Polyurethane foam based biofilter media for toluene removal

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Abstract Polyurethane foam medium was manufactured and analyzed to determine its suitability as a solid support medium for use in gas-phase biofilters. Physical and chemical studies were conducted to determine the medium’s characteristics. The medium’s ability to support an active biofilm capable of degrading volatile organic compounds was assessed using a laboratory scale biofilter fed a model waste stream containing toluene for more than 250 days with empty bed residence times (EBRTs) ranging from two to four minutes. Results are presented that show how a polyurethane foam medium with high porosity, suitable pore size, low density, and an ability to sorb water was able to remove over 99% of the influent toluene when fed at a concentration of 200 ppmv. An operating strategy is described which effectively prevented two problems common to conventionally operated biofilter systems: nutrient limitations and biosolid accumulation.

Keywords Air pollution control; biofiltration; polyurethane foam; toluene; VOCs

Introduction

Wastewater and solid waste treatment facilities and industrial manufacturing operations are often responsible for releasing gaseous volatile organic compounds (VOCs) to the air. Many of these VOCs are regulated and/or are responsible for odor complaints from the public. Because of this, destruction of VOCs that contaminate air streams has become increasingly important in pollution control and environmental cleanup. VOC concentrations in many air waste streams are low enough to make conventional physical-chemical treatment options (e.g., incineration or carbon adsorption) difficult and expensive. Biofiltration is a possible solution to some of these problems (Bohn, 1992).

The concept of using biological methods to treat waste gases is similar to other forms of biological waste treatment. In biofiltration, a fan or blower forces gases containing biodegradable VOCs through a packed bed that contains an unsaturated solid medium that supports a biologically active aqueous layer. As contaminated air flows through the support medium and past the aqueous biofilm, contaminants partition to the aqueous or solid phases where they are transformed by microorganisms into innocuous products such as carbon dioxide, water, and biosolids.

While packing media used in conventional biofilter beds consist mostly of peat or compost, a wide variety of other materials have been used. These include soil, wood chips, bark, sawdust, activated carbon, ceramic, ground tires, polystyrene beads (Ergas et al., 1995) and polyurethane foam (Moe et al., 1997; Moe and Irvine, 2000a, 2000b). In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms (Kinney et al., 1997).

High porosity, appropriate pore size, low density, and the ability to sorb water are features important to the proper operation of packed bed biofilters. High porosity permits the uniform gas flow distribution needed for maximum contact between the gas stream contaminants and the microbial population. Pore size is directly related to head loss and...
plugging problems that often result from microbial growth. Low density, an obvious advantage in construction, helps minimize compaction of the bed due to the weight of the packing material itself (Ergas et al., 1992). Because microorganisms grow best on wet surfaces, the ability of filter material to absorb water is also an important factor in medium selection.

In spite of their increasing popularity, three problems are commonly cited for conventionally designed and operated biofilter systems. The first, excessive microbial growth in overloaded systems or systems operated for long periods of time under normal loading, often causes clogging. The second, inadequate moisture control, results in decreased biofilter performance. The third, nutrient content of filter beds, is sometimes difficult to control.

Several methods have been developed to alleviate the problem of biofilter clogging. Sorial et al. (1995) developed a successful backwashing procedure for biofilters packed with ceramic pellets but the daily downtime was appreciable and full-bed fluidization was required. Holubar et al. (1995) controlled clogging by limiting the addition of nutrients at the expense of biofilter performance. Farmer et al. (1995) investigated a system of three biofilters in series where the lead biofilter receiving contaminated inflow was periodically switched. Although this decreased net biomass production in biofilters not in the lead position, clogging was still a problem. Holubar et al. (1995) also tested terminating contaminant flow and extending periods of endogenous respiration but found that several weeks of aeration were not sufficient to unclog the biofilter. Severin et al. (1995) sparged air and water through a biofilter and successfully dislodged excess biosolids.

