatic VOCs, e.g. toluene and o-xylene, which are designated as hazardous air pollutants (HAPs) under the 1990 Clean Air Act Amendment (CAAA) of the US environmental protection agency (EPA) [4]. With the stringent environmental regulations and potentially significant problems associated with the release of VOCs [5,6], waste gases containing VOCs and HAPs require treatments prior to being emitted to the atmosphere.

Numerous investigations have focused on the treatment of air streams contaminated with relatively low concentrations of aromatic VOCs, e.g. toluene and o-xylene [1–3,5–11]. Many efforts, in particular, have examined green technologies such as biofiltration [2,6,12–15]. Depending on the specific aromatic VOC being treated, biofilters were able to provide maximum elimination capacities (EC$_{max}$) ranging between 10 and 150 g m^{-3} h^{-1} [16–20]. All these studies reported o-xylene as the most recalcitrant BTEX (benzene, toluene, ethyl benzene, xylene) that demonstrated the lowest biodegradability in biofilters [15,17–20]. The maximum reported EC for o-xylene was about 65 g m^{-3} h^{-1} [17]. In addition, when mixtures of toluene and o-xylene were treated in biofilters, o-xylene inhibited the biodegradation of toluene, resulting in significant drop (up to a factor of 2) in the overall biofilter performance [2,20]. Such inhibitory and toxic effects of mixtures of VOCs on each other and on microorganisms undermine the viability of standalone biofiltration as effective air treatment technology. Nonetheless,

these limitations present an opportunity for developing processes that utilize the benefits of biofiltration while enhancing the removal of mixtures of VOCs, especially those with lower biodegradability.

One such improvement could come from utilizing UV photolysis upstream the biofilters. UV photolysis, which involves the use of UV irradiation to oxidize the pollutants [10], is an environmentally benign technology capable of oxidizing a wide range of contaminants including non-biodegradable and recalcitrant VOCs [1,10,11]. The use of UV photolysis as a standalone technology, however, is limited in its application due to its tendency to produce by-products [10,21–23] that might be of health or environmental concern [24–27]. However, such by-products are often more water soluble and biodegradable than the parent compounds [24,27,28] and hence, could be removed effectively via biofiltration, operating downstream of the UV photooxidation [1,10,11].

The synergistic effect of the coupled UV and biofiltration has already been demonstrated on few VOCs, including o-xylene, when treated individually [1,11]. Mohseni and Zhao [1] obtained much higher degradation of o-xylene by coupling UV photolysis with biofiltration. In addition, the UV-coupled biofilter receiving pretreated o-xylene demonstrated substantially greater EC_{max} (up to about 100% more than that by the standalone biofilter), an indication of the synergy between the two treatment processes [1]. In this current study, the coupling of UV photolysis and biofiltration was examined for the removal of mixtures of aromatic VOCs, toluene (C_6H_8) and o-xylene (C_8H_{10}). In particular, the work involved examining the inhibitory effects of VOCs on one another after UV photolysis. Furthermore, the impact of ozone, generated due to the photolysis of oxygen by 185 nm UV, on biofilter performance was investigated. The results demonstrate how UV photooxidation can breakdown toluene and o-xylene, improve their biotreatability, and overcome the inhibitory effects of o-xylene on toluene metabolism. The results also show that ozone produced in the UV pho-

toreactor may control the accumulation of biomass and so, the pressure drop through the biofilter bed. The results presented herein complement our previous work [1] and demonstrate that by integrating photolysis and biofiltration, one could overcome technological limitations of biofiltration for the treatment of mixtures of VOCs that possess low biodegradability.

2. Materials and methods

2.1. Experimental unit

The complete description of the experimental set-up (Fig. 1), consisting of two parallel biofilters and a UV annular photoreactor is presented elsewhere [1]. The UV photoreactor (custom made) had dimensions of 24.5 mm OD and 15.5 mm i.d. (also the OD of the lamp), and an effective length of 48 cm. It was equipped with two ozone producing low pressure mercury vapor lamps ($UV_{254+185\,nm}$) having the maximum emission at 254 nm and around 2% of the maximum intensity at 185 nm (G10T51/2/VH, Light Sources Inc., CT, USA). The UV irradiance was $7.79 \times 10^{-3}\,W\,cm^{-2}$ that was the average of measurements at the lamp surface and the outer wall of the photoreactor using a research radiometer (IL1700, International Light Inc., $\lambda = 254$ nm).