Proper control of moisture content is also critical to biofilter performance. Some biofilter support materials, including peat and compost, are hydrophobic when dry and are not easily re-wetted (Sorial et al., 1995) while others, such as polyurethane foam (Hampshire Chemical Corp., 1992), are produced from hydrophilic materials that are easily re-wetted. While an optimum range of moisture content can be determined experimentally for each material, moisture content is difficult to maintain in practice. For example, direct application of water may result in flooded zones, and humidification of the influent air is inadequate if microbially induced temperature rises reduce the air’s relative humidity to less than 100%. Nutrient limitations can have a negative impact on contaminant removal (Severin et al., 1995; Moe and Irvine, 1999; Moe and Irvine, under review). In many applications, nutrients are added to biofilters either with the packing material before biofilter assembly or in a nutrient solution sprayed on or mixed with the packing material after construction (Kinney et al., 1997). Because nutrients are added in aqueous solution, simultaneous control of moisture and nutrient levels is difficult when using most conventional packing materials. A medium such as polyurethane foam allows nutrients to be adjusted independently from moisture content.

In order to overcome limitations associated with conventional biofilter design and operation, experiments were conducted to examine a new biofilter medium, polyurethane foam. Moe et al. (1997) used digital image analysis to study pore size distribution in the foam and found that homogenous polyurethane foam could be made in the laboratory with porosity and surface area that compares favorably to materials traditionally used in packed bed reactors. The new medium also permits use of novel nutrient addition and biosolids wasting strategies. The polyurethane foam biofiltration system reported on herein is similar to the Captor™ Process for liquid treatment in which reticulated polyurethane foam sponge blocks served as solid supports for microbial attachment (Golla et al., 1994; Kondo et al., 1992; Heidman et al., 1988). In such a system, biosolids are removed by violent agitation of the medium or by squeezing the pads between rollers.

**Methods**

In this study, foam was produced without the aid of sophisticated mixing or casting machinery. Polyurethane foam was produced from Hypol™ 3000 prepolymer (Hampshire
Chemical Co., Lexington, MA). Pluronics™ P-65 Surfactant (BASF Corp., Parsippany, NJ) was dissolved in deionized water (at P-65 concentrations ranging from 2 g/L to 40 g/L), then cooled to 4ºC. Hypol 3000 was heated to 55ºC and maintained at that temperature for at least 2 hours prior to use. 110 g prepolymer and 110 g surfactant solution were combined in a disposable plastic cup and vigorously mixed using a plastic spoon for 20 seconds. The mixture was then poured into cylindrical cardboard molds 11 cm in diameter and 18 cm tall. The resulting foam was air dried before the mold was removed, and the foam was rinsed repeatedly with deionized water to remove surfactant before further testing.

An equilibrium isotherm from an aqueous solution of toluene (HPLC grade, Aldrich Chemical Co., Milwaukee, WI) was determined at 23ºC. Foam cut into pieces of approximately 0.5 cm × 0.5 cm × 0.5 cm was added to 10 glass bottles (0.26 L). The bottles were completely filled with 50 mg/L toluene solution, covered with Teflon-lined caps, and placed on a rotary shake table for 72 hours. A preliminary batch transient experiment indicated adsorption equilibrium was reached within 72 hours of contact with no appreciable further decrease in bulk toluene concentration for time periods of up to 7 days. Toluene concentrations at equilibrium in the bulk fluid were measured to quantify sorption.

Laboratory studies employed the biofilter depicted in Figure 1. The glass column reactor had an inner diameter of 10.5 cm and an overall height of approximately 1.5 m. The column consisted of a top, a bottom, and five 24 cm sections. Each section was filled with 20 cm of biofilter medium to provide a total bed depth of one metre. Gas sampling ports, located in a plenum below the filter medium in each filter section, were filled with Thermogreen™ LB-1 half-hole type septa (Supelco, Bellefonte, PA) that were replaced on a regular basis. The biofiltration column was assembled by placing Viton™ o-rings between the sections and clamping the assembly together using horseshoe type clamps with 3 tightening screws.

Compressed air from the laboratory air tap flowed through Tygon™ tubing to a Supelco Supelpure activated carbon filter to remove unwanted contaminants. A pressure regulator reduced pressure to 35 kPa before the airflow was split into two parts. 95% of the air was humidified as it passed through an aeration stone submerged in a 20 L glass carboy filled with water and heated by electrical heating tape. A KD Scientific model 1000 syringe pump (Boston, MA) delivered toluene from a glass gas-tight syringe (Hamilton Co., Reno, NV) through a 32 gauge needle into the remaining 5%. Flow meters (Manostat, New York, NY) measured and regulated gas flow rates. All surfaces that contacted contaminated air were made of glass, stainless steel, Teflon™, or Viton™. Small pieces of stainless steel mesh were placed in the bottom of the column to ensure mixing of the two gas streams in the plenum before entering the filter medium.