The two bench scale biofilter columns were made of Plexiglas and each consisted of three equal segments of 20 cm in height and 10 cm in diameter. The effective height of the packing materials in each segment was 16 cm which resulted in a total bed volume of 1.26 L. There were several points that allowed for sampling the gas streams along the biofilter columns. The biofilters were packed with a previously conditioned mixture of wood chips (3–30 mm) and compost (from yard waste) at 50:50 volume ratio. Controlled-release fertilizer pellets (Nutricote 14-14-14) containing 14% nitrogen were mixed with the medium at $9\,kg\,m^{-3}$ to supply nutrient requirements of microorganisms.
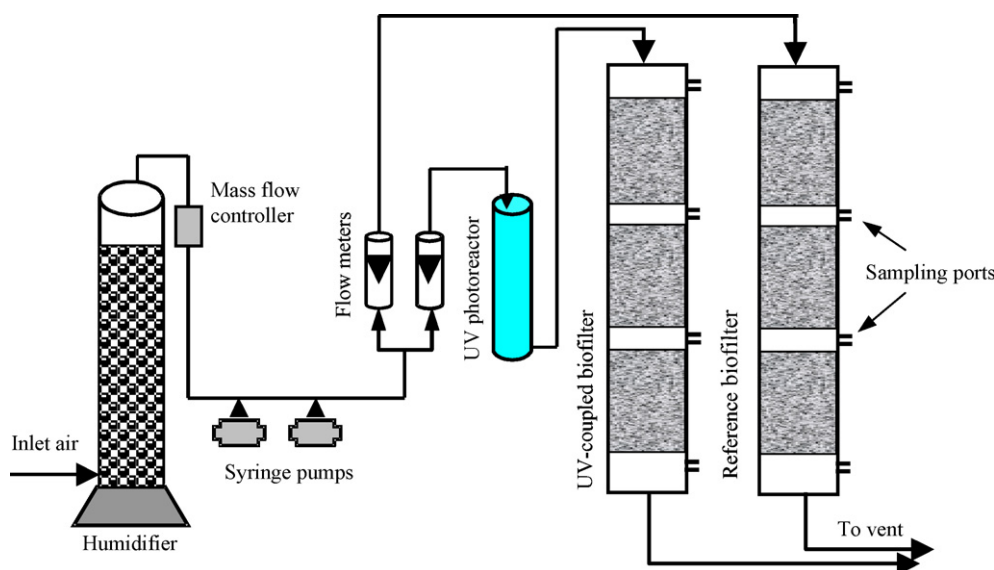

Fig. 1. Experimental set-up for the integrated UV-biofiltration experiments.

Table 1
Operational runs during the course of experimental study

Run ID	Description	Operating conditions[a]
Run 1 (days 4–34)	Start-up period. Pollutant concentrations were increased gradually	EBRT = 45 s, UV RT = 1.5 s, toluene concentration = 44.7 ppm, o-xylene concentration = 29.8 ppm
Run 2 (days 35–62)	Low VOC load, high UV fluence (12 mJ cm^{-2})	EBRT = 45 s, UV RT = 1.5 s, toluene concentration = 85.6 ppm, o-xylene concentration = 82.3 ppm
Run 3 (days 63–71)	High VOC load, high UV fluence (12 mJ cm^{-2})	EBRT = 45 s, UV RT = 1.5 s, toluene concentration = 103.5 ppm, o-xylene concentration = 104.9ppm
Run 4 (days 72–82)	Low VOC load, low UV fluence (6 mJ cm^{-2})	EBRT = 45 s, UV RT = 0.75 s, toluene concentration = 79.8 ppm, o-xylene concentration = 66.9 ppm
Run 5 (days 83–90)	High VOC load, low UV fluence (6 mJ cm^{-2})	EBRT = 45 s, UV RT = 0.75 s, toluene concentration = 121.4 ppm, o-xylene concentration 132.7 ppm
Run 6 (days 91–96)	High VOC load, lowered EBRT low UV fluence (6 mJ cm^{-2})	EBRT = 30 s, UV RT = 0.5 s, toluene concentration = 107.2 ppm, o-xylene concentration = 106.4 ppm
Run 7 (days 97–127)	Biofilters were switched. Reference biofilter → UV-biofilter, UV-biofilter → reference biofilter	EBRT = 45 s, UV RT = 0.75 s

[a] EBRT = empty bed retention time in the biofilters; RT = retention time.

2.2. Experimental procedure

The experiments were carried out using the two parallel systems of with and without UV pretreatments (Fig. 1) for a period of more than 4 months and under various operating conditions. Table 1 describes the operating conditions of various runs carried out in this investigation. The contaminated streams were generated by injecting toluene and o-xylene into the clean air stream using two syringe pumps (Model 220, KDScientific, New Hope, PA, USA). The desired concentration of the contaminants in the gas stream was achieved via controlling the injection rate of toluene and o-xylene. Contaminated air was then divided into two equal streams, one flowing through the UV-biofiltration unit and the second stream entering the reference biofilter. All the reactors operated in a down flow mode, receiving the contaminated air from the top. The temperature was maintained relatively constant at about 30 °C using heating tapes rapped around the tubing. The contaminated humid air entering the biofilters contained a relative humidity of greater than 95%. To prevent drying of the biofilter beds due to the entering air streams having less than 100% relative humidity, each biofilter was sprayed once a day with about 100 mL of water.

2.3. Analytical procedure

Concentrations of toluene and o-xylene in the gas stream were measured daily using a gas chromatograph equipped with mass spectrophotometer (GC/MS, Saturn 2200, Varian Inc., USA). The GC was equipped with a megabone capillary column (CPSil-8 CP5860) and helium at a flow rate of 1 mL min^{-1} was used as a carrier gas. The injector temperature was constant at 200 °C, and oven temperature was held constant at 50 °C for 2 min, increased to 150 °C at the rate of 40 °C min^{-1}, and then held constant for 5 min. On-line gas samples were taken via suction created by a vacuum pump (Model 400-1901, Barnant, Barrington, IL, USA) and injected into the GC using a six-port sampling/injection valve (Valco Instruments, Huston, TX, USA). The average of triplicate measurements was used as a VOC concentration in the sampled location. Measurements

of temperature and pressure drop were carried out using sampling ports along the height of the biofilter columns. Temperature measurements were made using standard thermometers inserted in the bed. Pressure measurements were made using a U-tube manometer filled with water.

Partial oxidation of toluene and o-xylene in the UV photoreactor was investigated by sparging a measured volume of the air into 250 mL of distilled water. Detailed explanation of the apparatus and sampling procedure is presented elsewhere [10]. Potassium iodide (KI) was added into the distilled water in order to remove ozone, which could cause experimental error owing to its powerful oxidative effect on most organic compounds [29]. The solution in the sparger was then analyzed for the total organic carbon (TOC analyzer, TOC-VCPH, Shimadzu) to measure the amount of water soluble organics and photolysis by-products captured in the solution. The presence of specific by-products (e.g. aldehydes) was investigated by analyzing aliquots of the sparger solution for these compounds using the GC/MS and according to the PFBHA liquid–liquid extraction gas chromatographic method [30]. Ozone produced in the UV photoreactor and its destruction at different sections of the downstream biofilter was analyzed by absorption in a KI solution and then titration against sodium thiosulfate (Na$_2$S$_2$O$_3$) [30].

3. Results and discussion

3.1. UV-biofilter versus reference biofilter

The performance of the coupled UV-biofiltration in removing mixtures of toluene and o-xylene was compared with that of the standalone biofilter, operating as reference. The experiments were carried out for 127 days and under different operating conditions (i.e. different experimental runs shown in Table 1), including inlet contaminant concentrations and gas retention times in the reactors.