Figure 1  Schematic diagram of laboratory biofilter apparatus
Gas-phase toluene concentrations were measured using a SRI model 8610 gas chromatograph with a photoionization detector (PID). A 60 m × 0.53 mm Restek column was used with helium carrier gas at a flow rate of 18 ml/min. Temperature was held constant at 100ºC for 2 minutes, followed by an increase of 10ºC/min to 200ºC where the temperature remained constant for 4 minutes. Gas samples were transferred using glass gas-tight syringes equipped with Teflon Luer Lock Valves (Hamilton Co., Reno, NV). Gas-phase carbon dioxide concentrations were measured using a Varian model 3700 gas chromatograph with thermal conductivity detector (TCD) operated isothermally at 40ºC. A Supelco 6’ × 1/8” stainless steel packed column with 60/80 Chromosorb 102 was used with helium carrier gas at a flow rate of 30 ml/min. Carbon dioxide eluted at approximately 1 minute. Gas samples were transferred using Tedlar gas sampling bags (Supelco, Bellefonte, PA), and glass gas-tight syringes (Hamilton Co., Reno, NV) were used to inject 100 µL samples. Because the influent biofilter carbon dioxide concentration fluctuated over time, the carbon dioxide readings are reported as increases over ambient laboratory levels.

A Varian model 3400 gas chromatograph equipped with a purge and trap and flame ionization detector (FID) was used to quantify toluene concentrations in liquid samples. An 8’ × 1/8” stainless steel Supelco 1% SP-1000 column with 60/80 Carbopack™ B was used. Helium gas was supplied at a flow rate of 20 ml/min. The airflow to the FID was 30 ml/min and hydrogen flow to the FID was 30 ml/min. The temperature began at 100ºC, increased by 15ºC /min to 220ºC, and held at 220ºC for 7 minutes. A Tekmar purge and trap was used with a Supelco volatile purge trap for USEPA method 624 (1 cm 3% SP™-2100 on 60/80 Chromosorb™ WAW, 15 cm Tenax™ TA, and 8 cm 35/60 Silica Gel (Gd-15). Liquid samples were purged for 12 minutes and then dry purged for 4 minutes. The trap was preheated to 175ºC before desorbing for 5 minutes at 180ºC, and baking for 8 minutes at 225ºC. Toluene eluted at approximately 12 minutes.

Analysis of aqueous samples was conducted according to *Standard Methods for the Examination of Water and Wastewater* (1995). Because the polyurethane foam scorched at the standard temperature for measuring dry mass and moisture content, dry mass was determined by drying the foam at 60ºC for at least 24 hours, and cooling in a desiccator. Relative humidity was measured using a HI 9161C microprocessor controlled printing thermohygrometer (Hanna Instruments). A water manometer was used to measure pressure drop across the foam medium at various flow rates.

Activated sludge from the South Bend, IN, municipal wastewater treatment plant was used to seed a 4.0 L laboratory Sequencing Batch Reactor (SBR) operated to enrich for the microbial culture used in the biofilter. The operating strategy was based on a 6-hour cycle consisting of 0.5 h fill, 4 h react, 1 h settle, 0.5 h draw plus idle. Feed for the SBR consisted of the following compounds in tap water (mg/L): KH₂PO₄ (727.6), Na₂HPO₄ (305.3), MgSO₄ (36.1), CaCl₂·2H₂O (4.0), (NH₄)₆Mo₇O₂₄·4H₂O (0.04), FeSO₄·7H₂O (2.0), ZnSO₄·7H₂O (2.0), MnSO₄·H₂O (0.4), CuSO₄·5H₂O (0.04), Co(NO₃)₂·6H₂O (0.04), CoCl₂·6H₂O (0.033), Na₂B₄O₇·10H₂O (0.04), EDTA (1.0), KNO₃ (2500), toluene (100 to 200). Feed was prepared daily, and the SBR was operated for 3 weeks prior to biofilter inoculation.