Fig. 2 shows the percentage removal of the two contaminants in terms of total organic carbon over the course of investigation (runs 1–6). The percentage removals of the individual VOCs (i.e. toluene and o-xylene) followed similar trends. Run 1,
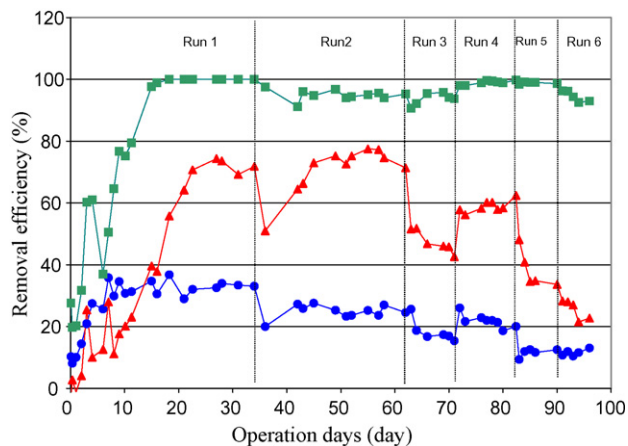
Fig. 2. Removal efficiencies of mixtures of toluene and *o*-xylene in terms of organic carbon, (●) UV photolysis, (■) UV-biofilter, and (▲) reference biofilter.

days 1–34, included the start-up phase during which the performance of the biofilters gradually increased despite the constant VOC loads in the inlet streams (about 45 ppmv of toluene and 30 ppmv of *o*-xylene). Also, the performance of the biofilters was somewhat unstable in the first 10 days of the experiment likely due to the instability of the system and/or microbial community. Nonetheless, both biofilters reached steady state by day 25 and before the end of run 1. Fig. 2 also shows that the UV-coupled biofilter had a shorter start-up period and achieved 100% removal efficiency (and likely steady state condition) within 2 weeks. The reference biofilter, on the other hand, did not reach steady state until day 25 and its total removal efficiency did not exceed 80%.

The UV-biofilter system maintained its superior performance and contaminant removal efficiencies over the entire experimental period and under various operating conditions of contaminant loadings, air flow rates, and UV fluences. In fact, the improvements in toluene and *o*-xylene removal were more pronounced during runs 3, 5, and 6 where the organic loadings were high (refer to Table 1). In addition, Fig. 2 shows that the UV-biofiltration process performed significantly better than the reference system, in the first 2–3 weeks of the experiment (e.g. during the start-up/acclimation period) and during the transition periods following spikes in the inlet loads/concentrations (e.g. days 34, 62, 71, 83, and 89). Pretreatment with UV photolysis acted as buffer and diminished the sudden changes in the loading to the biofilter; hence, reducing the transient effects and durations.

A detailed analysis of the results in Fig. 2 shows that UV had a synergistic effect on the downstream biofilter. That is, the enhanced removal of VOCs in the UV-biofilter was greater than sum of the removals obtained by the UV photolysis and the reference biofilter. This is particularly evident for runs 3, 5, and 6 where the systems received high contaminant loadings. During run 3, while the UV photolysis and the reference biofilter had removal efficiencies of about 17% and 45%, respectively, the combined UV-biofilter process offered removal efficiencies of more than 90% for toluene and *o*-xylene. This represented an added removal of about 30% provided by the UV-biofilter.

This difference was more pronounced in runs 5 and 6 where the added removal efficiencies were 50% and 57%, respectively. These results suggest that there was a direct correlation between the VOC loading and the synergistic effect of UV photolysis on biofilter performance. Consistent with the results obtained on the removal of single VOCs [1], it can be concluded that coupling UV photolysis with a conventional biofilter substantially enhances the performance of the biofilter treating mixtures of hardly biodegradable contaminants. This is especially the case at higher VOC loadings, conditions under which conventional biofilters would not perform well.

3.2. Elimination capacities

Fig. 3 compares the elimination capacities of the two biofilters (reference biofilter versus the UV-coupled biofilter receiving pretreated air) with respect to the toluene and *o*-xylene. For the inlet loadings of up to 48 $g_{toluene}$ m^{-3} h^{-1} and 46 $g_{o\text{-}xylene}$ m^{-3} h^{-1}, the UV-coupled biofilter provided near complete removal of both contaminants. The EC for this biofilter closely followed the inlet loadings and reached 45 $g_{toluene}$ m^{-3} h^{-1} and 43 $g_{o\text{-}xylene}$ m^{-3} h^{-1} for toluene and *o*-xylene, respectively. The fact that the EC of the UV-coupled biofilter did not reach a plateau over the range of contaminant loading demonstrates that greater toluene and *o*-xylene removals would have been achieved had higher loadings of contaminants been applied to the system.
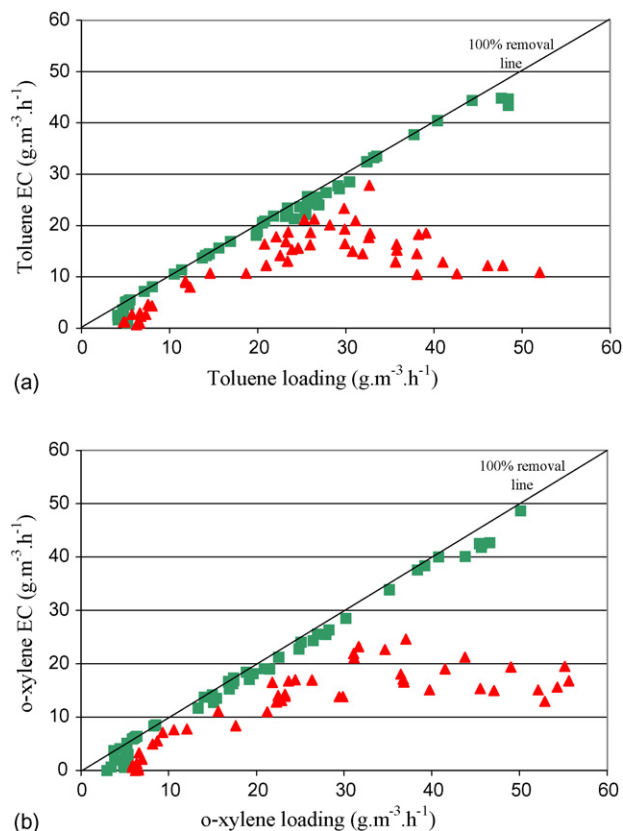

Fig. 3. Elimination capacities of toluene (a) and *o*-xylene (b) with respect to inlet contaminant loadings; (■) UV-coupled biofilter, and (▲) reference biofilter.

Unlike the UV-coupled biofilter, the reference biofilter showed variable and significantly lower performance. The EC_{max} of the reference biofilter did not exceed $25\,g\,m^{-3}\,h^{-1}$ for either contaminant, a value far less than that provided by the UV-coupled biofilter. In addition, Fig. 3(a) shows that increasing the loading of toluene beyond $35\,g\,m^{-3}\,h^{-1}$ resulted in gradual decline in its EC. The decline in the EC_{max} of toluene from a maximum of $25\,g\,m^{-3}\,h^{-1}$ to about $10–15\,g_{toluene}\,m^{-3}\,h^{-1}$ was likely due to the inhibitory effects of o-xylene on toluene biodegradation at higher concentrations. Such inhibitory effects of xylene isomers on toluene removal have been previously observed by other researchers, when the two compounds were treated as mixtures in biofilters [2,7,20].

From the results presented in Figs. 2 and 3, it can be concluded that UV-biofiltration of mixtures of slowly biodegradable aromatic VOCs not only enhances the overall removal efficiency of the organics, but also reduces/eliminates the inhibitory effects of one compound on the biodegradation of the others. The latter is a particularly important aspect of this work as it demonstrates a simple technique to overcome the inhibitory effects of VOCs during the biofiltration of waste gas streams from a variety of industrial operations and contaminated sites that contain mixtures of pollutants. The results from this research indicate that the application of relatively small fluences of UV (i.e. about $6–12\,mJ\,cm^{-2}$) could enhance the performance of the biofilters by more than 100%, especially at higher VOC loadings. Another advantage of UV is that it does not need to be operational at all times and can be used on an as-needed basis. In other words, the UV lamps can be energized when the VOC loading is high and more than the removal capacity of the biofilter, as well as during the transient operating conditions.