Start-up for the biofilter assembly consisted of placing the foam cylinders in a container with three litres of mixed liquor from the SBR and aerating for one hour. Foam was removed, adjusted to approximately 65% moisture content by squeezing, and placed in the biofilter column. Swelling of the wet foam held the cylinders in place. Three distinct periods of biofilter operation, identified as periods S, I, and II, and summarized in Table 1, were studied. Period S was a 63 day start-up period during which the target influent toluene concentration ranged from 100 to 200 ppmv, and the EBRT ranged from 2 to 4 minutes. During
Period I (days 64 to 158) the biofilter was operated with an inlet toluene concentration of 200 ppm, and an EBRT of 2 minutes. On day 159, when Period II began, the inlet toluene concentration was decreased to 50 ppm, and the EBRT kept at 2 minutes.

Beginning on Day 49 and continuing until the end of the study, nutrients were added and biosolids removed every 7 to 14 days by dismantling the column and placing the foam cylinders in a container with two litres of a concentrated nutrient solution as described by Moe and Irvine (1999; 2000b). The foam cylinders were squeezed 20 times each while submerged in the mineral salt solution. Moisture content was adjusted to approximately 65%, the foam cylinders returned to the biofilter, and the biofilter restarted with toluene loading. Suspended solids (SS) and volatile suspended solids (VSS) of the rinsate were measured to quantify biomass removal. While the biofilter was dismantled, the glass column and the stainless steel mesh from the plenum were removed and washed with hot tap water to minimize biomass accumulation on the experimental apparatus.

### Results and discussion

Head loss through one metre of polyurethane foam packing material was measured at various air flow rates using foam made using surfactant concentrations ranging from 4 g/L to 40 g/L. Although image analysis (Moe et al., 1997) showed that the average pore size was nearly identical for the different foam formulations, the results presented in Figure 2 clearly show that foam made with 10 to 40 g/L surfactant had less head loss than foam made with less. Microscopic inspection of the foam confirmed that reticulation was more complete in foam made with elevated surfactant levels than with reduced levels. While the foam formulation that used 40 g/L of Pluronics P-65 surfactant offered the lowest head loss, it tore when squeezed. The formulation using 10 g/L of Pluronics P-65 surfactant was selected for further study because it minimized surfactant use while exhibiting low head loss and favorable mechanical characteristics.

Head loss characteristics of the polyurethane foam compare favorably with head loss characteristics of traditional biofilter materials which typically range from 5 to 10 cm water at surface loadings of 10 to 100 m³ m⁻² hr⁻¹ (Ottengraf, 1987; Leson and Winer, 1991). At

### Table 1  Biofilter operating parameters

<table>
<thead>
<tr>
<th>Period</th>
<th>EBRT (min)</th>
<th>Days of operation</th>
<th>Target toluene loading (ppmv)</th>
<th>Nutrient addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>2 to 4</td>
<td>0–63</td>
<td>100 to 200*</td>
<td>Varied*</td>
</tr>
<tr>
<td>I</td>
<td>2</td>
<td>64–158</td>
<td>200</td>
<td>Regular</td>
</tr>
<tr>
<td>II</td>
<td>2</td>
<td>159–259</td>
<td>50</td>
<td>Regular</td>
</tr>
</tbody>
</table>

Figure 2   Head loss through 1 m of polyurethane foam medium made using Pluronics P-65 surfactant (from Moe and Irvine, 2000a)
the loading rate typical of most biofilters, head loss across the polyurethane bed prepared with 10 g/L surfactant and adjusted to 65% moisture was less than 0.2 cm of water. Such a head loss is considerably less than that associated with conventional packing material.