3.3. Switching biofilters

The effectiveness of UV pretreatment at enhancing the performance of the downstream biofilter was confirmed by switching the biofilters during run 7. Starting on day 97 of the experiment, the biofilters were switched so that the UV photoreactor was coupled with the reference biofilter and the biofilter previously coupled with UV, operated as standalone system. This stage of the experiment lasted 30 days during which the two parallel systems operated with inlet pollutant concentration of $788\,mg_{carbon}\,m^{-3}$, UV fluence of $6\,mJ\,cm^{-2}$, and EBRT of $45\,s$ in the biofilters. Fig. 4 shows the change in the removal efficiencies of the two biofilters after switching their position with respect to UV pretreatment. Upon receiving UV pretreated air stream, the performance of the originally reference biofilter increased significantly from around 23% VOC removal to above 88% within 6 days after switching and then reached up to about 95% by the end of the experiment. On the other hand, the removal of contaminants in the other system decreased gradually from about 93% on day 97 (before switching the biofilters) to as low as 20% within 30 days. The significant shift in the performances of the two biofilters highlights the importance of UV pretreatment as key to the enhanced removal of VOCs in the coupled UV-biofiltration process. In other words, UV pretreatment increased the biodegradability of recalcitrant VOCs and
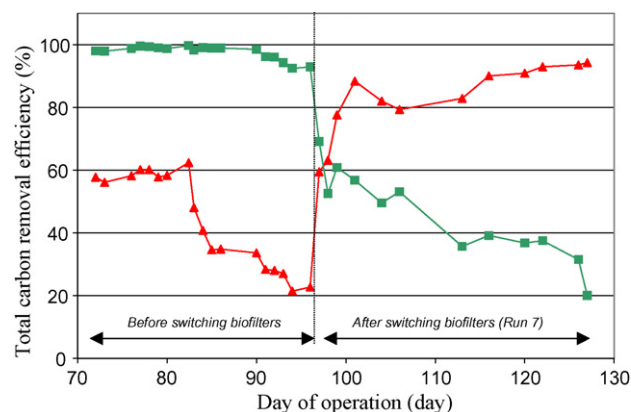

Fig. 4. Performance of the biofilters after switching, i.e. the UV photoreactor was placed ahead of the reference biofilter; (■) UV-coupled biofilter, and (▲) reference biofilter.

affected the dynamics of the microbial cultures within the biofilter such that it effectively eliminated the contaminants from the air stream.

3.4. UV photooxidation by-products

It is well established that photooxidation (photolysis) of organics with low UV fluences (similar to those applied in this work) leads to their partial oxidation and formation of water soluble and likely more biodegradable by-products [1,10,11]. Koh et al. [10] have already demonstrated more than 50% of hydrophobic organics converted in the photolysis stage were water soluble and biodegradable. The increased water solubility of the products of UV photolysis was further confirmed in this study by monitoring and comparing the TOC of the solutions sparged by the inlet and outlet streams of the UV photoreactor and biofilter. The results were similar to those presented by Mohseni and Zhao [1] and supported previous findings, indicating up to about 95% increase in the water solubility of the organics upon UV pretreatment. Also, the results indicated that soluble organics formed during the photolysis stage were biodegradable and hence, were removed very effectively in the biofilter.

Water-soluble organics captured in the sparging solution were analyzed further for the specific by-products of UV photolysis. Aldehydes were the most noticeable to be identified. Fig. 5 shows the concentrations of acetaldehyde and formaldehyde (two of the most common aldehydes associated with UV photolysis) captured in the sparged solution. Other intermediates identified, but not quantified due to their less significant presence, were propanal, glycolaldehyde, and benzyl alcohol. The formation of acetaldehyde and formaldehyde during the UV photolysis of toluene and o-xylene is quite evident from the sharp increase in the concentration of these intermediates in the outlet of the UV photoreactor. The presence of aldehydes is in agreement with literature reports suggesting these compounds as the most important intermediates of toluene and o-xylene photolysis [21,22]. As shown in Fig. 5, the concentration of these intermediates dropped significantly (to less than 3 ppbv which was the detection limit of the instrument) after the first segment of the
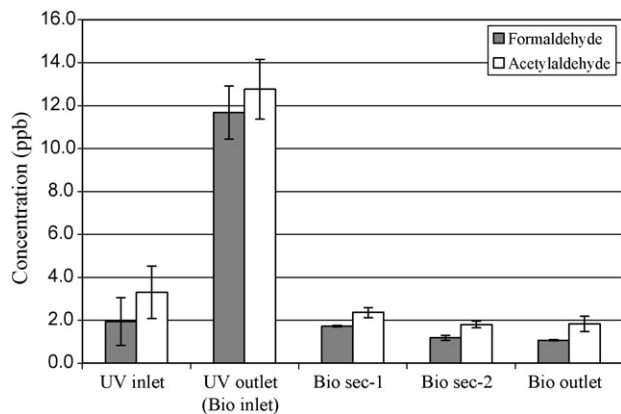
Fig. 5. Concentrations of formaldehyde and acetaldehyde in the coupled UV-biofiltration treatment process.

biofilter, indicating that all these compounds were biodegraded effectively. It is likely that these biodegradable intermediates also contributed indirectly to the removal of parent contaminants in the biofilter. That is, the presence of biodegradable compounds in the air stream may have affected/shifted the microbial community leading to greater degrees of toluene and o-xylene than it was observed in the reference biofilter.

3.5. Ozone formation and elimination

With the UV lamp emitting at 185 and 254 nm, ozone was produced as a result of the photolysis of oxygen present in the air. Fig. 6 shows the concentrations of ozone at the outlet of the UV photoreactor and at different segments along the downstream biofilter. It is important to note that the formation of ozone was to some extent inhibited due to the presence of humidity and the competitive absorption of the 185 nm UV by water molecules [31]. The highest concentration of ozone, 18.2 ppmv, was recorded in the outlet of the UV photoreactor for run 2, which corresponds to the UV fluence of 12 mJ cm^{-2} and inlet VOC concentration of 211 mg$_{carbon}$ m^{-3}. Increasing the concentration of organics in the inlet gas stream and/or decreasing the UV fluence led to lower ozone formation in the UV photoreactor (runs 2 through 6 in Fig. 6). For instance, in
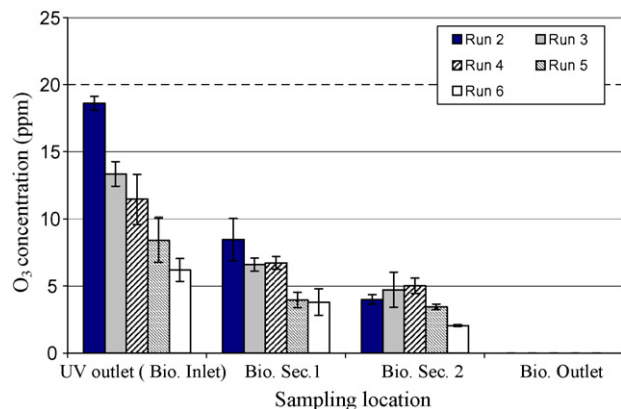
run 6 with the UV fluence of 6 mJ cm^{-2} and inlet concentration of 788 mg$_{carbon}$ m^{-3}, the amount of ozone produced was 5.4 ppmv. The lower formation of ozone with increasing contaminant concentration suggests that ozone was consumed while being produced. That is, ozone contributed to some extent in the partial oxidation of toluene and o-xylene. The extent of such contribution is not clear, as there was no investigation to quantify the effect of ozone on the removal of VOCs in the UV photoreactor.

Fig. 6 shows that the ozone produced in the UV photoreactor was removed along the biofilter in all the experimental runs. The absence of ozone in the outlet stream eliminates concerns over the release of ozone to the atmosphere from the UV-biofiltration process. More importantly, it demonstrates the fact that relatively low concentrations of ozone not only could be removed in the biofilters, but also did not compromise or negatively affect the activity of microorganisms at degrading the VOCs and/or their UV photolysis by-products. In fact, ozone may have contributed positively to the performance of the biofilter in two ways. First, ozone continued to react with toluene and o-xylene along the biofilter, converting them to more biodegradable molecules that could be simultaneously degraded by the microbial culture. Second, ozone, being a strong oxidant and disinfectant, controlled the growth and water content of the biofilm in the column allowing a more efficient uptake of hydrophobic toluene and o-xylene. The latter hypothesis was substantiated further through visual inspection of the biofilter medium and monitoring the pressure drops along the biofilters.