Low head loss is just one of the beneficial properties that can be incorporated into polyurethane foam based biofilter medium. Because the choice of starting molecules is great, the properties of the final polyurethane foam product are wide. Choice of the polyol has a major effect on foam properties, especially rigidity and flexibility (Braun et al., 1985). Foam density, cell structure, rate of wetting, and water retention can be modified to develop a wide range of foam characteristics by controlling the ratio of water to prepolymer, foaming temperature, pH, and the type and amount of surfactant (Havens and Rase, 1993). Sorption isotherm experiments carried out using polyurethane foam made with 10 g/L surfactant were used to quantify sorption characteristics of toluene on polyurethane foam. Freundlich parameter values were determined from a linear regression on the Freundlich equation (Metcalf and Eddy, 1991). $K_f$ was determined to be $4.8 \times 10^{-5}$ and $1/n$ equal to 0.98 with a correlation coefficient of 0.91. The low $K_f$ indicates this polyurethane foam has a low sorption capacity for toluene and, therefore, sorption would not be expected to be a significant sink for toluene in a biofilter made from this medium. However, by adding varying amounts of powdered activated carbon (PAC) or other sorbents to the foam mixture, the sorption characteristics may be altered.

At the start of Period I, the EBRT was adjusted to 2 minutes and the influent toluene to 200 ppmv. The biofilter quickly adapted to the new condition, and after 24 hours (when the first samples were collected), less than 1 ppmv toluene was detected in the effluent. This high removal remained consistent throughout Periods I and II. Figure 3 shows typical toluene and carbon dioxide concentration profiles within the biofilter as measured on day 110 (Period I) (from Moe and Irvine, 2000b).

![Figure 3: Toluene and CO2 profiles on day 110 (Period I)](image)

![Figure 4: Influent and effluent toluene concentrations during Periods I and II](image)
110. As would be expected, toluene removal was accompanied by concomitant production of carbon dioxide in an amount consistent with that expected from biodegradation. After initiation of a regular nutrient addition and biomass wasting strategy during Period S, there was no further evidence of nutrient limitations. If such a nutrient addition strategy had not been employed, an eventual kinetic and stoichiometric limitation would have resulted (Moe and Irvine, 1999; Moe and Irvine, under review). Additional information on these biofilters, including performance for an inlet toluene concentration of 50 ppmv and an EBRT of 1 minute, have been described by Moe and Irvine (2000a; 2000b).

Inlet and outlet toluene concentrations for Periods I and II are shown in Figure 4. During Period I, the actual inlet toluene concentration ranged from 178 ppmv to 225 ppmv. During Period II, the actual concentration was between 45 ppmv and 57 ppmv. Variation in contaminant concentration was caused by the toluene delivery system. As toluene was dispensed into the air stream, small drops fell to the bottom of the injection chamber. As drops evaporated, a small increase in toluene concentration was observed; between drops a slight decrease was observed. In all cases however, toluene removal remained above 99%.

During the 259 days of operation, the measured head loss across the biofilter bed never exceeded 4 mm of water. This, combined with a mass balance on carbon, indicated that biosolids were not accumulating in the biofilter. This supports the notion that the nutrient addition and biomass wasting strategy used herein will prevent biomass accumulation and associated problems. Although the new medium offers several advantages over currently used media, strategies for biomass removal and nutrient addition for application in the full scale (e.g., mechanical systems for compressing the foam) were not tested in experiments described herein. Consequently, a direct comparison of costs and benefits of this medium in comparison to those used in other systems was not conducted.

Any additive that can tolerate water (in solution, suspended, emulsified, etc.) can be incorporated into polyurethane foam. Inclusion of activated carbon, nutrients, enzymes, pure cultures, etc. will create a wide range of biofilter media for use in different applications. This idea has been used by researchers to incorporate microorganisms into polyurethane foam matrices as a method of immobilization in treating contaminated liquids (Santo Domingo et al., 1997; Hu et al., 1994; Brookes et al., 1987). Other researchers have immobilized enzymes in the foam (Wood et al., 1982; Havens and Rase, 1993). Further development of such novel polyurethane-based media for use in biofilters may allow substantial improvements over conventional media.

Conclusions
Polyurethane foam with a high porosity, suitable pore size, low density, low head loss, and ability to sorb water and support biofilm growth can be made consistently and reliably. The polyurethane foam biofilter medium tested has favorable head loss characteristics compared to other biofilter media, and can be used effectively as a biofilter packing medium. Stable long-term operation is possible in polyurethane foam based biofilters when an appropriate nutrient addition and biosolid wasting strategy is implemented.

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