3.6. Biofilter pressure drops

Fig. 7 presents the pressure drops in millimeters H$_2$O per meter of the bed throughout the investigation (runs 1–7). The pressure drop of the reference biofilter increased over the course of experiment and reached about 7.3 mm H$_2$O m^{-1} of the bed for the air flow rate of 6.3 L min^{-1} (EBRT = 45 s). The accumulation of biomass, biofilm growth, and subsequent reduction in bed porosity were considered as primary contributors to the increase of the biofilter pressure drop [4]. When air flow rate was

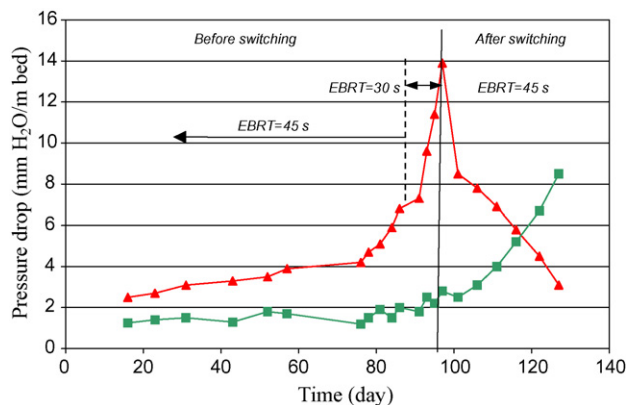Fig. 6. Ozone produced in the UV photoreactor and its profile along the downstream biofilter.

Fig. 7. Pressure drops profiles in the biofilters during the entire experimental work, (■) UV-coupled biofilter, and (▲) reference biofilter; note that after switching, the reference biofilter received UV pretreated stream.

increased to 9.4 L min^{-1} (EBRT = 30 s), pressure drop increased sharply to about 14 mm H$_2$O m^{-1} of the bed. Such increases in pressure drop at high flow rates would have significant implications for large-scale applications of biofiltration because of the major operating costs associated with the pumping of air through the system.

In comparison, the pressure drop in the UV-coupled biofilter increased very little and remained below 2.8 mm H$_2$O m^{-1} of the bed through the entire experimental period before switching. In other words, there was no indication of biomass accumulation in the bed, despite the higher activity of this biofilter with respect to VOC removal. It is believed ozone was the primary factor in controlling the growth of biomass and preventing pressure drop increase. As shown in Fig. 7, ozone was produced in the UV photolysis stage and entered the biofilter at concentrations of up to 18 ppmv. The presence of this amount of ozone was likely enough to control biomass growth, while maintaining a healthy population of organisms capable of degrading toluene and o-xylene, and their UV photooxidation by-products.

After day 97 and upon switching the biofilters, the pressure drop of the originally UV-coupled biofilter, which no longer received UV pretreated stream, started to increase steadily and reached up to 8.5 mm H$_2$O m^{-1} of the bed by the end of the experiment (Fig. 7). Pressure drop in the reference biofilter, on the other hand, decreased markedly upon the incorporation of UV before the biofilter. These observations further substantiated the role that ozone, formed in the UV photoreactor, played in controlling the growth of biomass/biofilm within the biofilter bed. Hence, they highlight yet another unique advantage of coupling UV and biofiltration. The combined process not only improves the biofilter performance and provides much higher removal of mixtures of recalcitrant VOCs, but also prevents excessive growth of biomass, thereby reducing the potentials for clogging of the biofilter beds and reducing maintenance costs associated with biofilter operations. Placing a UV photoreactor upstream of a biofilter eliminates the need for expensive chemical rinsing, backwashing, or nutrient limitation, which are the conventional means of pressure drop control proposed in the literature [32,33].

4. Conclusions

- Mixtures of toluene and o-xylene, two hardly biodegradable VOCs present in industrial air emissions, were effectively removed using an integrated UV-biofiltration process that demonstrated significant synergy between UV photolysis and biofiltration.
- For over 4 months of experimental period and the inlet contaminant concentrations ranging between 70 and 650 mg$_{carbon}$ m^{-3}, the integrated UV-biofiltration treatment provided greater than 95% removal efficiency which was up to 60% greater than sum of removals offered by UV and reference biofilter.
- The UV pretreatment partially oxidized a fraction of airborne toluene and o-xylene, converting them to more water soluble and biodegradable intermediates such as aldehydes which were removed effectively in the downstream biofilter.

- The biofilter receiving UV pretreated air stream experienced less biofilm accumulation and much lower pressure drop which has been associated with the presence of up to 20 ppmv ozone in the air stream produced in the photoreactor (with 185 nm UV).

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